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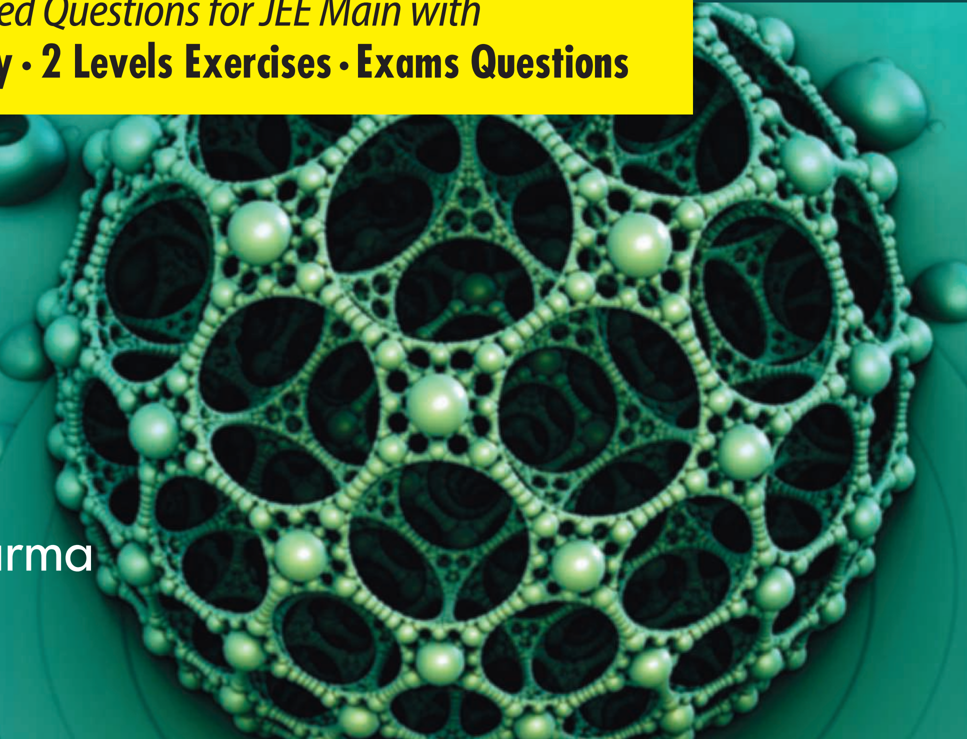

Sanjay Sharma

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SANJAY SHARMA

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ARIHANT PRAKASHAN (Series), MEERUT

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PREFACE

In sync with the recent changes in the test pattern and format of **JEE Main** (Joint Engineering Entrance), it is my pleasure to introduce **Master Resource Book in Chemistry for JEE Main**, for the Students aspiring a seat in a reputed Engineering College. JEE Main is a gateway examination for candidates expecting to seek admission in Bachelor in Engineering (BE), Bachelor of Technology (B.Tech) and Bachelor of Architecture (B.Arch) at Indian Institutes of Information Technology (IIITs), National Institutes of Technology (NITs), Delhi Technological University and other Centrally Funded Technical Institutes (CFTIs).

JEE Main is also an examination which is like screening examination for **JEE Advanced** (The gateway examination to India's most reputed Technical Institutes, Indian Institutes of Technology IITs). Only the top 2.2 lacs students passed in JEE Main will be able to attempt JEE Advanced.

Gradually, the number of students aspiring for the seat in the Engineering College has increased rapidly in the last 5 Years or so. This year nearly 10 lacs students appeared for JEE Main and only a few were able to reserve a seat in the college of their choice, so there is a cut throat competition among the aspirants. Thus, it calls for a systematic mastery of all the subjects of the test with paramount importance to problem-solving. Most of the books now in the market have become repetitive with scant respect to the needs of true and effective learning. This book has been designed to fulfill the perceived needs of the students as such.

- This book comprehensively covers all the topics of **JEE Main Chemistry** syllabus. The chapters have been sequenced according to the **syllabus of class 11th & 12th**. Each chapter has essential theoretical discussion of the related concepts with sufficient number of solved examples, practice problems and other solved problems. In each chapter previous years' questions of AIEEE and JEE Main have been included to help students know the difficulty levels and nature of questions asked in competitive exams at this level.
- All types of questions have been included in this book: **Single Correct Answer Types, Multiple Correct Answer Types, Reasoning Types, Matches, Passage-based Questions** etc.
- This is the only book which has its subject matter divided as per class 11th & 12th syllabus. It covers almost all questions of **NCERT Textbook & NCERT Exemplar problems**.

It is hoped this new effort will immensely benefit the students in their goal to secure a seat in the prestigious engineering college, and would be convenient to teachers in planning their teaching programmes. Suggestions for further improvement are welcome from the students and teachers.

Sanjay Sharma

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Equation, liquefaction of gases, critical constants.

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Elementary ideas of quantum mechanics, quantum mechanical model of atom, its important features, ψ and $\psi2$, concept of atomic orbitals as one electron wave functions; Variation of ψ and $\psi2$ with r for 1s and 2s orbitals; various quantum numbers (principal, angular momentum and magnetic quantum numbers) and their significance; shapes of s, p and d - orbitals, electron spin and spin quantum number; rules for filling electrons in orbitals – aufbau principle, Pauli's exclusion principle and Hund's rule, electronic configuration of elements, extra stability of half-filled and completely filled orbitals.

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Catalysis Homogeneous and heterogeneous, activity and selectivity of solid catalysts, enzyme catalysis and its mechanism.

Colloidal state distinction among true solutions, colloids and suspensions, classification of colloids - lyophilic, lyophobic; multi molecular, macromole-cular and associated colloids (micelles), preparation and properties of colloids Tyndall effect, Brownian movement, electrophoresis, dialysis, coagulation and flocculation; Emulsions and their characteristics.

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UNIT 14 *s* - Block Elements

(Alkali and Alkaline Earth Metals)

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General introduction, electronic configuration and general trends in physical and chemical properties of elements, anomalous properties of the first element of each group, diagonal relationships.

Preparation and properties of some important compounds - sodium carbonate, sodium chloride, sodium hydroxide and sodium hydrogen carbonate; Industrial uses of lime, limestone, Plaster of Paris and cement; Biological significance of Na, K, Mg and Ca.

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Group 13 to Group 18 Elements

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Group wise study of the p – block elements

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Group 14 Tendency for catenation; Structure, properties and uses of allotropes and oxides of carbon, silicon tetrachloride, silicates, zeolites and silicones.

Group 15 Properties and uses of nitrogen and phosphorus; Allotrophic forms of phosphorus; Preparation, properties, structure and uses of ammonia nitric acid, phosphine and phosphorus halides,(PCl_3, PCl_5); Structures of oxides and oxoacids of nitrogen and phosphorus.

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atomic radii, colour, catalytic behaviour, magnetic properties, complex formation, interstitial compounds, alloy formation; Preparation, properties and uses of $K_2Cr_2O_7$ and $KMnO_4$.

Inner Transition Elements Lanthanoids Electronic configuration, oxidation states, chemical reactivity and lanthanoid contraction.

Actinoids Electronic configuration and oxidation states.

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Introduction to coordination compounds, Werner's theory; ligands, coordination number, denticity, chelation; IUPAC nomenclature of mononuclear coordination compounds, isomerism; Bonding Valence bond approach and basic ideas of Crystal field theory, colour and magnetic properties; importance of coordination compounds (in qualitative analysis, extraction of metals and in biological systems).

Unit 18 Environmental Chemistry

Environmental pollution Atmospheric, water and soil. Atmospheric pollution Tropospheric and stratospheric.

Tropospheric pollutants : Gaseous pollutants Oxides of carbon, nitrogen and sulphur, hydrocarbons; their sources, harmful effects and prevention; Green house effect and Global warming; Acid rain;

Particulate pollutants Smoke, dust, smog, fumes, mist; their sources, harmful effects and prevention.

Stratospheric pollution Formation and breakdown of ozone, depletion of ozone layer - its mechanism and effects.

Water pollution Major pollutants such as, pathogens, organic wastes and chemical pollutants their harmful effects and prevention.

Soil pollution Major pollutants such as: Pesticides (insecticides, herbicides and fungicides), their harmful effects and prevention.

Strategies to control environmental pollution.

Section- C *(Organic Chemistry)*

UNIT 19 Purification & Characterisation of Organic Compounds

Purification Crystallization, sublimation, distillation, differential extraction and chromatography principles and their applications.

Qualitative analysis Detection of nitrogen, sulphur, phosphorus and halogens.

Quantitative analysis (basic principles only) Estimation of carbon, hydrogen, nitrogen, halogens, sulphur, phosphorus.

Calculations of empirical formulae and molecular formulae; Numerical problems in organic quantitative analysis.

UNIT 20 Some Basic Principles of Organic Chemistry

Tetravalency of carbon; Shapes of simple molecules hybridization (s and p); Classification of organic compounds based on functional groups: —C=C—,—C=C— and those containing halogens, oxygen, nitrogen and sulphur, Homologous series; Isomerism - structural and stereoisomerism.

Nomenclature (Trivial and IUPAC)

Covalent bond fission Homolytic and heterolytic free radicals, carbocations and carbanions; stability of carbocations and free radicals, electrophiles and nucleophiles.

Electronic displacement in a covalent bond Inductive effect, electromeric effect, resonance and hyperconjugation.

Common types of organic reactions Substitution, addition, elimination and rearrangement.

UNIT 21 Hydrocarbons

Classification, isomerism, IUPAC nomenclature, general methods of preparation, properties and reactions.

Alkanes Conformations: Sawhorse and Newman projections (of ethane); Mechanism of halogenation of alkanes.

Alkenes Geometrical isomerism; Mechanism of electrophilic addition: addition of hydrogen, halogens, water, hydrogen halides (Markownikoff's and peroxide effect); Ozonolysis, oxidation, and polymerization.

Alkynes acidic character; addition of hydrogen, halogens, water and hydrogen halides; polymerization.

Aromatic hydrocarbons Nomenclature, benzene structure and aromaticity; Mechanism of electrophilic substitution: halogenation, nitration, Friedel – Craft's alkylation and acylation, directive influence of functional group in mono-substituted benzene.

UNIT 22 Organic Compounds Containing Halogens

General methods of preparation, properties and reactions; Nature of C—X bond; Mechanisms of substitution reactions. Uses/environmental effects of chloroform, iodoform

UNIT 23 Organic Compounds Containing Oxygen

General methods of preparation, properties, reactions and uses.

Alcohols, Phenols and Ethers

Alcohols Identification of primary, secondary and tertiary alcohols; mechanism of dehydration.

Phenols Acidic nature, electrophilic substitution reactions: halogenation, nitration and sulphonation, Reimer - Tiemann reaction.

Ethers Structure.

Aldehyde and Ketones Nature of carbonyl group;

Nucleophilic addition to >C=O group, relative reactivities of aldehydes and ketones; Important reactions such as - Nucleophilic addition reactions (addition of HCN, NH_3 and its derivatives), Grignard reagent; oxidation; reduction (Wolff Kishner and Clemmensen) acidity of α-hydrogen, aldol condensation, Cannizzaro reaction, Haloform reaction; Chemical tests to distinguish between aldehydes and Ketones.

Carboxylic Acids Acidic strength and factors affecting it.

UNIT 24 Organic Compounds Containing Nitrogen

General methods of preparation, properties, reactions and uses.

Amines Nomenclature, classification, structure basic character and identification of primary, secondary and tertiary amines and their basic character. Diazonium Salts Importance in synthetic organic chemistry.

UNIT 25 Polymers

General introduction and classification of polymers, general methods of polymerization-addition and condensation, copolymerization; Natural and synthetic rubber and vulcanization; some important polymers with emphasis on their monomers and uses - polythene, nylon, polyester and bakelite.

UNIT 26 Biomolecules

General introduction and importance of biomolecules.

Carbohydrates Classification: aldoses and ketoses; monosaccharides (glucose and fructose), constituent monosaccharides of oligosacchorides (sucrose, lactose, maltose) and polysaccharides (starch, cellulose, glycogen).

Proteins Elementary Idea of α-amino acids, peptide bond, . polypeptides; proteins: primary, secondary, tertiary and quaternary structure (qualitative idea only), denaturation of proteins, enzymes.

Vitamins Classification and functions.

Nucleic Acids Chemical constitution of DNA and RNA. Biological functions of Nucleic acids.

UNIT 27 Chemistry in Everyday Life

Chemicals in medicines Analgesics, tranquilizers, antiseptics, disinfectants, antimicrobials, antifertility drugs, antibiotics, antacids, antihistamins - their meaning and common examples.

Chemicals in food Preservatives, artificial sweetening agents - common examples.

Cleansing agents Soaps and detergents, cleansing action.

UNIT 28 Principles Related to Practical Chemistry

- Detection of extra elements (N, S, halogens) in organic compounds; Detection of the following functional groups: hydroxyl (alcoholic and phenolic), carbonyl (aldehyde and ketone), carboxyl and amino groups in organic compounds.
- Chemistry involved in the preparation of the following
- Inorganic compounds Mohr's salt, potash alum.
- Organic compounds Acetanilide,
  p-nitroacetan ilide, aniline yellow, iodoform.
- Chemistry involved in the titrimetric excercises - Acids bases and the use of indicators, oxali acid vs $KMnO_4$, Mohr's salt vs $KMnO_4$.
- Chemical principles involved in the qualitative salt analysis
- Cations — Pb^{2+}, Cu^{2+}, Al^{3+}, Fe^{3+}, Zn^{2+}, Ni^{2+}, Ca^{2+}, Ba^{2+}, Mg^{2+} NH^{4+}. Anions – CO_3^{2-}, S^{2-}, SO_4^{2-}, NO_2, NO_3, Cl^-, Br^-, I^- (Insoluble salts excluded).
- Chemical principles involved in the following experiments

1. Enthalpy of solution of $CuSO_4$
2. Enthalpy of neutralization of strong acid and strong base.
3. Preparation of lyophilic and lyophobic sols.
4. Kinetic study of reaction of iodide ion with hydrogen peroxide at room temperature.

PART - I

Chapters from Class 11th Syllabus

1 Some Basic Concepts in Chemistry

JEE Main MILESTONE

- Matter and Its Nature
- Physical Quantities and Their Measurements in Chemistry
- Atomic and Molecular Masses
- Equivalent Mass or Equivalent Weight
- Empirical and Molecular Formulae
- Stoichiometric Problems of Different Kinds

1.1 Matter and Its Nature

Matter is anything which occupies space and has mass. All the things around us *e.g.,* water, air, book, table etc., are matter.

There are five states of matter namely solid, liquid, gases, plasma and Bose-Einstein condensate. Out of these, three states *i.e.,* solid, liquid and gas are general states and taught in our schools. These three states provide a basis for the physical classification of matter.

Solids have a definite volume and shape; liquids have a definite volume but not definite shape; gases have neither a definite volume nor a definite shape.

Chemistry is the branch of science which deals with the composition, properties and interaction of all kinds of matter such as air, water, rocks, plants, earth, etc.

These three states of matter are the result of competition between intermolecular interactions (attractive force between molecules) and thermal energy (responsible for repulsion between molecules).

On heating, a solid usually changes to a liquid and the liquid on further heating changes to the gaseous (or vapour) state. In the reverse process, a gas on cooling liquifies to the liquid and the liquid on further cooling freezes to the solid.

Plasma is seen as a state containing gaseous ions and free electrons and exists when gaseous state is taken to very high temperatures (say 1000 to 1,000,000,000°C). Here, it is necessary that the entire gas as a whole have no charge and is not of too much density. So, in short we can say **plasmas** as **low density ionised gases at very high temperatures**. Plasmas can be seen in northern lights or ball lightenings, flames, lightenings, neon lights, stars in particular sun, clouds of gas and dust around stars.

BE condensate was predicted in 1924 by **Satyendra Nath Bose** and **Albert Einstein** but due to lack of equipments, it was only created in 1935 by **Cornell, Ketterle** and **Weimann.** Its concept and existence is totally opposite to plasmas. The state is conceptualised at supercold conditions.

The supercold above means only a few billionth of a degree above absolute zero. Cornell and Weimann developed BEC at such temperature with **rubidium.**

Dalton's Atomic Theory

J. Dalton in 1803, proposed the atomic theory of matter on the basis of laws of chemical combinations. (which are given later in this chapter)

According to which

(i) matter is made up of indivisible and indestructible particles, called **atoms.**

(ii) all atoms of an element have identical mass and similar chemical properties. (Atoms of different elements have different masses and different chemical properties).

(iii) when atoms combine, they do so in the ratio of small whole numbers to form compound atoms or simply **compounds** or **molecules**. Compounds formed by such combinations are alike in every respect.

(iv) chemical reactions involve only combination, separation or rearrangement of atoms.

(v) atoms are neither created nor destroyed in the course of an ordinary chemical reaction.

Limitations of Dalton's Atomic Theory

(i) It failed to explain how atoms of different elements differ from each other.

(ii) It failed to explain how and why atoms of elements combine with each other to form compound atoms or molecules.

(iii) It failed to explain the nature of forces that bind together different atoms in a molecule.

(iv) It did not make any distinction between ultimate particle of an element that takes part in reaction (atoms) and the ultimate particle that has independent existence (molecules).

The hypothesis of Dalton is even accepted today by the scientific community with two modifications only.

1. Atom is divisible and destructible.
2. All atoms of an element are not identical in mass.

Atoms *and* Molecules

An **atom** is defined as "the smallest particle of matter which may or may not exist independently but can take part in a chemical reaction."

A **molecule** is defined as "the smallest particle of matter which can exist independently but cannot take part in a chemical reaction."

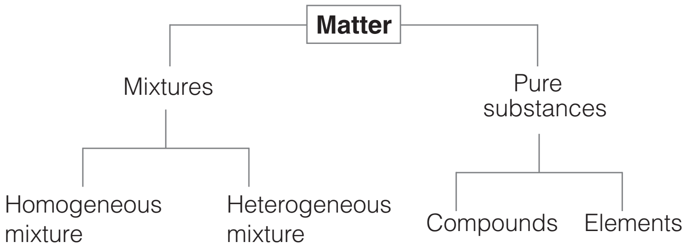
Both atoms and molecules are basic constituents of matter with the condition that atoms combine to form the molecules.

The molecules may be

(i) monoatomic, *i.e.,* contain 1 atom only, *e.g.,* Na, K etc.
(ii) diatomic, *i.e.,* contain 2 atoms, *e.g.,* N_2, O_2 etc.
(iii) triatomic, *i.e.,* contain 3 atoms, *e.g.,* O_3 etc.
(iv) polyatomic, *i.e.,* contain more than 3 atoms *e.g.,* P_4, S_8 etc.

Chemical Classification of Matter

On the basis of chemical composition and properties, matter can be classified as



(a) Mixtures

These have variable composition and variable properties due to the fact that components retain their characteristic properties. These may be separated into pure components by applying physical methods.

These can be of two types

(i) The **homogeneous mixtures**, have same composition throughout and their components are indistinguishable, *e.g.,*a liquid solution of sugar and water etc.

(ii) A **heterogeneous mixture,** on the other hand, do not have the same composition throughout and the components here are distinguishable, *e.g.,* a mixture of grains of sand and salt. Here particles of each component maintain their own identity.

(b) Pure Substances

These have fixed composition and non-variable properties. These cannot be separated into simpler substances by physical methods.

An **element** is a substance that contains only one type of atoms whereas a **compound** is formed when atoms of different elements combine in a fixed ratio.

Compounds and elements can be differentiated as the former can be decomposed into simple substances by chemical methods while later cannot be decomposed into simpler substances by chemical methods.

Sample **Problem 1** *Which one of the following is not an element?*

(a) *Graphite* (b) *Silica*
(c) *Diamond* (d) *Plasma sulphur*

Interpret (*b*) Elements contain only one type of atoms. Graphite and diamond both contain only C (carbon), plastic sulphur contains only S but silica (SiO_2) contains two different atoms, *i.e.*, Si and O, so it is not an element.

1.2 Physical Quantities and Their Measurements in Chemistry

The description, interpretation and prediction of the behaviour of chemical substances can be done on the basis of the knowledge of their physical and chemical properties determined from careful experimental measurements. The properties like mass, length, time, temperature etc., are physical quantities and their measurement does not involve any chemical reaction. These properties are expressed in numerals with suitable units.

The measurement of any physical quantity is represented by a number followed by units in which it is measured. For example length of a room can be represented as 12 m; here 12 is the number and m denotes metre-the unit in which the length is measured.

Precision and Accuracy

Precision is the measure of reproducibility of an experiment while accuracy is the measurement of closeness of a result to its true value. *Good accuracy means good precision but reverse is not always true.*

i.e., precision = individual value – arithmetic mean value

Accuracy = mean value – true value

Sample **Problem 2** *Two students performed the same experiment separately and each one of them recorded two readings of mass which are given below. Correct reading of mass is* 3.0 g. *On the basis of given data mark the correct option out of the following statements.* **[NCERT Exemplar]**

Student	**Readings** (i)	(ii)
A	3.01	2.99
B	3.05	2.95

(a) *Results of both the students are neither accurate nor precise.*
(b) *Results of student A are both precise and accurate.*
(c) *Results of student B are neither precise nor accurate.*
(d) *Results of student B are both precise and accurate.*

Interpret (*b*) Results of student *A* are close to true value as well as to each other, that's why these are precise as well as accurate.

Scientific Notation

In scientific notation, all numbers (however large or small) are expressed as a number between 1.000 and 9.999 multiplied or divided by 10, *i.e.*, here a number is generally expressed in the form

$$N \times 10^n$$

Here, N is called **digit term.** It is a number between 1.000 and 9.999.

n is called an **exponent.** If decimal is shifted towards left, the value of n is positive (and is equal to the number of places by which decimal is shifted) and if decimal is shifted towards right, the value of n is negative.

e.g., 138.42 can be written as 1.3842×10^2

or 0.013842 can be written as 1.3842×10^{-2}

Significant Figures

The digits in a properly recorded measurement are known as **significant figures** or in other words, we can say that significant figures are the meaningful digits in a measured or calculated quantity.

A significant figure includes all those digits that are known with certainty plus one more which is uncertain or estimated. Always remember that **greater the number of significant figures in a reported result, smaller the uncertainty**.

There are certain rules for determining the number of significant figures. These are as follows

1. All non-zero digits are significant. *e.g.*, in 852 cm, there are three significant figures and in 0.25 L there are two significant figures.
2. Zeros preceding to first non-zero digit are not significant. Such zero indicates the position of decimal point. *e.g.*, 0.03 has one significant figure and 0.0052 has one significant figure.
3. Zeros between two non-zero digits are significant *e.g.*, 3.007 has four significant figures.
4. Zeros at the end or right of a number are significant provided they are on the right side of the decimal point. *e.g.*, 0.200 g has three significant figures.

   But, if otherwise, the terminal zeros are not significant if there is no decimal point. *e.g.*, 100 has only one significant figure, but 10.0 has three significant figures and 100.0 has four significant figures. Such numbers are better represented in scientific notation. We can express the number 100 as 1×10^2 for one significant figure, 1.0×10^2 for two significant figures and 1.00×10^2 for three significant figures.
5. Counting numbers of objects, for example, 2 balls or 20 eggs, have infinite significant figures as these are exact numbers and can be represented by writing infinite number of zeros after placing a decimal *i.e.*, 2 = 2.000000 or 20 = 20.000000
6. In numbers written in scientific notation, all digits are significant *e.g.*, 4.01×10^2 has three significant figures.

Significant Figures in Calculations

1. **When adding or subtracting**, the number of decimal places in the answer should not exceed the number of decimal places in either of the numbers. *e.g.*,

$$\begin{array}{rl} 0.13 & \text{2 significant figures} \\ 1.5 & \text{2 significant figures} \\ 20.911 & \text{5 significant figures} \\ \hline 22.541 & \end{array}$$

   1.5 has only one digit after the decimal point and the result should be reported only up to one digit after the decimal point which is 22.5.

2. **In multiplication and division,** the significant figures in the answer should be the same as that in the quantity with the least number of significant figures.

   e.g.,

$$\frac{0.01208}{0.0236} = 0.512$$

   The number 0.0236 has only three significant figures that's why the answer must also be limited to three significant figures. Similarly, the product

$$132.07 \times 0.12 = 15.8484$$

   The answer 15.8484 should be reported as 15 because 0.12 has only two significant figures.

3. **When a number is rounded off,** the number of significant figures is reduced. The last digit retained is increased by 1 only if the following digit is > 5 and is left as such if the following digit is ≤ 4. *e.g.*,

$$12.696 \text{ can be written as } 12.7$$
$$13.93 \text{ can be written as } 13.9$$

   If the following digit is 5, left the number as such if it is even or add 1 if it is odd. *e.g.*,

$$18.35 \text{ can be written as } 18.4$$

Caution Point *While calculating the significant figures of numbers, it is better to convert them into scientific notation because exponential term does not contribute to the significant figures.*

Sample Problem 3 *If the density of a solution is 3.12 g* mL^{-1}*, the mass of 1.5 mL solution in significant figures is*

[NCERT Exemplar]

(a) 4.7 *g*
(b) 4680×10^{-3} *g*
(c) 4.680 *g*
(d) 46.80 *g*

Interpret (*a*) Mass = volume × density = 1.5 mL × 3.12 g mL^{-1}

= 4.68 g

The digit 1.5 has only two significant figures, so the answer must also be limited to two significant figures. Hence, it is rounded off to reduce the number of significant figures. Hence, the answer is reported as 4.7g.

Sample Problem 4 *How many significant figures should be present in the answer of the following calculations?* **[NCERT Exemplar]**

$$\frac{2.5 \times 1.25 \times 3.5}{2.01}$$

(*a*) 1
(*b*) 2
(*c*) 3
(*d*) 4

Interpret (*b*) Since the number with least significant figure *i.e.*, 2.5 or 3.5, has two significant figures, so answer must also be reported in two significant figures.

Note Here is no need to do complete calculation.

Various Systems of Measurement

(a) CGS System

It is also called **Gaussian system** and is based on centimetre (cm), gram (g) and second (s) as the units of length, mass and time respectively.

(b) FPS System

It is a British system which used foot (ft), pound (lb) and second (s) as the fundamental units of length, mass and time.

(c) MKS System

It is called MKSA system later on. It is the system, which uses metre (m), kilogram (kg) and second (s) respectively for length, mass and time; Ampere (A) was added later on for electric current.

(d) SI System

It is internationally accepted system in 1960s, hence called International system of units and contains following 7 basic and 2 supplementary units.

(i) **Basic units** includes metre (m) for length, kilogram (kg) for mass, second (s) for time, ampere (A) for electric current, kelvin (K) for thermodynamic temperature, mole (mol) for amount of substance and candela (Cd) for luminous intensity.

(ii) **Supplementary units** includes radian (rad) for angle and steradian (sr) for solid angle.

Sometimes submultiples and multiples are used to reduce or enlarge the size of the different units. The names and symbols of sub-multiples and multiples are listed in the table given below.

Table 1.1 **SI Prefixes**

Multiple	Prefix	Symbol	Multiple	Prefix	Symbol
10^{24}	yotta	Y	10^{-1}	deci	d
10^{21}	zetta	Z	10^{-2}	centi	c
10^{18}	exa	E	10^{-3}	milli	m
10^{15}	peta	P	10^{-6}	micro	μ
10^{12}	tera	T	10^{-9}	nano	n
10^{9}	giga	G	10^{-12}	pico	p
10^{6}	mega	M	10^{-15}	femto	f
10^{3}	kilo	k	10^{-18}	atto	a
10^{2}	hecto	h	10^{-21}	zepto	z
10	deca	da	10^{-24}	yocto	y

Derived Units

The units of all other quantities, which are derived from the above mentioned units, called the **fundamental units,** are called the derived units. *e.g,*

Units of volume $=$ length $\times$ breadth $\times$ height $= \mathrm{m}\times\mathrm{m}\times\mathrm{m} = \mathrm{m}^3$

Table 1.2 **Some Derived Properties and their Units**

Quantity	Definition of quantity	Expression in terms of SI base units
Area	Length squared	m^2
Volume	Length cubed	m^3
Density	Mass per unit volume	$\mathrm{kg / m^3}$ or $\mathrm{kg\ m^{-3}}$
Velocity	Distance travelled per unit time	m/s or $\mathrm{ms^{-1}}$
Acceleration	Velocity changed per unit time	$\mathrm{m/s^2}$ or $\mathrm{ms^{-2}}$
Force	Mass times acceleration of object	$\mathrm{kg\ m/s^2}$ or $\mathrm{kg\ ms^{-2}}$ (newton, N)
Pressure	Force per unit area	$\mathrm{kg/(ms^2)}$ or $\mathrm{kg\ m^{-1}s^{-2}}$ (pascal, Pa)
Energy (work, heat)	Force times distance travelled	$\mathrm{kg\ m^2/s^2}$ or $\mathrm{kg\ m^2s^{-2}}$ (joule, J)
Electric charge	Ampere times second	A-s (coulomb, C)
Electric potential	Energy per unit charge	J/(A-s) potential difference (volt, V)

Dimensional Analysis

In calculations, generally there is a need to convert units from one system to other. This can be done with the help of conversion factor, so the method used to accomplish this is called **factor label method** or **unit factor method** or **dimensional analysis.**

Information sought $=$ information given $\times$ CF

Some conversion factors [CCF] are as follows.

$$1\,\mathrm{m} = 39.37\ \mathrm{inch}$$
$$1\ \mathrm{inch} = 2.54\,\mathrm{cm}$$
$$1\mathrm{L} = 1000\ \mathrm{mL} = 1000\ \mathrm{cm}^3$$
$$= 10^{-3}\mathrm{m}^3 = 1\mathrm{dm}^3$$
$$1\,\mathrm{lb} = 453.59237\mathrm{g}$$
$$1\mathrm{J} = 1\mathrm{N-m} = 1\ \mathrm{kgm}^2\mathrm{s}^{-2}$$
$$1\mathrm{cal} = 4.184\ \mathrm{J} = 2.613\times 10^{19}\mathrm{eV}$$
$$1\mathrm{eV} = 1.602\times 10^{-19}\mathrm{J}$$
$$1\mathrm{eV/atom} = 96.485\ \mathrm{kJ\ mol^{-1}}$$
$$1\ \mathrm{u} = 1.66\times 10^{-27}\ \mathrm{kg}$$
$$= 931.5\ \mathrm{MeV}$$
$$1\ \mathrm{J} = 10^7\ \mathrm{erg}$$
$$1\ \mathrm{dyne} = 10^{-5}\ \mathrm{N}$$
$$1\ \mathrm{atm} = 101325\ \mathrm{Nm^{-2}} = 101325\ \mathrm{Pa}$$
$$1\ \mathrm{bar} = 1\times 10^5\ \mathrm{Nm^{-2}} = 1\times 10^5\ \mathrm{Pa}$$
$$1\ \mathrm{L\text{-}atm} = 101.3\ \mathrm{J} = 24.21\ \mathrm{cal}$$
$$1\ \mathrm{mol\ (gas)} = 22.4\ \mathrm{L\ at\ STP}$$
$$1\ \mathrm{mol\ (substance)} = N_A\ \mathrm{molecules}$$
$$1\ \mathrm{g\text{-}atom} = N_A\ \mathrm{atoms}$$
$$1\ \mathrm{K} = t^\circ\mathrm{C} + 273.15$$
$$t(^\circ\mathrm{F}) = \frac{9}{5}t^\circ\mathrm{C} + 32$$
$$1\ \mathrm{D\ (Debye)} = 1\times 10^{-18}\ \mathrm{esu\text{-}cm}$$
$$1\ \mathrm{g\text{-}cm^{-3}} = 1000\ \mathrm{kg\ cm^{-3}}$$

Caution Point *Remember that* CF *must always have the numerator and denominator representing equivalent quantities.*

Sample Problem 5 *If the speed of light is* $3.0\times 10^8\mathrm{ms^{-1}}$, *calculate the distance covered by light in* 2.00 *ns.*

[NCERT Exemplar]

(*a*) 6.0×10	(*b*) 0.6×10
(*c*) 0.06×10	(*d*) 60.0×10^{-1}

Interpret (*c*) $1\mathrm{ns} = 10^{-9}\mathrm{s}$

$$\text{Conversion factor} = \frac{10^{-9}\mathrm{s}}{1\mathrm{ns}}$$

$$2.00\mathrm{ns} = 2.00\mathrm{ns}\times\frac{10^{-9}\mathrm{s}}{1\mathrm{ns}}$$
$$= 2.00\times 10^{-9}\mathrm{s}$$

$$\text{Distance covered} = \text{speed x time}$$
$$= 3.0\times 10^8\ \mathrm{ms^{-1}}\times 2.0\times 10^{-9}\mathrm{s}$$
$$= 6.0\times 10^{-1}\ \mathrm{m} = 0.6\ \mathrm{m}$$

Sample Problem 6 *The relationship between picometer (pm) and nanometer (nm) is*

(*a*) 1 *nm* = 100.0 *pm*
(*b*) 1 *nm* = 10 *pm*
(*c*) 1 *pm* = 10 *nm*
(*d*) 1 *pm* = 100 *nm*

Interpret (*a*) $1\ \mathrm{pm} = 10^{-12}\ \mathrm{m}, 1\ \mathrm{nm} = 10^{-9}\ \mathrm{m}$

$$\text{Conversion factor} = \frac{10^{-12}\mathrm{m}}{1\mathrm{pm}}\ \text{and}\ \frac{1\mathrm{nm}}{10^{-9}\mathrm{m}}$$

$$1\mathrm{pm} = 10^{-12}\mathrm{m}\times\frac{1\mathrm{nm}}{10^{-9}\mathrm{m}}$$

$\Rightarrow$ $\quad 1\ \mathrm{pm} = 10^{-3}\mathrm{nm}$

or $\quad 1\ \mathrm{nm} = 1000\ \mathrm{pm}$

Sample Problem 7 *Pressure is determined as force per unit area of the surface. The SI unit of pressure, pascal is as shown below.*

$$1\ \text{Pa} = 1\ \text{Nm}^{-2}$$

If the mass of air at sea level is 1034gcm^{-2}, *calculate the pressure in pascal.* **[NCERT]**

(a) 1.01×10^5
(b) 1.01×10^4
(c) 2.32×10^5
(d) 1.03×10^5

Interpret (a) Pressure is the force or weight per unit area.

$$\text{Pressure} = \frac{1034\text{g}\times 9.8\text{ms}^{-2}}{\text{cm}^2}$$

$$= \frac{1034\ \text{kg}\times 100\times 100\times 9.8\ \text{ms}^{-2}}{1000\ \text{m}^2}$$

$$= 101332.0\ \text{Nm}^{-2} \qquad (1\ \text{N} = \text{kg ms}^{-2})$$

$$= 1.01332\times 10^5\ \text{Pa}$$

Laws of Chemical Combinations

The combination of elements to form compounds is governed by following basic laws.

Law of Conservation of Mass
(by Lavoisier)

According to this law the matter can neither be created nor destroyed in a chemical reaction.

Law of Definite Proportions (by J. Proust)

"A sample of a pure compound always consists of the same elements combined in same proportions by mass, whatever be its source."

e.g., ammonia always has the formula NH_3 *i.e.*, one molecule of NH_3 always contains one atom of nitrogen and three atoms of hydrogen or 17.0 g of NH_3 always contains 14 g of nitrogen and 3 g of hydrogen. These findings always remain the same for NH_3.

Law of Multiple Proportions
(by John Dalton)

An element may form more than one compound with another element. For a given mass of an element, the masses of other elements (in two or more compounds) come in the ratio of small integers."

This is called law of multiple proportions. *e.g.*, in NH_3, 14 g of nitrogen requires 3 g of hydrogen and in hydrazine (N_2H_4) 14 g of nitrogen requires 2 g of hydrogen. Hence, fixed mass of nitrogen requires hydrogen in the ratio 3 : 2 in two different compounds (3 : 2 is a simple ratio). Thus, this is in agreement with "law of multiple proportions".

Gay Lussac's Law of Gaseous Volumes

The volume of reactants and products in a large number of chemical reactions are related to each other by small integers, provided the volumes are measured at same temperature and pressure".

These lines are considered as the law of definite proportions by volume given by Gay-Lussac, a French chemist. *e.g.*, in the reaction of hydrogen with oxygen to produce water, it was found that 2 vol of H_2 combines with 1 vol of O_2 to form 2 vol of H_2O (steam). This simply means that 100 mL of H_2 gas combines with 50 mL of O_2 to produce exactly 100 mL of steam (if volume of all the gases are measured at same temperature and pressure).

Avogadro's Law

"The volume of a gas (at constant pressure and temperature) is proportional to the number of moles (or molecules) of gas present".

According to this law

$$V \propto n$$

where, $n =$ number of moles of gas

In simpler words, the law can also be stated as "equal volumes of all gases, under the same conditions of temperature and pressure contain equal number of molecules" which is infact 6.023×10^{23} or in multiples of it.

Caution Point *Law of definite proportions and law of multiple proportions do not hold good when same compound is prepared by different isotopes of the same element, e.g.,* H_2O *and* D_2O *or* $H_2\overset{16}{O}$ *and* $H_2\overset{18}{O}$. *Moreover, law of conservation of mass does not hold good for nuclear reactions.*

Sample Problem 8 *Which of the following reactions is not correct according to the law of conservation of mass?* **[NCERT Exemplar]**

(a) $2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$
(b) $C_3H_8(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(g)$
(c) $P_4(s) + 5O_2(g) \longrightarrow P_4O_{10}(s)$
(d) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$

Interpret (b) In equation,

$$\begin{array}{ccc} C_3H_8(g) + O_2(g) & \longrightarrow & CO_2(g) + H_2O(g) \\ 44\text{g}\ +32\text{g} & & 44\ +18 \end{array}$$

i.e., mass of reactants ≠ mass of products. Hence, law of conservation of mass is not followed.

Sample Problem 9 *The following data are obtained when dinitrogen and dioxygen react together to form different compounds.*

S. No.	Mass of dinitrogen	Mass of dioxygen
(*i*)	14g	16g
(*ii*)	14g	32g
(*iii*)	28g	32g
(*iv*)	28g	80g

Which law of chemical combination is obeyed by the above experimental data? [**NCERT**]

(a) *Law of multiple proportions*

(b) *Law of conservation of mass*

(c) *Law of definite proportions*

(d) *All of the above*

Interpret (*a*) On fixing the mass of dinitrogen as 28g, the masses of dioxygen combined are 32, 64, 32 and 80 in the given four oxides. These are in the simple whole number ratio *i.e.*, 2 : 4 : 2 : 5. Hence, the given data obey the law of multiple proportions.

1.3 Atomic and Molecular Masses

Atomic Mass

Dalton gave the idea of atomic masses in relative terms, *i.e.*, the average mass of one atom relative to the average mass of the other. We can make accurate measurement of mass by comparing mass of an atom with the mass of a particular atom chosen as standard. On the present atomic mass scale, ^{12}C is chosen as standard and is arbitrarily assigned the mass of 12 atomic mass unit (amu).

$\therefore$ Atomic mass

$$= \frac{\text{mass of one atom of the element}}{\frac{1}{12}\text{th part of the mass of one atom of C}-12}$$

Therefore, one amu or u (unified mass) is equal to exactly the 1/12th of the mass of ^{12}C atom.

$$1\text{ u} = \frac{1}{12} \times \frac{12\text{ g}}{6.022 \times 10^{23}}$$

$$= 1.66 \times 10^{-24}\text{ g}$$

Since most of the elements have isotopes, the atomic mass of an element is, infact, the average of masses of its all the naturally occurring isotopes, so generally in fractions e.g., If an element exists in three isotopic forms having atomic masses, m_1, m_2 and m_3 in the ratio, x, y and z, the average atomic mass,

$$M_{av} = \frac{m_1 \times x + m_2 \times y + m_3 \times z}{x + y + z}$$

If in place of ratio, relative abundance is given, the

$$M_{av} = \frac{m_1 \times r_1 + m_2 \times r_2 + m_3 \times r_3}{r_1 + r_2 + r_3}$$

Here, r_1, r_2 and r_3 = relative abundances of the isotopes.

The approximate atomic mass of solid elements except Be, B, C and Si, is related to specific heat as

$$\text{Average atomic mass} = \frac{6.4}{\text{specific heat}}$$

This is called **Dulong and Petit's method.**

Mass spectrometer is used to determine the atomic mass experimentally.

Molecular Mass

Molecular mass is the sum of atomic masses of the elements present in a molecule. It is obtained by multiplying the atomic mass of each element by the number of its atoms and adding them together *e.g.*,

Molecular mass of glucose ($C_6H_{12}O_6$)

$$= 6(12.011\text{u}) + 12(1.008\text{u}) + 6(16.00\text{u})$$

$$= (72.066\text{u}) + (12.096\text{u}) + (96.00\text{u})$$

$$= 180.162\text{u}$$

Formula Mass

The formula mass of a substance is the sum of the atomic masses of all atoms in the formula unit of the compound. It is normally calculated for ionic compounds. *e.g.*, formula mass of NH_3 is $14 + 3 = 17$ amu or 17u

or formula mass of NaCl is

$$23 + 35.5 = 58.5\text{ amu or } 58.5\text{u}.$$

Check Point 1

1. How many millimetres are there in 14.0 cm?
2. Explain why in calculations involving more than one arithmetic operation, rounding off to the proper number of significant figures may be done once at the end if all the operations are multiplications or divisions or if they are all additions and subtractions, but not if they are combinations of additions or subtractions with divisions or multiplications?
3. Why do atomic masses of most of the elements in atomic mass unit be in fractions?
4. On analysis it was found that the black oxide of copper and red oxide of copper contain 79.9% and 88.8% of copper respectively. This data is in accordance with which law of combination?

1.4 **Equivalent Mass** or **Equivalent Weight**

The number of parts of a substance that combines with or displaces, directly or indirectly, 1.008 parts by mass of hydrogen or 35.5 parts by mass of chlorine or 8 parts by mass of oxygen is called the equivalent mass of the substance. Mathematically,

$$\frac{\text{Eq. wt. of substance } A}{\text{Eq. wt. of substance } B} = \frac{\text{Wt. of substance } A}{\text{Wt. of substance } B}$$

If A is metal and B is H (or O or Cl) then

$$\text{Eq. wt. of metal } = \frac{\text{mass of metal}}{\text{mass of hydrogen displaced}} \times 1.008$$

$$\text{or} \quad = \frac{\text{mass of metal}}{\text{mass of oxygen combined}} \times 8.0$$

$$\text{or} \quad = \frac{\text{mass of metal}}{\text{mass of chlorine combined}} \times 35.5$$

Equivalent weight of acid

$$= \frac{\text{molecular weight of acid}}{\text{basicity (number of replaceable H}^+)}$$

e.g., Equivalent weight of $H_2SO_4 = \frac{98}{2} = 49$

Equivalent weight of base

$$= \frac{\text{molecular weight of base}}{\text{acidity (number of replaceable OH}^-)}$$

e.g., Equivalent weight of $NaOH = \frac{40}{1} = 40$

$$\text{Eq. wt. of salt} = \frac{\text{molecular weight of salt}}{\text{total positive valency of metal atoms}}$$

e.g., Equivalent weight of $NaCl = \frac{58.5}{1} = 58.5$

Equivalent weight of $Na_2CO_3 = \frac{106}{2} = 53$

Equivalent weight of a substance that undergoes

$$\text{oxidation/ reduction} = \frac{\text{molecular weight}}{\text{change in oxidation number}}$$

e.g., When $KMnO_4$ reacts under acidic conditions, change in oxidation number (from +7 to +2) is 5, hence;

Equivalent weight of $KMnO_4$ in acidic medium

$$= \frac{158}{5} = 31.6$$

For volatile metal chlorides, eq. wt. and atomic weight are related as

$$\text{Atomic wt.} = \text{eq. wt.} \times \text{valency}$$

Caution Points

(*i*) *Atomic and molecular masses of elements and compounds are always constant but equivalent mass may vary with change of valency.*

(*ii*) *The valencies of elements forming isomorphous compounds (i.e., the compounds that have similar constitution and chemical formulae) are same. e.g., valencies of* Cr, Se *and* S *in* K_2CrO_4, K_2SeO_4 *and* K_2SO_4 *are same.*

Sample **Problem 10** 0.5 *g of a metal on oxidation gave* 0.79 *g of its oxide. The equivalent weight of the metal is*

(*a*) 10 (*b*) 14
(*c*) 20 (*d*) 40

Interpret (*b*) $\text{Eq. wt.} = \frac{\text{wt. of metal}}{\text{wt. of oxygen combined}} \times 8$

$$= \frac{0.5}{0.79 - 0.5} \times 8 \approx 14$$

Sample **Problem 11** *The equivalent weight of iron in* Fe_2O_3 *would be*

(*a*) 18.6 (*b*) 28
(*c*) 56 (*d*) 112

Interpret (*a*) $\text{Eq. wt. of metal} = \frac{\text{atomic wt.}}{\text{valency}} = \frac{56}{3} = 18.6$

Hot Spot 1

MOLE Concept

Mole concept is an important topic for JEE Main examination and a small practice can help you in solving problems based on this topic very quickly as the level of questions is easy to average.

While solving problems based on mole concept, always keep in mind

(i) Convert all in same unit, *i.e.*, mol/atoms/mass and then compare.
(ii) Moles $\propto$ molecules

The word **mole** was introduced around 1896 by **W. Ostwald** who derived it from Latin word **moles** means a **heap** or **pile.** In 1967 this word was accepted as a unit of chemical substances under SI system. It is represented by the symbol **mol.**

One mole of object will always mean 6.023×10^{23} of those objects. The number of object per mole, 6.023×10^{23} mol^{-1} is called **Avogadro's Number/Constant** represented by N_A.

Thus, one mole of any substance is defined as

(i) The amount which weighs exactly same as its formula weight in gram or atomic mass in gram or molecular mass in gram.
(ii) The amount which has same number of entities (atoms, molecules or other particles) as there are atoms in exactly 0.012 kg (or 12 g) of carbon-12 isotope (*i.e.,* 6.023×10^{23} entities).
(iii) The amount which occupies 22.4 L at STP (if it is taken for a gas).

The formulae used to convert amount of substance into moles are

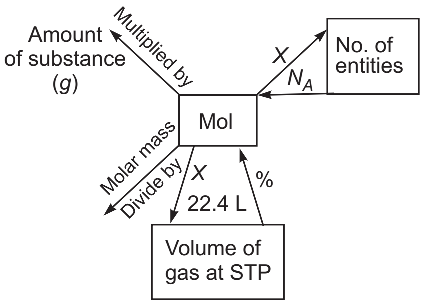
$$\text{Number of moles of molecule} = \frac{\text{weight in gram}}{\text{molecular weight}}$$

$$\text{Number of moles of atoms} = \frac{\text{weight in gram}}{\text{atomic weight}}$$

$$\text{Number of moles} = \frac{\text{number of particles}}{\text{Avogadro's number}}$$

$$\text{or Number of moles of gases} = \frac{\text{volume of gas at STP (in L)}}{22.4}$$

As in atoms and molecules, mole concept is also applicable to ionic compounds, which do not contain molecules. In such cases, the formula of any ionic compound is representation of ratio between constituent ions. One mole of an ionic compound is represented by 6.023×10^{23} formula units.



Flow chart showing conversion of mole in other units

One mole of NaCl = 6.023×10^{23} NaCl units

$= 6.023 \times 10^{23}$ units of $Na^+ + 6.023 \times 10^{23}$ units of Cl^-

Mass of one mole of NaCl $= 23.0\text{g} + 35.5\text{g}$

$= 58.5$ g NaCl

Sample **Problem 12** *The number of atoms present in one mole of an element is equal to Avogadro number. Which of the following element contains the greatest number of atoms?* **[NCERT Exemplar]**

(*a*) 4 g He (*b*) 46 g Na
(*c*) 0.4 g Ca (*d*) 12 g He

Interpret (*d*) For comparing number of atoms, first we calculate the moles as all are monoatomic and hence, moles $\times N_A =$ number of atoms.

$$\text{Moles of 4g He} = \frac{4}{4} = 1 \text{ mol}$$

$$\text{46g Na} = \frac{46}{23} = 2 \text{ mol}$$

$$\text{0.40 g Ca} = \frac{0.40}{40} = 0.1 \text{ mol}$$

$$\text{12g He} = \frac{12}{4} = 3 \text{ mol}$$

Therefore, number of atoms are highest in 12g He as it has the maximum number of moles.

Various Concentration Terms

Different concentration terms are given below:

(a) **Normality** (N)

It is defined as the number of g-equivalents of solute per litre of solution or as the number of mg-equivalents of a substance per millilitre of solution. *e.g.,* 0.12 N H_2SO_4 means a solution which contains 0.12 g-equivalent of H_2SO_4 per litre of solution. This also means that each millilitre of this solution can react, for example, with 0.12 mg eq. of CaO or with 0.12 mg-eq. of Na_2CO_3.

Thus,

$$\text{Normality } N = \frac{\text{g-equivalent of solute}}{\text{volume of solution (in L)}}$$

or

$$= \frac{\text{g-equivalent of solute}}{\text{volume of solution (in mL)}} \times 1000$$

If specific gravity is known, normality is calculated as

$$\text{Normality} = \frac{\text{specific gravity} \times \%\text{ strength} \times 10}{\text{equivalent weight}}$$

(b) **Molarity** (*M*)

It is defined as the number of moles of solute per litre of solution or the same numerically, as the number of mg-molecules per millilitre of solution. The molarity is usually designated by *M, e.g.,* if the molarity of H_3PO_4 is 0.18, it means a concentration corresponding to 0.18 mol of H_3PO_4 per litre of solution.

Thus, molarity is given as

$$\text{Molarity, } M = \frac{\text{moles of solute}}{\text{volume of solution (in L)}}$$

If specific gravity is given,

$$\text{Molarity} = \frac{\text{specific gravity} \times \%\text{ strength} \times 10}{\text{molecular weight}}$$

(c) **Formality** (*F*)

It is practically same as molarity.

$$\text{Formality} = \frac{\text{gram formula weight}}{\text{volume in litre}}$$

(d) **Molality** (*M*)

It is defined as the number of moles of solute dissolved in 1000 g of the solvent. It is designated by *m*. Molality is independent of temperature, as it depends only upon the mass which does not vary with temperature.

$$\text{Molality, } m = \frac{\text{moles of solute}}{\text{weight of solvent (in g)}} \times 1000$$

Formulae Used to Calculate the **Number of Moles**

1. Number of millimoles = molarity × volume in mL

or $$\text{Moles} = \frac{\text{millimoles}}{1000}$$

2. Number of equivalents of a substance

$$= \frac{\text{weight (g)}}{\text{equivalent weight}}$$

3. Number of milli-equivalent

$$(\text{Meq}) = \frac{1000 \times \text{weight (g)}}{\text{equivalent weight}}$$

$$= \text{normality} \times \text{volume (mL)}$$

4. Normality = molarity × balance factor (*y*).
where, *y* = acidity/basicity/number of replaceable H-atoms/change in oxidation number.

5. Number of equivalents = *y* × number of moles

6. Number of milli-equivalents = *y* × number of millimoles
where, *y* is same as for formula (4).

7. Mole fraction of solute in the solution $= \frac{n}{n+N}$

where, *n* = moles of solute, *N* = moles of solvent

For very dilute solutions,

$$\text{Mole fraction of solute in solution} = \frac{Mm}{1000}$$

where, *M* = molecular weight of solvent, *m* = molality

8. Density of solution

$$= \text{molarity}\left(\frac{1}{\text{molality}} + \frac{\text{molecular weight of solute}}{1000}\right)$$

9. Per cent by weight of solute in solution

$$= \frac{\text{weight of solute (g)} \times 100}{\text{weight of solution (g)}}$$

10. Percent by volume of solute in solution

$$= \frac{\text{weight of solute (g)} \times 100}{\text{volume of solution (mL)}}$$

11. 1 mL, 1 N $KMnO_4 \equiv$ 1 mL, 1 N H_2O_2

12. 1 mL, 1 N $Na_2S_2O_3 \equiv$ 1 mL, 1 N I_2 solution

13. 1 volume H_2O_2 = 0.1785 N H_2O_2

14. If two compounds *A* and *B* neutralise completely each other then

milli-equivalents of *A* = milli-equivalents of *B*

15. Molecular weight = 2 × vapour density (for gaseous phase).

Sample Problem 13 *If the concentration of glucose ($C_6H_{12}O_6$) in blood is 0.9 g L^{-1} what will be the molarity of glucose in blood?* **[NCERT Exemplar]**

(*a*) 5 M (*b*) 50 M (*c*) 0.005 M (*d*) 0.5 M

Interpret (*c*) 0.9 gL^{-1} means,

1000 mL (or 1L) solution contains glucose = 0.9 g glucose

$$= \frac{0.9}{180} \text{ mol glucose}$$

$$= 5 \times 10^{-3} \text{ mol glucose}$$

i.e., 1 L solution contains 0.005 mole glucose or the molarity of glucose is 0.005 M.

Sample Problem 14 *Calculate the mass of sodium acetate,* CH_3COONa *required to make 500 mL of 0.375 molar aqueous solution. Molar mass of sodium acetate is* 82.0245 g mol^{-1}. **[NCERT]**

(*a*) 18.12 g (*b*) 15.38 g
(*c*) 16.19 g (*d*) 12.11 g

Interpret (*b*) $\text{Molarity} = \dfrac{w \times 1000}{m \times \text{volume of solution(mL)}}$

where, w = mass of solute and *m* = molar mass of solute
Given, molarity of the solution = 0 .375 M
Molar mass of solute, *M* = 82.0245g mol^{-1}
Volume of solution = 500 mL

$$\therefore \text{ Mass of solute, } w = \frac{0.375 \times 82.0245 \times 500}{1000}$$

$$= 15.379 \text{ g} \approx 15.38\text{g}$$

Sample Problem 15 *Calculate the concentration of nitric acid in mol per litre in a sample which has a density,* 1.41 g mL^{-1} *and the mass per cent of nitric acid in it being* 69%. **[NCERT]**

(*a*) 15.4 M (*b*) 10.9 M (*c*) 5.43 M (*d*) 18.21 M

Interpret (*a*)

Given, $d = 1.14$ g mL^{-1}, mass % of HNO_3 = 69%

69% HNO_3 means 100g of its solution contains 69 g HNO_3 (nitric acid).

Hence, mass of HNO_3 (solute) = 69 g

Molar mass of nitric acid,

$$HNO_3 = 1.0079 + 14.0067 + (3 \times 16.00)$$

$$= 63.0146 \text{ g mol}^{-1}$$

$$\text{Density,} \quad d = \frac{m}{V}$$

$$\text{or} \quad V = \frac{m}{d} = \frac{100 \text{ g}}{1.41 \text{ g mL}^{-1}} = \frac{100}{1.41} \text{ mL}$$

$$\text{Molarity} = \frac{w \times 1000}{m \times \text{volume of solution (mL)}}$$

$$= \frac{69 \times 1000 \times 1.41}{63.0146 \times 100} = 15.439\text{M}$$

Note Concentration of a substance in mol per liter is known as molarity.

Alternative method

$$\text{Molarity} = \frac{\text{density} \times \text{mass per cent} \times 10}{\text{molar mass of solute}}$$

$$= \frac{1.14 \times 69 \times 10}{63.0146} = 15.439 \text{ M}$$

Sample Problem 16 *Sulphuric acid reacts with sodium hydroxide as follows.*

$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$$

When 1 L of 0.1 M sulphuric acid solution is allowed to react with 1 L of 0.1 M sodium hydroxide solution, the amount of sodium sulphate formed and its molarity in the solution obtained are **[NCERT Exemplar]**

(*a*) 0.1 mol L^{-1}, 3.55 g (*b*) 0.025 mol L^{-1}, 7.10 g
(*c*) 0.01 mol L^{-1}, 5.33 g (*d*) 0.25 mol L^{-1}, 5.33 g

Interpret (*b*) Moles of H_2SO_4 = 1L × 0.1M = 0.1 mol

moles of NaOH = 1L × 0.1M = 0.1 mol

$$\begin{array}{cccc} H_2SO_4 + & 2NaOH & \longrightarrow & Na_2SO_4 + 2H_2O \\ 1\text{mol} & 2 \text{ mol} & & 1 \text{ mol} \\ 0.1\text{mol} & 0.1\text{mol} & & 0.05 \text{ mol} \end{array}$$

$$\therefore \text{Molarity mass of } Na_2SO_4 = 0.05 \times 142$$

$$= 7.1\text{g } (\because \text{Molar mass of } Na_2SO_4 = 142 \text{ mol g mol}^{-1})$$

$$\text{Molarity} = \frac{\text{moles of } Na_2SO_4}{\text{volume of solution}} = \frac{0.05}{1+1} = 0.025 \text{ mol L}^{-1}$$

Sample Problem 17 *If 500 mL of a 5 M solution is diluted to 1500 mL, what will be the molarity of the solution obtained?* **[NCERT Exemplar]**

(*a*) 1.5 M (*b*) 1.66 M (*c*) 0.017 M (*d*) 1.59 M

Interpret (*b*) For dilution,

$$\underset{\text{(before dilution)}}{M_1V_1} = \underset{\text{(after dilution)}}{M_2V_2}$$

$$500 \times 5\text{M} = 1500 \times M$$

$$M = \frac{5}{3} = 1.66 \text{ M}$$

Sample Problem 18 *Calculate the molarity of a solution of ethanol in water in which the mole fraction of ethanol is* 0.040. **[NCERT]**

(*a*) 2.314 (*b*) 1.123 (*c*) 3.139 (*d*) 1.762

Interpret (*a*) Molarity is defined as the moles of solute (ethanol) in 1 L of the solution.

1 L of ethanol solution (as it is diluted) = 1 L of water

$$\text{Number of moles of } H_2O \text{ in 1 L water} = \frac{1000 \text{ g}}{18} = 55.55 \text{ moles}$$

For a binary solution (binary solution contains two components)

$$X_1 + X_2 = 1$$

$$\text{Hence,} \quad X_{H_2O} = 1 - X_{C_2H_5OH}$$

$$X_{H_2O} = 1 - 0.040 = 0.96$$

$$X_{H_2O} = \frac{n_{H_2O}}{n_{H_2O} + n_{C_2H_5OH}}$$

$$0.96 = \frac{55.55}{55.55 + n_{C_2H_5OH}}$$

$$53.328 \;+ 0.96 n_{C_2H_5OH} \;=\; 55.55$$

$$0.96 n_{C_2H_5OH} \;=\; 55.55 - 53.328 \;=\; 2.222$$

$$n_{C_2H_5OH} \;=\; \frac{2.222}{0.96}\; 2.3145 \text{ mol}$$

Sample Problem 19 *One mole of any substance contains* 6.022×10^{23} *atoms/molecules. Number of molecules of* H_2SO_4 *present in 100 mL 0.02M* H_2SO_4 *solution is* **[NCERT Exemplar]**

(a) 12.044×10^{20} molecules (b) 6.022×10^{23} molecules
(c) 1×10^{23} molecules (d) 12.044×10^{23} molecules

Interpret (a) Number of millimoles of H_2SO_4 = molarity × volume in mL

$$= 0.02 \times 100 = 2 \text{ millimol} = 2 \times 10^{-3} \text{ mol}$$

$$\text{Number of molecules } = \text{Number of moles} \times N_A$$
$$= 2 \times 10^{-3} \times 6.022 \times 10^{23} = 12.044 \times 10^{20} \text{ molecules}$$

Sample Problem 20 *Mole fraction of* I_2 *in benzene is 0.1. The molality of* I_2 *in* C_6H_6 *is*

(a) 1.42 (b) 3.205
(c) 2.06 (d) 1.86

Interpret (a) Mole fraction of $I_2 = \left[\dfrac{n}{n+N}\right] = 0.1$ ...(i)

$$\text{Mole fraction of benzene } = \left[\frac{N}{n+N}\right] = 0.9 \qquad \text{...(ii)}$$

where, n and N are moles of I_2 and C_6H_6 in solution respectively.

$$\text{molality,} \qquad m = \frac{1000 \times \text{mole fraction of } I_2}{(1 - \text{mole fraction of } I_2) \times M}$$

$$= \frac{1000 \times 0.1}{0.9 \times 78} = 1.42 \text{ m}$$

Molar Mass and Molar Volume

Molar mass of an element is defined as mass of 1 mole of that element, *i.e.*, mass of 6.023×10^{23} entities or particles of that element. *e.g.*, molar mass of oxygen = 32 g/mol, that means 6.023×10^{23} molecules of oxygen weigh 32 g, or molar mass of Na = 23 g/mol, that means 6.023×10^{23} monoatomic molecules of Na weigh 23 g.

When molar mass is divided by density, molar volume is obtained. It is the volume of one mole of a substance. Since molar volumes of solids and liquids do not vary much with temperature and pressure, these can be calculated easily by the following relation :

$$\text{Molar volume} = \frac{\text{molar mass}}{\text{density}}$$

The molar volumes of gases, change considerably with temperature and pressure. For an ideal gas, the molar volume at $0°C$ and 1 atm pressure is 22.4 L.

Percentage Composition of Compounds

Percentage composition of the compounds is the relative mass of the each of the constituent elements in 100 parts of it. It is readily calculated from the formula of the compound. Mass percentage of an element

$$= \frac{\text{mass of that element in the compound} \times 100}{\text{molar mass of the compound}}$$

Sample Problem 21 *What is the mass per cent of carbon in carbon dioxide?* **[NCERT Exemplar]**

(a) 0.034% (b) 3.4%
(c) 27.27% (d) 28.7%

Interpret (c) In order to solve such problem, first write the formula of molecule/compound.

The formula of carbon dioxide = CO_2

Molecular mass of $CO_2 = 12.0 + 16.0 \times 2 = 44 \text{ g mol}^{-1}$

$$\text{Atomic mass of C} = 12.0 \text{ g atom}^{-1}$$

$$\text{Percentage of C} = \frac{12}{44} \times 100 = 27.27\%$$

Sample Problem 22 *How much copper can be obtained from 100 g of copper sulphate* $(CuSO_4)$ *?* **[NCERT]**

(a) 63.54 g (b) 31.77 g
(c) 39.81 g (d) 79.62 g

Interpret (c) Molar mass of $CuSO_4 = 63.54 + 32.06 + (4 \times 16)$
$= 159.6 \text{ g mol}^{-1}$

$$159.6 \text{ g } CuSO_4 \text{ contains } 63.54 \text{ g Cu}$$

$$1 \text{ g } CuSO_4 \text{ contains } \frac{63.54}{159.6} \text{ g Cu}$$

$$100 \text{ g } CuSO_4 \text{ contains } \frac{63.54 \times 100}{159.6} = 39.81 \text{g Cu}$$

1.5 Empirical and Molecular Formulae

The chemical formula of a compound which shows relative number of atoms in its simplest ratio is called **empirical formula.**

The chemical formula of a compound which gives the actual number of atoms of each element in a molecule is called its **molecular formula.** It is important to note that the molecular formula is generally an integral multiple of the empirical formula, *i.e.*,

$$\text{Molecular formula} = (\text{empirical formula}) \times n$$

where, $n = 1, 2, 3, \ldots$ etc.

The molecular formula conveys two informations mainly :

1. The relative number of each type of atoms in a molecule.
2. The total of atoms of each element in the molecule.

Deriving Molecular & Empirical Formula

Use the following steps to determine the empirical formula of the compound.

1. Calculate the amount of elements and their percentage composition.
2. Divide the percentage of each element by its atomic mass. It gives atomic ratio of the elements present in the compound.
3. Divide the atomic ratio of each element by the minimum value of atomic ratio as to get simplest ratio of the atoms of elements present in the compound.
4. If the simplest ratio is fractional, then multiply the values of simplest ratio of each element by a smallest integer to get a simplest whole number for each of the element.
5. To get the empirical formula, write symbols of various elements present side by side with their respective whole number ratio as a subscript to the lower right hand corner of the symbol.

Deriving Molecular Formula

The molecular formula of a substance may be determined from the empirical formula if the molecular mass of the substance is known. The molecular formula is always a simple multiple of empirical formula and the value of simple multiple is obtained by dividing molecular mass with empirical formula mass.

Sample **Problem 23** *A welding fuel gas contains carbon and hydrogen only. Burning a small sample of it in oxygen gives* 3.38 *g carbon dioxide,* 0.690 *g of water and no other products. A volume of* 10.0 *L (measured at STP) of this welding gas is found to weigh* 11.6 *g. The molecular formula of the compound is* **[NCERT]**

(*a*) CH (*b*) CH_2

(*c*) C_2H_2 (*d*) CH_4

Interpret (*c*) (i) 44 g CO_2 contains 12 g carbon

$$3.38 \text{ g } CO_2 \text{ contains } \frac{12}{44} \times 3.38 \text{ g} = 0.9218 \text{ g carbon}$$

$$18 \text{ g } H_2O \text{ contains } 2 \text{ g hydrogen}$$

$$0.690 \text{ g } H_2O \text{ contains } \frac{2}{18} \times 0.690 \text{ g} = 0.0767 \text{ g hydrogen}$$

Total mass of compound = 0.9218 + 0.0767 = 0.9985g (because compound contains only carbon and hydrogen).

$$\text{Percentange of C in the compound} = \frac{0.9218}{0.9985} \times 100 = 92.32$$

$$\text{Percentange of H in the compound} = \frac{0.0767}{0.9985} \times 100 = 7.68$$

Calculation for Empirical Formula

Element	Per cent by mass	Atomic mass	Relative number of moles of elements	Simplest molar ratio
C	92.32	12	$\frac{92.32}{12} = 7.69$	$\frac{7.69}{7.68} \approx 1$
H	7.68	1	$\frac{7.68}{1} = 7.68$	$\frac{7.68}{7.68} = 1$

Hence, empirical formula = CH

(ii) Calculation for molar masss of the gas

10.0 L of the given gas at STP weigh = 11.6 g

∴ 22.4 L of the given gas at STP will weigh

$$= \frac{11.6 \times 22.4}{10} = 25.984 \text{ g}$$

$$\text{Molar mass} = 25.984 \approx 26 \text{ g mol}^{-1}$$

(iii) Empirical formula mass (CH) = 12 + 1 = 13

$$\therefore \quad n = \frac{\text{molecular mass}}{\text{empirical formula mass}} = \frac{26}{13} = 2$$

Hence, molecular formula $= n \times CH = 2 \times CH = C_2H_2$

Sample **Problem 24** *A compound having empirical formula* $(C_3H_4O)_n$ *has vapour density* 84. *The molecular formula of this compound is*

(*a*) C_3H_4O

(*b*) $C_6H_8O_2$

(*c*) $C_6H_{12}O_3$

(*d*) $C_9H_{12}O_3$

Interpret (*d*) Molecular mass $= 2 \times VD = 2 \times 84 = 168$

$$n = \frac{\text{molecular mass}}{\text{empirical formula mass}} = \frac{168}{12 \times 3 + 4 + 16} = \frac{168}{56} = 3$$

Thus, molecular formula $= (C_3H_4O)_3 = C_9H_{12}O_3$

Hot Spot 2

CHEMICAL EQUATIONS and Stoichiometry

Stoichiometry is the most important topic of this chapter. Generally questions are seen from this topic. The level of question is from moderate to typical.

Calculations based on the quantitative relationship between the reactants and products are referred as **stoichiometry.** (Stoichiometry from Greek words *stoichion* = element; *metron* = measure). Solving of stoichiometric problems require a firm grasp of mole concept, balancing chemical equations and care in consistent use of units.

The numerals used to balance a chemical equation are called **stoichiometric coefficients.** The goal of these calculations is to predict the relationship between the amounts of the reactants and products of chemical reaction.

Always remember, never lose your goal while solving such problems. Use mole concept carefully and then also find type of stoichiometric problem before solving.

To solve out stoichiometric problems, follow a right approach that is based on a few relatively easy ground rules, which can be understood by following sample problem.

Sample **Problem 25** *Predict the amount of oxygen that must be inhaled to digest (burn) 100 of sugar. The sugar burns according to the following equation.*

$$C_{12}H_{22}O_{11}\,(s) + 12\,O_2\,(g) \longrightarrow 12\,CO_2\,(g) + 11H_2O(l)$$

(*a*) 95.28 *g*
(*b*) 112. 28 *g*
(*c*) 125 *g*
(*d*) 35.12 *g*

Interpret (*b*) Follow the following steps to solve such type of problems.

Step I	Identify the goal of the problem. *e.g.,* in the above problem.	Find out how many grams of O_2 are consumed when 100 g of sugar is burned?
Step II	Write down the key elements of the problem, or draw a simple picture that summarizes the key information in the problem.	We have 100 g of sugar. Sugar has formula $C_{12}H_{22}O_{11}$. We know molar equation.
Step III	Try to do what can be done.	We can convert the mass (100 g) in moles, as we know molar mass of $C_{12}H_{22}O_{11}$. *i.e.,* $\frac{100}{342} = 0.29$ mol
Step IV	Do not try to do impossible.	There is no way to get moles of oxygen directly form moles of sugar in one step.
Step V	Never lose sight of what you have accomplished.	*What else we can do*? We know the molar relationship of O_2 and sugar in balance chemical equation. We can calculate the number of moles of oxygen needed to burn 0.29 mole of sugar as, $0.29 \times \frac{12}{1} = 3.48$ mole of O_2.
Step VI	Don't try to work the problem in your head. Write down all the intermediate steps.	Now we can calculate the weight of O_2 as $3.48 \times 32 = 112.28$ g O_2

Limiting Reactant or Limiting Reagent

If a reaction involves two or more reactants, the reactant that is consumed first is called **limiting reagent** or **limiting reactant** as it limits the amount of product formed. *e.g.,* A limiting reactant is like a part in an automobile factory, if there are 1000 head lights and 600 car bodies, then the maximum number of automobile will be limited by the number of headlights. Because each body requires two headlights and the headlights are available only for 500 cars. So the headlights play the role of limiting reagents.

Calculation of Limiting Reagent

This can be best understood by considering the following sample problem.

Sample **Problem 26** *Dinitrogen and dihydrogen react with each other to produce ammonia according to the following chemical equation,*

$$N_2(g) + 3H_2\,(g) \longrightarrow 2NH_3(g)$$

Calculate the mass of ammonia produced if 2.00×10^3 *g dinitrogen reacts with* 1.00×10^3 *g of dihydrogen.*

[NCERT]

(*a*) 8.1 *g*
(*b*) 3.4 *g*
(*c*) 1.8 *g*
(*d*) 2.4 *g*

Interpret (*d*) To find the limiting reagent, we have to follow the following sequence of steps

Step I Consider the possibility that there may be a limiting amount of one of the reactants. *e.g.,* in the above problem, dihydrogen appears as a limiting reagent because its amount is less than dinitrogen.

Step II Assume that one of the reactants is the limiting reagent. Let dihydrogen is the limiting reagent.

Step III See if you have enough of the other reactant to consume the material you have assumed to be the limiting reactant. If you do, your original assumption was correct.

$$\underset{\substack{1\text{ mol}\\28\text{ g}}}{N_2(g)} + \underset{\substack{3\text{ mol}\\6\text{ g}}}{3H_2(g)} \longrightarrow \underset{\substack{2\text{ mol}\\34\text{ g}}}{2NH_3(g)}$$

$\because$ 6g dihydrogen (H_2) reacts with dinitrogen (N_2) = 28 g

$$\because\ 1\times10^3\text{ g } H_2 \text{ will react with } N_2 = \frac{28\times1\times10^3}{6}\text{ g}$$

$$= 4.66\times10^3\text{ g}$$

But the available amount of N_2 is = 2.00×10^3 g which is less than 4.66×10^3 g. That means, our assumption is not correct.

Note If your assumption is true, left the step IV.

Step IV If you don't, assume that another reagent is the limiting reagent and test this assumption.

$$\underset{\substack{1\text{ mol}\\28\text{ g}}}{N_2(g)} + \underset{\substack{3\text{ mol}\\6\text{ g}}}{3H_2(g)} \longrightarrow \underset{\substack{2\text{ mol}\\34\text{ g}}}{2NH_3(g)}$$

28 g N_2 reacts with 6 g H_2

1 g N_2 reacts with $\frac{6}{28}$ g H_2

$$\therefore\ 2000\text{ g } N_2 \text{ will reacts with } \frac{2000\times6}{28}$$

$$= 428.57\text{ g } H_2$$

Hence, N_2 is the limiting reagent and H_2 is in excess. N_2 limits the amount of ammonia produced.

Amount of H_2 remain unreacted

$$=1000 - 428.57 = 571.43\text{ g}$$

Step V Once you have identified the limiting reagent, calculate the amount of the product formed.

28 g N_2 produces 34 g NH_3

1 g N_2 produces $\frac{34}{28}$ g NH_3

$$\therefore\ 2000\text{ g } N_2 \text{ will produce } \frac{34}{28}\times2000 = 2428.57\text{ g } NH_3$$

$$= 2.42\text{ kg } NH_3$$

Thus, the amount of NH_3 produced by the reaction of 2.00×10^3 g N_2 and 1.00×10^3 g H_2 = 2.42 kg

Sample **Problem 27** *The reactant which is entirely consumed in reaction is known as limiting reagent. In the reaction $2A + 4B \rightarrow 3C + 4D$, whein 5 moles of A react with 6 moles of B, then the amount of C formed is* **[NCERT Exemplar]**

(a) 3 *mol* (b) 4 *mol*

(c) 5.5 *mol* (d) 4.5 *mol*

Interpret (*d*) $2A + 4B \rightarrow 3C + 4D$

According to the above equation, 2 moles of '*A*' require 4 moles of '*B*' for the reaction.

Hence, for 5 moles of '*A*' the moles of '*B*' required

$$= 5\text{moles of } A \times \frac{4\text{ moles of } B}{2\text{ moles of } A}$$

$$= 10\text{ mol } B$$

But we have only 6 moles of '*B*' hence, '*B*' is the limiting reagent. So amount of '*C*' formed is determined by amount of '*B*'.

Since 4 moles of '*B*' give 3 moles of '*C*'.

Hence, 6 moles of '*B*' will give

$$6\text{ moles of } B \times \frac{3\text{ moles of } C}{4\text{ moles of } B} = 4.5\text{ moles of } C$$

1.6 Stoichiometric Problems of Different Kinds

Depending on the units, stoichiometric problems may be classified into the following relationship

(a) mass-mass relationship-gravimetric analysis
(b) mass-volume relationship
(c) volume-volume relationship

Such relations further be classified as

(i) Gas-gas analysis or eudiometry
(ii) Solutions-volumetric analysis or titration

I Calculations Based on Mass-mass Relationship

In making necessary calculations, following methods can be used

(a) **Mole Method** (Based on mole concept)

It involves the following steps

Step I Write the complete and balanced chemical reaction concerned in the problem.

Step II The stoichiometric coefficients in the balanced chemical reactions represent the relative number of moles of the different reaction components. Relate the amounts of the reaction components concerned, with the help of mole.

Step III Calculate the unknown amount of substance using unitary method.

Sample **Problem 28** *Calculate the weight of carbon dioxide formed by complete combustion of* 1.5 g *ethane.*

(*a*) 22 *g* (*b*) 2.2 *g* (*c*) 44 *g* (*d*) 4.4 *g*

Interpret (*d*) $\underset{\substack{1\text{ mol}\\=30\text{ g}}}{C_2H_6} + \frac{7}{2}O_2 \longrightarrow \underset{\substack{2\text{ mol}\\=2\times44\text{ g}}}{2CO_2} + 3H_2O$

$\because$ 30 g C_2H_6 produces 2×44 g CO_2 on complete combustion

$\therefore$ 1.5 g C_2H_6 will produce $\frac{2\times44}{30}\times1.5 = 4.4$ g CO_2

(b) Principle of Atomic Conservation (POAC) Method

This is another approach of solving problems by mole method, without balancing the reaction. As the reactions are balanced by conserving the atoms of each element, the mole of atoms of each element in the reactant side should be equal to that in the product side. On applying the conservation of atoms of each element with the help of mole, we may get relations needed to solve the problem.

For example, the sample problem 28 may be solved by POAC method as

Moles of C-atoms in C_2H_6 = moles of C- atoms in CO_2

or $2\times$ mole of C_2H_6 = $1\times$mole of CO_2

or $$2\times\frac{1.5}{30} = 1\times\frac{w}{44}$$

$\therefore$ $$w = 4.4\,\text{g}$$

(c) Factor-label Method

In this method, the required amount is determined directly by first converting the given amount of substance into its moles, then relating the moles of given substance with the moles of required substance as per balanced chemical equation or atomic conservation and finally converting the moles into the amount of the required substance.

For example, the sample problem 28 may be solved by factor label method as

Procedure

$$\text{Mass of } C_2H_6 \text{ (given)} \xrightarrow[\text{into}]{\text{Convert}} \text{Moles of } C_2H_6$$

$$\xrightarrow[\text{moles of } CO_2]{\text{Relate with}} \text{moles of } CO_2$$

$$\xrightarrow[\text{into}]{\text{Convert}} \text{Mass of } CO_2 \text{ (required)}$$

Application

$$\text{Mass of } CO_2 = (1.5\text{g } C_2H_6)\times\left(\frac{1 \text{ mol } C_2H_6}{30\text{ g } C_2H_6}\right)\times\left(\frac{2\text{ mol } CO_2}{1\text{ mol } C_2H_6}\right)\times\left(\frac{44\text{g } CO_2}{1\text{ mol } CO_2}\right)$$

$$= 4.4\,\text{g}$$

(d) Equivalent Method

(Based on equivalent concept)

The number of gram-equivalents of each reactants reacted will be same and the same number of gram-equivalents of each products will form. The sample problem 28 may be solved by equivalent concept as

no. of g-equivalents of C_2H_6 = no. of g-equivalents of CO_2

or $$\frac{1.5}{\left(\frac{30}{14}\right)} = \frac{w}{\left(\frac{44}{7}\right)}$$

$$w = 4.4\,\text{g}$$

$\therefore$ The factors 14 and 7 are changes in oxidation states of carbon for C_2H_6 and CO_2 respectively.

Sample **Problem 29** *Oxygen is prepared by catalytic decomposition of potassium chlorate* ($KClO_3$). *Decomposition of potassium chlorate gives potassium chloride* (KCl) *and oxygen* (O_2). *How many grams of* $KClO_3$ *are required to produce* 2.4 *moles of* O_2?

(*a*) 122.5 *g* (*b*) 196 *g* (*c*) 245 *g* (*d*) 98 *g*

Interpret (*b*) Decomposition of $KClO_3$ takes place as,

$$2KClO_3(s) \longrightarrow 2KCl(s) + 3O_2(g)$$

$$2 \text{ moles of } KClO_3 \equiv 3\text{moles of } O_2$$

$\because$ 3 moles of O_2 are formed by 2 moles of $KClO_3$

$\therefore$ 2.4 moles of O_2 will be formed by $\left(\frac{2}{3}\times2.4\right)$ moles of $KClO_3$

$$= 1.6 \text{ mol } KClO_3$$

$$\text{Mass of } KClO_3 = \text{Number of moles}\times\text{molar mass}$$

$$= 1.6\times122.5 = 196\text{ g}$$

Sample **Problem 30** *How many grams of oxygen are required to burn completely* 570 *g of octane?*

(*a*) 570 *g* (*b*) 5 *mol* (*c*) 25×32 *g* (*d*) 2000 *g*

Interpret (*d*) Balanced equation,

$$\underset{\substack{2\text{ mol}\\=2\times114}}{2C_8H_{18}} + \underset{\substack{25\text{ mol}\\=25\times32}}{25O_2} \longrightarrow 16CO_2 + 18H_2O$$

$\therefore$ ***First method*** For burning 2×114 g of octane, oxygen required

$$= 25\times32\text{ g}$$

For burning 1g octane, oxygen required $= \frac{25\times32}{2\times114}$ g

Thus, for burning 570 g of octane, oxygen required

$$= \frac{25\times32}{2\times114}\times570\text{g} = 2000\text{ g}$$

Mole method Number of moles of octane in 570 g $= \frac{570}{114} = 5.0$

For burning 2.0 moles of octane, oxygen required

$$= 25\text{ mol} = 25\times32\text{ g}$$

For burning 5 moles octane, oxygen required

$$= \frac{25\times32}{2.0}\times5.0\text{g} = 2000\text{ g}$$

Proportion method Let x g of oxygen be required for burning 570.0 g of octane. It is known that 2×114 g of the octane require 25×32 g of oxygen; then, the proportion,

$$\frac{25\times 32\text{ g oxgen}}{2\times 114\text{g octane}}=\frac{x}{570.0\text{ g octane}}$$

$$x=\frac{25\times 32\times 570}{2\times 114}=2000\text{ g}$$

Calculation Involving Per cent Yield

In general, when a reaction is carried out in the laboratory we do not obtain actually the theoretical amount of the product. The amount of the product that is actually obtained is called the **actual yield**. Knowing the actual yield and theoretical yield the per cent yield can be calculated by using the formula,

$$\text{Per cent yield}=\frac{\text{Actual yield}}{\text{Theoretical yield}}\times 100$$

Sample **Problem 31** *For the reaction,*

$$CaO + 2HCl \longrightarrow CaCl_2 + H_2O$$

1.23 *g of* CaO *is reacted with excess of hydrochloric acid and* 1.85 *g of* $CaCl_2$ *is formed. What is the per cent yield?*

(*a*) 76.1 (*b*) 86.3
(*c*) 95.1 (*d*) *None of these*

Interpret (*a*) The balanced equation is

$$\underset{\substack{1\text{ mol}\\56\text{ g}}}{CaO} + 2HCl \longrightarrow \underset{\substack{1\text{ mol}\\111\text{ g}}}{CaCl_2} + H_2O$$

56 g of CaO produces $CaCl_2$ = 111 g

1.23 g of CaO will produce $CaCl_2=\frac{111}{56}\times 1.23 = 2.43$ g

Thus, theoretical yield = 2.43 g

Actual yield = 1.85 g

$$\text{Per cent yield}=\frac{1.85}{2.43}\times 100=76.1$$

Calculations Involving Per cent Purity

Depending upon the mass of the product, the equivalent amount of the reactant present can be determined with the help of a chemical equation. Knowing the actual amount of the reactant taken and the amount calculated with the help of a chemical equation, the percentage purity can be determined as

$$\%\text{ purity}=\frac{\text{wt. of reactant required}}{\text{wt. of reactant taken}}\times 100$$

Sample **Problem 32** *Chlorine evolved by the reaction of* 45.31 *g of pyrolusite (impure) and excess of* HCl *is found to combine completely with the hydrogen produced by the reaction of* 10 *g of magnesium and excess of dilute hydrochloric acid. Find the percentage purity of* MnO_2 *in the given pyrolusite.*

(*a*) 98 (*b*) 95 (*c*) 70 (*d*) 80

Interpret (*d*) $\underset{24\text{ g}}{Mg} + \underset{(2\times 36.5)\text{ g}}{2HCl} \longrightarrow MgCl_2 + \underset{2\text{ g}}{H_2}$

$$\underset{87\text{ g}}{MnO_2} + 4HCl \longrightarrow MnCl_2 + \underset{71\text{ g}}{Cl_2} + 2H_2O$$

$$\underset{2\text{ g}}{H_2} + \underset{71\text{ g}}{Cl_2} \longrightarrow 2HCl$$

2g of hydrogen obtained by using 24 g of Mg will combine completely with 71 g of chlorine produced from 87 g of pure MnO_2. Thus, when 10 g of Mg are used,

the mass of pure MnO_2 required is $=\frac{87}{24}\times 10=36.25$ g

So, 45.31 g of pyrolusite contain MnO_2 (pure) = 36.25 g

$\therefore$ 100 g of pyrolusite contain MnO_2 (pure)

$$=\frac{36.25}{45.31}\times 100=80.004\text{ g}$$

$\therefore$ Percentage of purity = 80.00

Analysis of Mixtures

In such problems, one of the components is supposed to be x g and the other will be the difference from the total. Balanced chemical equations for the reactions of both the components are now written and the total amount of the common product produced by the components of the mixture is calculated. It is equated with the data given and the unknown factors are, thus, worked out.

Sample **Problem 33** *A solid mixture* (5.0 g) *consisting of lead nitrate and sodium nitrate was heated below* 600° C *until the mass of the residue was constant. If the loss in mass is* 28.0 *per cent, find the amount of lead nitrate in the mixture.*

(*a*) 1.67 (*b*) 3.32 (*c*) 1.40 (*d*) 5.00

Interpret (*b*) Let the amount of $NaNO_3$ in the mixture be xg.

$\therefore$ The amount of $Pb(NO_3)_2$ in the mixture = $(5.0-x)$ g

$$\underset{(2\times 85)\text{ g}}{2NaNO_3} \xrightarrow{\text{Heat}} 2NaNO_2 + \underset{32\text{ g}}{O_2}$$

$$\underset{\substack{(2\times 331)\text{ g}\\662\text{ g}}}{2Pb(NO_3)_2} \xrightarrow{\text{Heat}} 2PbO + \underbrace{\underset{(4\times 46)\text{ g}}{4NO_2} + \underset{32\text{ g}}{O_2}}_{216\text{ g}}$$

170 g of $NaNO_3$ evolve oxygen = 32 g

x g of $NaNO_3$ evolve oxygen $=\frac{32}{170}\ x$g

662 g of $Pb(NO_3)_2$ evolve gases = 216 g

$(5.0-x)$ g of $Pb(NO_3)_2$ evolve gases $=\frac{216}{662}\times(5.0-x)$ g

$\therefore$ Total loss $=\frac{32}{170}\times x+\frac{216}{662}\times(5.0-x)$

Loss given in the problem $=\frac{28}{100}\times 5=1.4$ g

$\therefore$ Total loss $=\frac{32}{170}x+\frac{216}{662}(5.0-x)=1.4$

On solving, x=1.676 g

Thus, mass of $NaNO_3$ = 1.676 g

Mass of $Pb(NO_3)_2$ = (5.0 −1.676)g = 3.324 g

Reactions in Succession

In such problems, the amount of any one of the reaction component belonging from a reaction is to be determined from the given amount of some other reaction component belonging from some other reaction with the help of some common components.

Sample **Problem 34** *How many gram of ethylene can be burnt completely by the oxygen gas produced from complete decomposition of* 49 g $KClO_3$*?*

(*a*) 96 g (*b*) 9.6 g
(*c*) 5.6 g (*d*) 6.5 g

Interpret (*c*) **Method I** Solve each concerned reaction separately. First determine the amount of oxygen gas produced by the complete decomposition of $KClO_3$.

$$\begin{array}{ccc} 2KClO_3 & \longrightarrow 2KCl + & 3O_2 \\ 2\text{ mol} & & 3\text{ mol} \\ = 2\times 122.5\text{ g} & & = 3\times 32\text{ g} \\ = 245\text{ g} & & = 96\text{ g} \end{array}$$

$\because$ 245 g $KClO_3$ will produce 96 g O_2

$$\therefore \quad 49\text{ g } KClO_3 \text{ will produce } O_2 = \frac{96}{245}\times 49$$

$$= 19.2\text{ g } O_2$$

Now, determine the amount of ethane which can be burnt completely by the oxygen gas produced.

$$\begin{array}{ccc} C_2H_4 & + \; 3O_2 & \longrightarrow 2CO_2 + 2H_2O \\ 1\text{ mol} & 3\text{ mol} & \\ = 28\text{ g} & = 3\times 32\text{ g} & \\ & = 96\text{ g} & \end{array}$$

$\because$ 96 g O_2 will burn 28g C_2H_4

$\therefore$ 19.2 g O_2 will burn $\dfrac{28}{96}\times 19.2 = 5.6\text{ g } C_2H_4$

Method II Add or subtract the concerned reactions properly such that the common compound, by which the reactions are related cancels out. The reaction, thus obtained, may be a hypothetical reaction but it will give the true molar relation.

$$\begin{array}{l} 2KClO_3 \longrightarrow 2KCl + 3O_2 \\ C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O \\ \hline 2KClO_3 + C_2H_4 \longrightarrow 2KCl + 2CO_2 + 2H_2O \\ \;\;2\text{ mol} \qquad\; 1\text{ mol} \end{array}$$

$= 2\times 122.5$ g $= 28$ g

$$\therefore 49\text{ g } KClO_3 \text{ will react with } \frac{28}{2\times 122.5}\times 49 = 5.6\text{ g } C_2H_4$$

Method III Relate the moles of the component of given amount with the component of required amount, with the help of common substance, with the help of balanced chemical reactions.

$2\text{ mol } KClO_3 \equiv 3\text{ mol } O_2 \equiv 1\text{ mol } C_2H_4$

$= 2\times 122.5\text{ g} = 28\text{ g}$

$\therefore$ 49 g $KClO_2$ will react with

$$\frac{28}{2\times 122.5}\times 49 = 5.6\text{ g } C_2H_4$$

Method IV Factor-Lable method

Mass of C_2H_4

$$= (49\text{ g } KClO_3)\times\left(\frac{1\text{ mol } KClO_3}{122.5\text{ g } KClO_3}\right)\times\left(\frac{3\text{ mol } O_2}{2\text{ mol} KClO_3}\right)\times\left(\frac{1\text{ mol } C_2H_4}{3\text{ mol } O_2}\right)\times\left(\frac{28\text{ g } C_2H_4}{1\text{ mol } C_2H_4}\right)$$

$= 5.6$ g

Sample **Problem 35** 0.2415 g *sample of a mixture of* $MgSO_4\cdot 7H_2O$ *and* $MgCl_2\cdot 6H_2O$ *containing inert impurities was subjected to suitable treatment, as a result of which there were obtained* 0.1362 g *of* $BaSO_4$ *and* 0.1129 g *of* $Mg_2P_2O_7$. *Calculate the percentage impurity in the original mixture.*

(*a*) 5% (*b*) 4% (*c*) 3% (*d*) 8%

Interpret (*b*) Let the original sample contains *a* mol $MgSO_4\cdot 7H_2O$ and *b* mol $MgCl_2\cdot 6H_2O$. As $BaSO_4$ will form only from $MgSO_4\cdot 7H_2O$, from the conservation of SO_4^{2-} ion, a mole of $BaSO_4$ will form.

From question, $a\times 233 = 0.1362$ ... (i)

Now, as $Mg_2P_2O_7$ will form from both $MgSO_4\cdot 7H_2O$ and $MgCl_2\cdot 6H_2O$, from the conservation of Mg-atom, mole of $Mg_2P_2O_7$ formed $= a/2 + b/2$.

From question, $\left(\dfrac{a}{2}+\dfrac{b}{2}\right)\times 222 = 0.1129$ ...(ii)

From Eq. (i) and (ii), $a = 0.000585$ and $b = 0.000432$

Hence, the composition of original mixture

$MgSO_4\cdot 7H_2O = 0.000585\text{ mol} = 0.000585\times 246 = 0.1439\text{ g}$

$$\text{Percentage purity} = \frac{0.1439}{0.2415}\times 100 = 59.59\%$$

$$MgCl_2\cdot 6H_2O = 0.000432\text{ mol} = 0.000432\times 203 = 0.0877\text{ g}$$

$$\text{Percentage purity} = \frac{0.0877}{0.2415}\times 100 = 36.31\%$$

$$\text{Impurity} = 100 - (59.59 + 36.31) = 4.1\%$$

(ii) Calculations Involving Mass-volume Relationship

In such calculations masses of reactants are given and volume of the product is required and *vice-versa*. 1 mole of a gas occupies 22.4 L volume at STP thus, mass of a gas can be related to volume according to the following gas equation

$$pV = nRT$$

$$pV = \frac{w}{m}RT$$

Sample **Problem 36** *Hydrogen gas is prepared in the laboratory by reacting dilute* HCl *with granulated zinc. Following reaction takes place*

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$

Calculate the volume of hydrogen gas liberated at STP when 32.65 g *of zinc reacts with* HCl. *I mole of a gas occupies 22.7 L volume at STP; atomic mass of* Zn = 65.3 *u*. **[NCERT Exemplar]**

(a) 22.7 L (b) 22.4 L (c) 11.3L (d) 5.2 L

Interpret (*c*) From the equation, 65.3 g of zinc liberates 22.7 L of hydrogen. So 32.65 g zinc will liberate

$$32.65 \text{ g Zn} \times \frac{22.7 \text{ L } H_2}{65.3 \text{ g Zn}} = \frac{22.7}{2} \text{ L} = 11.35 \text{L}$$

Sample Problem 37 *A vessel contains* 1.6 *g of dioxygen at STP* (273.15 *K*, 1 *atm pressure*). *The gas is now transferred to another vessel at constant temperature, where pressure becomes half of the original pressure. The volume of the new vessel, and number of molecules of dioxygen, are respectively.* **[NCERT Exemplar]**

(*a*) $2.24, 6.02 \times 10^{23}$ (*b*) $1.12, \ 3.01 \times 10^{22}$

(*c*) $2.24, 3.01 \times 10^{21}$ (*d*) $2.24, \ 3.01 \times 10^{22}$

Interpret (*d*) (i) $p_1 = 1$ atm $T_1 = 273 \text{K}, \ V_1 = ?$

32 g of oxygen occupies 22.4 L of volume at STP.

Hence, 1.6 g of oxygen will occupy,

$$1.6 \text{ g oxygen} \times \frac{22.4 \text{ L}}{32 \text{ g oxygen}} = 1.12 \text{ L volume}$$

$$V_1 = 1.12 \text{L}$$

$$p_2 = \frac{p_1}{2} = \frac{1}{2} = 0.5 \text{ atm.}$$

$$V_2 = ?$$

According to Boyle's law

$$p_1V_1 = p_2V_2$$

$$\therefore \quad V_2 = \frac{p_1 \times V_1}{p_2} = \frac{1 \text{ atm} \times 1.12 \text{ L}}{0.5 \text{ atm}} = 2.24 \text{L}$$

(ii) Number of molecules of oxygen in the vessel

$$= \frac{6.022 \times 10^{23} \times 1.6}{32} = 3.011 \times 10^{22}$$

(iii) Calculations Based on Volume-volume Relationship

For Gases

These calculations are based on two laws

(i) Avogadro's law (ii) Gay-Lussac's law

(See Topic 1.3 for laws.)

Sample Problem 38 *What volume of air containing* 21% *oxygen by volume is required to completely burn* 1 *kg of carbon containing* 100% *combustible substances?*

(*a*) 888.85 *L* (*b*) *8.8885 L*

(*c*) 88.885 *L* (*d*) *None of these*

Interpret (*b*) Combustion of carbon may be given as

$$\underset{\substack{1 \text{ mol} \\ 12 \text{ g}}}{C(s)} + \underset{\substack{1 \text{ mol} \\ 1 \text{ mol}}}{O_2(g)} \longrightarrow CO_2(g)$$

$\because$ 12 g carbon requires 1 mole of O_2 for complete combustion.

$\therefore$ 1000 g carbon will require $\frac{1}{12} \times 1000$ mol O_2 for combustion, *i.e.*, 83.33 mol O_2

Volume of O_2 at NTP $= 83.33 \times 22.4 \text{ L} = 1866.592 \text{ L}$

$\because$ 21 L O_2 is present in 100 L air

$\therefore$ 1866.592 L O_2 will be present in $\frac{100}{21} \times 1866.592$ L air

$$= 8888.5 \text{ L} = 8.8885 \times 10^3 \text{ L}$$

For Solutions

(i) **Simple titrations** In a simple titration, a solution of substance *A* of unknown concentration is made to react with a solution of *B* whose concentration is known, so that the concentration of *A* may be calculated. The two are reacted in such a way that the volume of *B* required to completely react with *A* can be found out by using some indicators.

If the normality of *B* is N_1 and its volume used is V_1 then the gram-equivalents of *B* reacted $= N_1V_1$.

According to the law of equivalents, the gram-equivalents of *A* would be equal to that of *B*.

$\therefore$ Gram equivalents of $A = N \times V$

If the volume of *A* is *V* then the normality of *A* would be $\frac{N_1V_1}{V}$.

Sample Problem 39 *What volume of* 2.5 *M* H_2SO_4 *is required to neutralize a solution containing* 2.5 *g* NaOH?

(*a*) 10.2 *mL* (*b*) 18.4 *mL*

(*c*) 12.5 *mL* (*d*) 11.89 *mL*

Interpret (*c*) 2.5 g NaOH $= \frac{2.5}{40}$ equivalent of

$$\text{NaOH} = \left(\frac{2.5}{40} \times 1000\right) \text{mill. equivalents of NaOH} = 62.5$$

Now meq of H_2SO_4 = Meq of NaOH

Let the volume of H_2SO_4 required is *V* mL

or $2.5 \times 2 \times V = 62.5$

($\because$ *n* factor for $H_2SO_4 = 2$)

$$V = \frac{62.5}{5} = 12.5 \text{ mL}$$

(ii) **Back titration** Let us assume that we have a solid *C* which is impure and we want to calculate the percentage purity. We are given two reagents *A* and *B*, where the concentration of *A* is unknown while that of *B* is known (N_1).

A certain volume of *A* is taken in a beaker and it is titrated with *B*. Let the volume of *B* used be V_1. Again fresh *A* (same volume) is taken in a beaker and the solid *C* is added to it. The resulting solution is again titrated with *B* and let the volume of *B* consumed be V_2.

For back titration to work the following *two conditions should be satisfied.*

I. *A*, *B* and *C* should be such that *A* reacts with *B*, *A* reacts with *C* and the product of *A* and *C* cannot react with *B*.

II. The amount of *A* taken in the beaker before adding *C* to it should be such that the gram-equivalents of *A* in it should be either greater than or equal to gram-equivalent of *C*.

$\therefore$ It can be seen that the gram-equivalents of *B* that reacted with *A* in the first titration = N_1V_1 which is also equal to the gram-equivalents of *A*. The gram equivalents of *B* in the second titration = N_2V_2 which is equal to the gram-equivalents of *A* that were left in excess after reacting with *C*.

$\therefore$ Gram-equivalents of *A* consumed by $C = N_1V_1 - N_2V_2$ which is also equal to gram-equivalents of *C*. If the '*n*' factor of *C* is × then the moles of *C* is $\left(\frac{N_1V_1 - N_2V_2}{x}\right)$.

The mass of *C* would be $\left(\frac{N_1V_1 - N_2V_2}{x}\right)\times M = m$.

If the sample of *C* weighed *W* grams then the percentage of *C* in it $= \frac{m}{W}\times 100$.

Sample Problem 40 *1.6 g of pyrolusite ore was treated with 50 cc of 1.0 N oxalic acid and some sulphuric acid. The oxalic acid left undecomposed was raised to 250 cc in a flask. 25 cc of this solution when titrated with 0.1 N* $KMnO_4$ *required 32 cc of the solution. Find out the percentage of pure* MnO_2 *in the sample.*

(a) 49% (b) 50% (c) 81% (d) 62%

Interpret (a) Meq of excess dil oxalic acid in 25 cc = Meq. of $KMnO_4 = 0.1\times 32$

$\therefore$ Meq of oxalic acid in 250 cc dilute solution = 32

Meq of MnO_2 = Meq. of oxalic acid added − Meq of excess oxalic acid $= 1\times 50 - 32 = 18$

$\therefore$ Let the weight of MnO_2 is *Wg*.

$$\therefore \qquad \frac{W}{E}\times 1000 = 18$$

$$\therefore \qquad \frac{W}{87/2}\times 1000 = 18 \quad \text{or} \quad W = \frac{18\times 87}{2000} = 0.783\text{ g}$$

$$\%\text{ of } MnO_2 = \frac{0.783}{1.6}\times 100 = 48.93$$

(iii) **Double titration** This is a titration of specific compound using different indicators.

This method involves two indicators namely phenolphthalein and methyl orange. These indicators are weak organic acids or bases which shows completion of reaction by changing its colour. Phenolphthalein acts as an indicator in weakly basic medium, but not in acidic medium. But methyl orange acts as an indicator both in acidic medium as well as in basic medium.

Extent of different bases with acid (HCl) using these two indicators is summarized as below.

Table 1.3 **Indicators Used with Different Bases**

	Indicators	
Bases	Phenolphthalein	Methyl orange
NaOH	100% reaction is indicated	100% reaction is indicated
Na_2CO_3	50% of reaction up to $NaHCO_3$ stage is indicated	100% reaction is indicated
$NaHCO_3$	No reaction is indicated	100% reaction is indicated $NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$

Suppose, the volume of given standard acid solution (HCl) is required,

for complete reaction of NaOH $= V_a$ mL

for complete reaction of $Na_2CO_3 = V_b$ mL

for complete reaction of $NaHCO_3 = V_c$ mL

There may be different combinations of mixture of bases are possible. We will opt the following two methods,

Method I We carry two titration separately with two different indicators.

Method II We carry single titration but adding second indicator after first end point is reached.

Table 1.4 **Results with Two Indicators**

Mixture	Method I		Method II	
	Volume of HCl used with indicator		Volume of HCl used with indicator	
	Phenolphthalein	Methyl orange	Phenolphthalein	Methyl orange added after the first end point is reached
$NaOH + Na_2CO_3$	$V_a + \frac{V_b}{2}$	$V_a + V_b$	$V_a + \frac{V_b}{2}$	$\frac{V_b}{2}$
$NaOH + NaHCO_3$	V_a	$V_a + V_c$	V_a	V_c
$Na_2CO_3 + NaHCO_3$	$\frac{V_b}{2}$	$V_a + V_c$	$\frac{V_b}{2}$	$\frac{V_b}{2} + V_a$

If mixture contains NaOH, Na_2CO_3 *and* $NaHCO_3$, *then these are the following cases with the following cases with the indicators.*

***Case* 1** The titre readings of HCl, using phenolphthalein from beginning $= V_a + \dfrac{V_b}{2}$

***Case* 2** If methyl orange is added after the first end point, then the titre readings of HCl $= \dfrac{V_b}{2} + V_c$

***Case* 3** If methyl orange is added from the very beginning, the titre readings of HCl $= V_a + V_b + V_c$

Sample Problem 41 *A solution contains a mixture of* Na_2CO_3 *and* NaOH. *Using phenolphthalein as indicator,* 25 *mL of mixture required* 19.5 *mL of* 0.995 *N* HCl *for the end point. With methyl orange, 25mL of solution required 25 mL of the same* HCl *for the end point. The grams per litre of* Na_2CO_3 *in the mixture is*

(*a*) 23.2 (*b*) 18.5 (*c*) 19.9 (*d*) 12.8

Interpret (*a*) Let the moles of Na_2CO_3 and NaOH in 25 mL mixture be *x* and y respectively.

***Case* 1** when HPh is used as indicator.

$$\underset{x}{NaOH} + \underset{x}{HCl} \longrightarrow NaCl + H_2O$$

$$\underset{y}{Na_2CO_3} + \underset{y}{HCl} \rightarrow NaHCO_3 + NaCl$$

So, $$x + y = 19.5 \times 10^{-3} \times (0.995 \times 1) \qquad \ldots(i)$$

***Case* 2** when MeOH is used as indicator.

$$\underset{x}{NaOH} + \underset{x}{HCl} \longrightarrow NaCl + H_2O$$

$$\underset{y}{Na_2CO_3} + \underset{2y}{2HCl} \longrightarrow 2NaCl + H_2O + CO_2 \qquad \ldots(ii)$$

$$x + 2y = 25 \times 10^{-3} \times 0.995 \times 1$$

On solving Eqs. (i) and (ii), we get,

$$x = 13.93 \times 10^{-3} \text{ mol and } y = 5.4725 \times 10^{-3} \text{ mol}$$

Now, weight of NaOH in 25 mL mixture

$$= 13.93 \times 10^{-3} \times 40 = 557.2 \times 10^{-3} \text{ g}$$

Weight of Na_2CO_3 in 25 mL mixture $= 5.4725 \times 10^{-3} \times 106$ $= 580.085 \times 10^{-3}$ g

$$\therefore \text{ Weight of NaOH per litre} = \frac{557.2 \times 10^{-3} \times 1000}{25} = 22.288 \text{ g/L}$$

$$\text{weight of } Na_2CO_3 \text{ per litre} = \frac{580.085 \times 10^{-3} \times 1000}{25}$$

$$= 23.2034 \text{ g/L}$$

(iv) **Iodimetry** This is a simple redox titration between a solution of iodine and $Na_2S_2O_3$ solution.

$$\underset{n\,=\,2}{I_2} + \underset{n=1}{2S_2O_3^{2-}} \longrightarrow 2I^- + S_4O_6^{2-}$$

(v) **Iodometry** This is an indirect way of doing iodimetry. An oxidizing agent *A* is made to react with excess of solid KI. The oxidizing agent oxidizes I^- to I_2. This iodine is then made to react with $Na_2S_2O_3$ solution. As can be seen the gram-equivalents of $Na_2S_2O_3$ would be equal to I_2 which in turn will be equal to that of reacted KI and this would be equal to the number of gram equivalents of *A*.

Sample Problem 42 5.7*g of bleaching powder was suspended in* 500*mL* of water . 25*mL* of this solution *on treatment with* KI *in the presence of* HCl *liberated iodine which reacted with* 24.35 *mL of* N/10 $Na_2S_2O_3$. *Calculate the percentage of available chlorine in the bleaching powder.*

(*a*) 30% (*b*) 25%

(*c*) 80% (*d*) 70%

Interpret (*a*) Millieq. of $Na_2S_2O_3 = 24.35 \times 1/10 = 2.435$

This would be the milliequivalent of I_2 and therefore that of Cl_2 (which liberates I_2 from KI).

Milliequivalents of Cl_2 in 500mL $= 2.435 \times 20 = 48.7$

Meq of Cl_2 = meq. of bleaching powder = Meq of available Cl_2 in the bleaching powder.

$$\text{Percentage of chlorine} = \frac{48.7}{1000} \times \frac{35.5}{5.7} \times 100$$

$$= 30.33\%$$

Check Point 2

1. How are 0.50 mole Na_2CO_3 and 0.50 M Na_2CO_3 different?
2. Write the empirical formula of the compounds having molecular formulae H_2O_2, B_2H_6 and Fe_2O_3.
3. Which reactant checks the amount of barium phosphate formed, when 2 moles each of barium chloride and sodium phosphate react?

WORKED OUT
Examples

Example 1 *10 g of hydrogen fluoride gas occupies 5.6 L of volume at NTP. The molecular formula of the gas is (at. mass of* F = 19)

(*a*) HF (*b*) H_3F_3 (*c*) H_2F_2 (*d*) H_4F_4

Solution (*c*) ∵ 5.6 L of volume is occupied by 10g hydrogen fluoride gas

∴ 22.4 L volume will be occupied by hydrogen fluoride

$$\text{gas} = \frac{10}{5.6} \times 22.4 = 40 \text{ g}$$

Among the given molecular formulae, molecular mass of H_2F_2 is 40. Thus, the molecular formula of the gas is H_2F_2.

Example 2 *A sample of pure compound contains* 2.04 g *of sodium,* 2.65×10^{22} *atoms of carbon and* 0.132 *mol of oxygen atoms. Its empirical formula is*

(*a*) $NaCO_2$ (*b*) $Na_2C_2O_4$
(*c*) Na_2CO_3 (*d*) *None of these*

Solution (*c*) Number of moles of

$$\text{Na} = \frac{2.04 \text{ g}}{23 \text{ g mol}^{-1}} = 0.0887 \text{ mol}$$

$$\text{Number of moles of C} = \frac{2.65 \times 10^{22} \text{ atoms}}{6.02 \times 10^{23} \text{ atoms mol}^{-1}} = 0.0440 \text{ mol}$$

Number of moles of O = 0.132 mol

Ratio of number of moles =

Na	:	C	:	0
0.0887	:	0.0440	:	0.132
2	:	1	:	3

∴ Empirical formula of the compound is Na_2CO_3.

Example 3 *One volume hydrogen combines with sulphur to give one volume of a gas X. If the vapour density of X is* 17*, the number of sulphur atoms in the gas X is*

(*a*) 1 (*b*) 2
(*c*) 3 (*d*) 4

Solution (*a*)

$$\underset{\substack{1 \text{ vol} \\ 1 \text{ molecule} \\ 2 \text{ atoms}}}{\text{Hydrogen}} + \text{Sulphur} \longrightarrow \underset{\substack{1 \text{ vol} \\ 1 \text{ molecule} \\ 1 \text{ molecule}}}{X}$$

∴ The formula of *X* is H_2S_n.

$$\begin{aligned} \text{Molecular mass of } X &= 1 \times 2 + n \times 32 = 2 + 32n \\ &= 2 \times \text{VD} \\ &= 2 \times 17 = 34 \\ \Rightarrow \quad 2 + 32n &= 34 \\ n &= 1 \end{aligned}$$

Example 4 *A cylinder of compressed gas contains nitrogen and oxygen in the ratio* 3 : 1*by mole. If the cylinder is known to contain* 2.5×10^4 *g of oxygen, what is the total mass of the gas mixture?*

(*a*) 781.25 (*b*) 6.5625×10^4
(*c*) 9.06×10^4 (*d*) 6.023×10^5

Solution (*c*) Number of moles of oxygen in the cylinder

$$= \frac{\text{mass in gram}}{\text{molecular mass in gram mol}^{-1}}$$

$$= \frac{2.5 \times 10^4}{32} = 781.25$$

∴ Number of moles of $N_2 = 3 \times 781.25 = 2343.75$

$$\begin{aligned} \text{Mass of nitrogen in the cylinder} &= 2343.75 \times 28 \\ &= 65625 \text{ g} = 6.5625 \times 10^4 \text{ g} \end{aligned}$$

Total mass of the gas in the cylinder

$$\begin{aligned} &= 2.5 \times 10^4 + 6.5625 \times 10^4 \\ &= 9.0625 \times 10^4 \text{ g} \end{aligned}$$

Example 5 *Two metallic oxides contain 27.6% and 30.0% oxygen respectively. If the formula of the first oxide is* M_3O_4, *then that of the second will be*

(*a*) M_2O_5 (*b*) M_2O_3 (*c*) MO (*d*) MO_2

Solution (*b*) As first oxide is M_3O_4,

72.4 parts of *M* = 3 atoms of *M*

and 27.6 parts of O = 4 atoms of O.

$$\therefore \quad 70 \text{ parts of } M = \frac{3}{72.4} \times 70 \text{ atoms of } M$$

$$= 2.9 \text{ atoms of } M$$

$$30 \text{ parts of O} = \frac{4}{27.6} \times 30 \text{ atoms of O}$$

$$= 4.35 \text{ atoms of O}$$

∴ Ratio of *M* : O in the second oxide

$$= 2.9 : 4.35 = 1 : 1.5 \text{ or } 2 : 3$$

Hence, the formula is M_2O_3.

Example 6 *The density of a gaseous element is 5 times that of oxygen under similar conditions. If the molecule of the element is triatomic, what will be its atomic mass?*

(*a*) 53.33 (*b*) 55.84 (*c*) 43.47 (*d*) 78.86

Solution (*a*) Molecular mass of oxygen = 32

$$\text{Vapour density of oxygen} = \frac{32}{2} = 16$$

Thus, vapour density of the gaseous element = 16 × 5 = 80

Molecular mass of the gaseous element = 80 × 2 = 160

$$\text{As the molecule is triatomic, its atomic mass} = \frac{\text{mol. mass}}{\text{atomicity}}$$

$$= \frac{160}{3} = 53.33$$

Example 7 *What is the empirical formula of vanadium oxide if 2.74 g of metal oxide contains 1.53 g of metal?*

(*a*) V_2O_3 (*b*) VO (*c*) V_2O_5 (*d*) V_2O_7

Solution (*c*) $\% \text{ of V} = \frac{1.53}{2.74} \times 100 = 55.84$

∴ % of O = 44.16

Element	Percentage	Atomic ratio	Simplest ratio
V	55.83	$\frac{55.84}{52} = 1.1$	$\frac{1.1}{1.1} = 1$
O	44.17	$\frac{44.16}{16} = 2.76$	$\frac{2.76}{1.1} = 2.5$

V : O = 2 : 5

Thus, empirical formula = V_2O_5

Example 8 *The sulphate of a metal contains 20% metal. This sulphate is isomorphous with zinc sulphate hepta hydrate. The atomic mass of the metal is*

(*a*) 30 (*b*) 12 (*c*) 24 (*d*) 36

Solution (*c*) $\frac{\text{mass of metal sulphate}}{\text{mass of metal}}$

$$= \frac{\text{eq. mass of } M + \text{eq. mass of } SO_4^{2-}}{\text{eq. mass of } M}$$

$$\frac{100}{20} = \frac{E + 48}{E}$$

$$5E = E + 48$$

$$4E = 48 \quad \text{or} \quad E = 12$$

As metal sulphate is isomorphous with $ZnSO_4 \cdot 7H_2O$,

Valency of *M* = Valency of Zn = 2

Hence, At. mass of *M* = Eq. mass × valency

$$= 12 \times 2 = 24$$

Example 9 *Hydrated sulphate of a divalent metal of atomic weight 65.4 loses 43.85% of its weight on dehydration. The number of molecules of water of crystallisation in the salt is*

(*a*) 5 (*b*) 7

(*c*) 14 (*d*) 9

Solution (*b*) Let the number of molecules of water of crystallisation is *x*.

Formula of divalent hydrated metal sulphate will be

$$MSO_4 \cdot xH_2O$$

Molecular mass of salt = 65.4 + 96 + 18*x*

= (161.4 + 18*x*)

$$\text{Percentage of water} = \frac{18x}{161.4 + 18x} \times 100 = 43.85$$

On solving, $x = 7$

Example 10 *1.020 g of metallic oxide contains 0.540 g of the metal. If the specific heat of the metal, M is 0.216 cal* $deg^{-1}g^{-1}$*, the molecular formula of its oxide is*

(*a*) *MO* (*b*) M_2O_3

(*c*) M_2O_4 (*d*) M_2O

Solution (*b*) Mass of oxygen in the oxide

= (1.020 − 0.540) = 0.480 g

$$\text{Equivalent mass of the metal} = \frac{0.540}{0.480} \times 8 = 9.0$$

According to Dulong and Petit's law,

$$\text{Approx, atomic mass} = \frac{6.4}{\text{sp. heat}} = \frac{6.4}{0.216} = 29.63$$

$$\text{Valency of the metal} = \frac{\text{at. mass}}{\text{eq. mass}} = \frac{29.63}{9.0} = 3$$

Hence, the formula of the oxide is M_2O_3.

Example 11 *The atomicity of a molecule, M, if 10 g of it combine with 0.8 g of oxygen to form an oxide, is (specific heat of the molecule, M is 0.033 cal* $deg^{-1}\ g^{-1}$ *and molecular mass of molecule is 199.87 g)*

(*a*) 1 (*b*) 2

(*c*) 3 (*d*) 8

Solution (*a*) Equivalent mass of *M*

$$= \frac{\text{mass of metal}}{\text{mass of oxygen}} \times 8$$

$$= \frac{10}{0.8} \times 8 = 100$$

$$\text{Approximate atomic mass} = \frac{6.4}{\text{sp. heat}} = \frac{6.4}{0.033}$$

$$= 193.93 \text{ g}$$

$$\text{Valency of } M = \frac{193.93}{100} = 2 \text{ (nearest whole number)}$$

So, accurate atomic mass = eq. mass × valency

$$= 100 \times 2 = 200 \text{ g}$$

$$\text{Atomicity} = \frac{\text{mol. mass}}{\text{at. mass}}$$

$$= \frac{199.87}{200} = 1$$

Start Practice for JEE Main

Round I (Topically Divided Problems)

Units and Significant Figures

1. The units J Pa^{-1} is equivalent to
(a) m^3 (b) cm^3
(c) dm^3 (d) None of these

2. In which of the following numbers all zeros are significant?
(a) 0.500 (b) 30.000
(c) 0.00030 (d) 0.0050

3. A measured temperature on Fahrenheit scale is 200F. What will this reading be on celsius scale? **[NCERT Exemplar]**
(a) 40°C (b) 94°C
(c) 93.3°C (d) 30°C

4. The number of significant figures in Avogadro's number is
(a) four (b) two
(c) three (d) can be any of these

5. In multiplication and division, the significant figures of answer must be same as that in the quantity with .... number of significant figures.
(a) maximum (b) 3
(c) 2 (d) minimum

6. Convert the following into basic units.
(i) 28.7 pm (ii) 15.15 µs
(iii) 25365 mg
The correct answer is **[NCERT]**
(a) 28.7×10^{-11}, 1.515×10^{-6}, 2.5365×10^{-3}
(b) 2.87×10^{-11}, 1.515×10^{-5}, 2.5365×10^{-2}
(c) 2.87×10^{-10}, 1.515×10^{-5}, 2.5365×10^{-3}
(d) 2.87×10^{-10}, 1.515×10^{-6}, 2.5365×10^{-2}

7. The result of which of the following has least significant figures? **[NCERT]**
(a) $\dfrac{0.02856\times 298.15\times 0.112}{0.5785}$
(b) 5×5.364
(c) $0.0125+0.7864+0.0215$
(d) All have same number of significant figures

Matter and its Classification

8. The smallest matter particle that can take part in chemical reaction is
(a) atom (b) molecule
(c) Both (a) and (b) (d) None of these

9. Matter is anything which occupies ...*A*... and has...*B*.... Here *A* and *B* are
(a) density and mass (b) volume and mass
(c) space and mass (d) None of these

10. The solid like conducting state of gases with free electrons is called
(a) sol state (b) gel state
(c) plasma state (d) All of these

11. Which of the following statements about a compound is incorrect? **[NCERT Exemplar]**
(a) A molecule of a compound has atoms of different elements
(b) A compound cannot be separated into its constituent elements by physical methods of separation
(c) A compound retains the physical properties of its constituent elements
(d) The ratio of atoms of different elements in a compound is fixed

12. Which of the following is not a mixture?
(a) Gasoline (b) Distilled alcohol
(c) LPG (d) Iodized table salt

Laws of Chemical Combinations

13. Which of the following statements is correct about the reaction given below? **[NCERT Exemplar]**

$$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(g)$$

(a) Total mass of iron and oxygen in reactants = total mass of iron and oxygen in product therefore it follows law of conservation of mass

(b) Total mass of reactants = total mass of product; therefore, law of multiple proportions is followed

(c) Amount of Fe_2O_3 can be increased by taking any one of the reactants (iron or oxygen) in excess

(d) Amount of Fe_2O_3 produced will decrease if the amount of any one of the reactants (iron or oxygen) is taken in excess

14. Carbon dioxide contains 27.27% of carbon, carbon disulphide contains 15.79% of carbon and sulphur dioxide contains 50% of sulphur. This data is an agreement with

(a) law of conservation of mass

(b) law of definite proportions

(c) law of multiple proportions

(d) law of reciprocal proportions

15. If 6.3 g of $NaHCO_3$ are added to 15.0 g CH_3COOH solution, the residue is found to weigh 18.0 g. What is the mass of CO_2 released in the reaction?

(a) 4.5 g (b) 3.3 g

(c) 2.6 g (d) 2.8 g

16. 45.4L of dinitrogen reacted with 22.7L of dioxygen and 45.4L of nitrous oxide was formed. The reaction is given below

$$2N_2(g) + O_2(g) \longrightarrow 2N_2O(g)$$

Which law is being obeyed in this experiment? **[NCERT Exemplar]**

(a) Law of definite proportion

(b) Law of conservation of mass

(c) Law of multiple proportion

(d) None of the above

17. The mass of nitrogen per gram hydrogen in the compound hydrazine is exactly one and half times the mass of nitrogen in the compound ammonia. The fact illustrates the

(a) law of conservation of mass

(b) multiple valency of nitrogen

(c) law of multiple proportions

(d) law of definite proportions

18. Zinc sulphate contains 22.65% of zinc and 43.9% of water of crystallization. If the law of constant proportions is true then the weight of zinc required to produce 20 g of the crystals will be

(a) 45.3 g (b) 4.53 g

(c) 0.453 g (d) 453 g

Mole Concept

19. What will be the molarity of a solution, which contains 5.85 g of NaCl(s) per 500 mL? **[NCERT Exemplar]**

(a) 4 mol L^{-1} (b) 20 mol L^{-1}

(c) 0.2 mol L^{-1} (d) 2 mol L^{-1}

20. The mass of 112 cm^3 of CH_4 gas at STP is

(a) 0.16 g (b) 0.8 g

(c) 0.08 g (d) 1.6 g

21. Out of 1.0 g dioxygen, 1.0 g (atomic) oxygen and 1.0 g ozone, the maximum number of molecules are contained in

(a) 1.0 g of atomic oxygen

(b) 1.0 g of ozone

(c) 1.0 g of oxygen gas

(d) All contain same number of atoms

22. The number of water molecules present in a drop of water (volume 0.0018 mL) at room temperature is

(a) 6.023×10^{19} (b) 1.084×10^{18}

(c) 4.84×10^{17} (d) 6.023×10^{23}

23. The number of sodium atoms in 2 moles of sodium ferrocyanide is

(a) 12×10^{23} (b) 26×10^{23}

(c) 34×10^{23} (d) 48×10^{23}

24. A signature written with carbon pencil weighs 1 mg. What is the number of carbon atoms present in the signature?

(a) 6.02×10^{20} (b) 0.502×10^{20}

(c) 5.02×10^{23} (d) 5.02×10^{20}

25. What will be the mass of one ^{12}C atom in gram?

(a) 6.02×10^{23} (b) 1.6×10^{-19}

(c) 1.99×10^{-23} (d) 1.67×10^{-23}

26. What will the molality of the solution containing 18.25 g of HCl gas in 500 g of water? **[NCERT Exemplar]**

(a) 0.1 m (b) 1 M (c) 0.5 m (d) 1 m

27. A sample of AlF_3 contains 3.0×10^{24} F^- ions. The number of formula units of this sample are

(a) 9.0×10^{24} (b) 3.0×10^{24}

(c) 0.75×10^{24} (d) 1.0×10^{24}

28. Which one of the following will have the largest number of atoms? **[NCERT]**

(a) 1 g Au (s) (b) 1 g Na (s)

(c) 1 g Li (s) (d) 1 g Cl_2 (g)

29. 19.7 kg of gold was recovered from a smuggler. How many atoms of gold were recovered (Au = 197)?

(a) 100 (b) 6.02×10^{23}

(c) 6.02×10^{24} (d) 6.02×10^{25}

30. Which of the following pairs contains equal number of atoms?

(a) 11.2 cc (STP) of nitrogen and 0.015 g of nitric oxide
(b) 22.4 L (STP) of nitrous oxide and 22.4 L of nitric oxide
(c) 1 millimole of HCl and 0.5 millimole of H_2S
(d) 1 mole of H_2O_2 and 1 mole of N_2O_4

31. The molecular weight of air will be (the components of air given as N_2—78%, O_2—21%, Ar—0.9% and CO_2—0.1%)

(a) 18.64 (b) 24.968
(c) 28.964 (d) 29.864

32. Calculate the number of moles left after removing 10^{21} molecules from 200 mg of CO_2.

(a) 0.00454 (b) 0.00166
(c) 2.88×10^{-3} (d) None of these

33. If H_2SO_4 ionises as

$$H_2SO_4 + 2H_2O \longrightarrow 2H_3O^+ + SO_4^{2-}$$

then total number of ions produced by 0.1 M H_2SO_4 will be

(a) 9.03×10^{21} (b) 3.01×10^{22}
(c) 6.02×10^{22} (d) 1.8×10^{23}

34. One atom of an element X weigh 6.643×10^{-23} g. Number of moles of atom in 20 kg is

(a) 140 (b) 150
(c) 250 (d) 500

35. The density of 3 molal solution of NaOH is 1.110 g mL^{-1} Calculate the molarity of the solution. **[NCERT Exemplar]**

(a) 2.97 M (b) 1.67 M
(c) 3.64 M (d) 2.32 M

36. If the density of methanol is 0.793 kg L^{-1}, what is its volume needed for making 2.5L of its 0.25M solution? **[NCERT]**

(a) 5 mL (b) 25.2 mL
(c) 50 mL (d) 2.525 mL

37. A sample of drinking water was found to be severely contaminated with chloroform, $CHCl_3$, supposed to be carcinogenic in nature. The level of contamination was 15 ppm (by mass) Determine the molarity of chloroform in the water sample. **[NCERT]**

(a) 1.45×10^{-4} (b) 1.27×10^{-4}
(c) 1.89×10^{-6} (d) 1.34×10^{-5}

38. Which of the following contains the maximum number of atoms? **[NCERT]**

(a) 52 moles of Ar
(b) 52 u of He
(c) 52 g of He
(d) All have equal number of atoms

39. A sample of ammonium phosphate, $(NH_4)_3PO_4$ contains 6.36 moles of hydrogen atoms. The number of moles of oxygen atom in the sample is

(atomic mass of N = 14.04, H = 1, P = 31, O = 16)

(a) 0.265 (b) 0.795
(c) 2.12 (d) 4.14

40. A sample of copper sulphate pentahydrate contains 8.64 g of oxygen. How many gram of Cu is present in this sample ? (Atomic mass of Cu = 63.6, S = 32.06, O = 16)

(a) 0.952 g (b) 3.816 g
(c) 3.782 g (d) 8.64 g

41. Cortisone is a molecular substance containing 21 atoms of carbon per molecule. The molecular weight of cortisone is 360.4. What is the percentage of carbon in cortisone?

(a) 59.9% (b) 75%
(c) 69.98% (d) None of these

42. How many moles of $MgIn_2S_4$ can be made from 1 g each of Mg, In and S? (Atomic mass : Mg = 24, In = 114.8, S = 32)

(a) 6.47×10^{-4} (b) 3.0×10^{-1}
(c) 9.17×10^{-2} (d) 8.7×10^{-3}

43. If an iodized salt contains 1% KI and a person takes 2 g of the salt every day, the iodide ions going into his body every day would be approximately

(a) 7.2×10^{21} (b) 7.2×10^{19}
(c) 3.6×10^{21} (d) 9.5×10^{19}

44. If the density of water is 1 g cm^{-3} then the volume occupied by one molecule of water is approximately

(a) 18 cm^{-3} (b) 22400 cm^{-3}
(c) 6.02×10^{-23} cm^3 (d) 3.0×10^{-23} cm^3

Masses, Chemical Stoichiometry, Molecular and Empirical Formulae

45. Which property of an element is always a whole number?

(a) Atomic volume (b) Atomic weight
(c) Atomic number (d) Equivalent weight

46. If w_1 g of a metal X displaces w_2 g of another metal Y from its salt solution and if the equivalent weights are E_1 and E_2 respectively, the correct expression for the equivalent weight of X is

(a) $E_1 = \frac{w_1}{w_2} \times E_2$ (b) $E_1 = \frac{w_2 \times E_2}{w_1}$
(c) $E_1 = \frac{w_1 \times w_2}{E_2}$ (d) $E_1 = \sqrt{\frac{w_1}{w_2} \times E_2}$

47. The empirical formula and molecular mass of a compound are CH_2O and 180 g mol^{-1} respectively. What will be the molecular formula of the compound? **[NCERT Exemplar]**

(a) $C_9H_{18}O_9$ (b) CH_2O
(c) $C_6H_{12}O_6$ (d) $C_2H_4O_2$

48. For the reaction,

$$X + 2Y \longrightarrow Z$$

5 moles of X and 9 moles of Y will produce

(a) 5 moles of Z (b) 8 moles of Z
(c) 14 moles of Z (d) 4 moles of Z

49. Calculate the mass per cent of Na present in sodium sulphate, Na_2SO_4. **[NCERT]**

(a) 32.37 (b) 22.57
(c) 16.18 (d) 45.06

50. If 0.5 mole of $BaCl_2$ is mixed with 0.2 mole of Na_3PO_4, the maximum number of moles of $Ba_3(PO_4)_2$ that can be formed is

(a) 0.7 (b) 0.5 (c) 0.03 (d) 0.10

51. In the reaction,

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

equivalent weight of iodine will be equal to

(a) molecular weight (b) 1/2 of molecular weight
(c) 1/4 of molecular weight (d) twice of molecular weight

52. 2.76 g of silver carbonate on being strongly heated yields a residue weighing

(a) 3.54 g (b) 3.0 g (c) 1.36 g (d) 2.16 g

53. An organic compound contains 20.0% C, 6.66% H, 47.33% N and the rest was oxygen. Its molar mass is 60 g mol^{-1}. The molecular formula of the compound is

(a) CH_4N_2O (b) $C_2H_4NO_2$
(c) CH_3N_2O (d) $CH_4N_2O_2$

54. Use the data given in the following table to calculate the molar mass of naturally occurring argon.

Isotope	Isotopic molar mass	Abundance
^{36}Ar	35.96755 g mol^{-1}	0.337%
^{38}Ar	37.96272 g mol^{-1}	0.063%
^{40}Ar	39.9624 g mol^{-1}	99.600%

The molar mass of argon is **[NCERT]**

(a) 39.948 (b) 39.665 (c) 38.678 (d) 38.442

55. In the following reaction,

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$$

2 moles of MnO_2 react with 4 moles of HCl to form 11.2 L Cl_2 at STP. Thus, per cent yield of Cl_2 is

(a) 25% (b) 50%
(c) 100% (d) 75%

56. Consider the reaction, $A + B_2 \longrightarrow AB_2$, A acts as the limiting reagent, in which of the following reactions are mixtures? **[NCERT]**

(a) 300 atoms of A + 200 molecules of B
(b) 2 moles of A + 3 moles of B
(c) 100 atoms of A + 100 molecules of B
(d) 5 moles of A + 2.5 moles of B

57. What is the number of moles of $Fe(OH)_3(s)$ that can be produced by allowing 1 mole of Fe_2S_3, 2 moles of H_2O and 3 moles of O_2 to react as

$$2Fe_2S_3 + 6H_2O + 3O_2 \longrightarrow 4Fe(OH)_3 + 6S\ ?$$

(a) 1 mol (b) 1.84 mol
(c) 1.34 mol (d) 1.29 mol

58. Calcium carbonate reacts with aqueous HCl to give $CaCl_2$ and CO_2 according to the reaction,

$$CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

What mass of $CaCO_3$ is required to react completely with 25 mL of 0.75 M HCl? **[NCERT]**

(a) 0.6844 (b) 0.9375
(c) 0.4265 (d) 0.2795

59. One atom of an element weighs 1.8×10^{-22} g. Its atomic mass is

(a) 29.9 (b) 18 (c) 108.36 (d) 154

60. Determine the molecular formula of an oxide of iron in which the mass per cent of iron and oxygen are 69.9 and 30.1 respectively. Given that molar mass of the oxide is 159.89 g mol^{-1}. **[NCERT]**

(a) FeO (b) FeO_2 (c) Fe_2O_3 (d) Fe_3O_2

61. Arsenic forms two oxides, one of which contains 65.2% and the other 75.7% of the element. Hence, equivalent masses of arsenic are in the ratio

(a) 1 : 2 (b) 3 : 5 (c) 13 : 15 (d) 2 : 1

62. The equivalent mass of chlorine is 35.5 and the atomic mass of copper is 63.5. The equivalent mass of copper chloride is 99.0. Hence, formula of copper chloride is

(a) CuCl (b) Cu_2Cl
(c) $CuCl_2$ (d) None of these

63. Insulin contains 3.4% sulphur. What will be the minimum molecular weight of insulin?

(a) 94.117 (b) 1884
(c) 941.176 (d) 976

64. Two oxides of a metal contain 50% and 40% metal (M) respectively. If the formula of first oxide is MO_2, the formula of second oxide will be

(a) MO_2 (b) MO_3 (c) M_2O (d) M_2O_5

65. Chlorine is prepared in the laboratory by treating manganese dioxide (MnO_2) with aqueous hydrochloric acid according to the reaction.

$$4HCl(aq) + MnO_2(s) \longrightarrow 2H_2O(l) + MnCl_2(aq) + Cl_2(g)$$

How many grams of HCl reacts with 5.0g of manganese dioxide? **[NCERT]**

(a) 36.5 g (b) 4.12 g
(c) 8.39 g (d) 13.25 g

66. If ten volumes of dihydrogen gas react with five volumes of dioxygen gas, how many volumes of water vapour would be produced? **[NCERT]**

(a) 5 (b) 10 (c) 2 (d) 20

67. 100 tons of Fe_2O_3 containing 20% impurities will give iron by reduction with H_2 equal to

(a) 112 tons (b) 80 tons
(c) 160 tons (d) 56 tons

68. Cyclohexanol is dehydrated to cyclohexene on heating with conc H_2SO_4. The cyclohexene obtained from 100 g cyclohexanol will be (if yield of reaction is 75%)

(a) 61.5 g (b) 75.0 g
(c) 20.0 g (d) 41.0 g

69. Equal weights of Zn metal and iodine are mixed together and I_2 is completely converted to ZnI_2. What fraction by weight of original Zn remains unreacted? ($Zn = 65, I = 127$)

(a) 0.34 (b) 0.74
(c) 0.84 (d) Unable to predict

70. 100 mL of 0.1 N hypo decolourised iodine obtained by the addition of x gram of crystalline copper sulphate to excess of KI. The value of 'x' is

(Molecular wt. of $CuSO_4 \cdot 5H_2O$ is 250.)

(a) 5.0 g (b) 1.25 g
(c) 2.5 g (d) 4 g

71. On analysis a certain compound was found to contain iodine and oxygen in the ratio of 254 g of iodine (at. mass 127) and 80 g oxygen (at. mass 16). What is the formula of the compound?

(a) IO (b) I_2O
(c) I_5O_3 (d) I_2O_5

Round II (Mixed Bag)

Only One Correct Option

1. A box contains some identical red coloured balls. labelled as *A*, each weighing 2g. Another box contains identical blue coloured balls, labelled as *B*, each weighing 5 g. In the combinations AB, AB_2, A_2B and A_2B_3 which law is applicable. **[NCERT Exemplar]**

(a) Law of definite proportion
(b) Law of multiple proportion
(c) Law of conservation of mass
(d) None of the above

2. The law of definite proportions is not applicable to nitrogen oxide because

(a) nitrogen atomic weight is not constant
(b) nitrogen molecular weight is variable
(c) nitrogen equivalent weight is variable
(d) oxygen atomic weight is variable

3. A 400 mg iron capsule contains 100 mg of ferrous fumarate, $(CHCOO)_2Fe$. The percentage of iron present in it is approximately

(a) 33% (b) 25% (c) 14% (d) 8%

4. The number of water molecules in 1 L of water is

(a) 18 (b) 18×1000
(c) N_A (d) $55.55\,N_A$

5. Haemoglobin contains 0.33% of iron by weight. The molecular weight of haemoglobin is approximately 67200. The number of iron atoms (at. wt. of $Fe = 56$) present in one molecule of haemoglobin is

(a) 6 (b) 1 (c) 4 (d) 2

6. If isotopic distribution of C-12 and C-14 is 98% and 2% respectively then the number of C-14 atoms in 12 g of carbon is

(a) 1.032×10^{22} (b) 3.01×10^{22}
(c) 5.88×10^{23} (d) 6.023×10^{23}

7. The number of moles of oxygen in 1 L of air containing 21% oxygen by volume, in standard conditions, is

(a) 0.186 mol (b) 0.21 mol
(c) 2.10 mol (d) 0.0093 mol

8. There are two isotopes of an element with atomic mass z. Heavier one has atomic mass $z + 2$ and lighter one has $z - 1$, then abundance of lighter one is

(a) 66.6% (b) 96.7% (c) 6.67% (d) 33.3%

9. Which of the following statements indicates that law of multiple proportion is being followed? **[NCERT Exemplar]**

(a) Sample of carbon dioxide taken from any source will always have carbon and oxygen in the ratio 1:2.

(b) Carbon forms two oxides namely CO_2 and CO, where masses of oxygen which combine with fixed mass of carbon are in the simple ratio 2:1
(c) When magnesium burns in oxygen, the amount of magnesium taken for the reaction is equal to the amount of magnesium in magnesium oxide formed
(d) At constant temperature and pressure 200 mL of hydrogen will combine with 100 mL oxygen to produce 200 mL of water vapour

10. A certain amount of a metal whose equivalent mass is 28 displaces 0.7 L of H_2 at STP from an acid. Hence, mass of the element is
(a) 1.75 g (b) 0.875 g
(c) 3.50 g (d) 7.00 g

11. 1.520 g of the hydroxide of a metal on ignition gave 0.995 g of oxide. The equivalent weight of metal is
(a) 1.520 (b) 0.995
(c) 19.00 (d) 9.00

12. 100 mL of 20.8% $BaCl_2$ solution and 50 mL of 9.8% H_2SO_4 solution will form $BaSO_4$
($Ba = 137, Cl = 35.5, S = 32, H = 1, O = 16$)

$$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HCl$$

(a) 23.3 g (b) 11.65 g
(c) 30.6 g (d) None of these

13. Calcium carbonate reacts with aqueous HCl to give $CaCl_2$ and CO_2 according to the reaction,

$$CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

In this reaction, 250 mL of 0.76 M HCl reacts with 1000 g of $CaCO_3$. Calculate the mass of $CaCl_2$ formed in the reaction. **[NCERT Exemplar]**
(a) 11.1 g (b) 10.54 g
(c) 5.25 g (d) 2.45 L

14. One gram of hydrogen is found to combine with 80 g of bromine. One gram of calcium (valency=2) combines with 4 g of bromine. The equivalent weight of calcium is
(a) 10 (b) 20
(c) 40 (d) 80

15. What quantity of ammonium sulphate is necessary for the production of NH_3 gas sufficient to neutralize a solution containing 292 g of HCl? [$HCl = 36.5$, $(NH_4)_2SO_4 = 132, NH_3 = 17$]
(a) 272 g (b) 403 g
(c) 528 g (d) 1056 g

16. The percentage of P_2O_5 in diammonium hydrogen phosphate, $(NH_4)_2HPO_4$ is
(a) 23.48 (b) 46.96
(c) 53.78 (d) 71.00

17. A mixture of CH_4, N_2 and O_2 is enclosed in a vessel of one litre capacity at 0°C. The ratio of partial pressures of gases is 1 : 4 : 2. Total pressure of the gaseous mixture is 2660 mm. The number of molecules of oxygen present in the vessel is
(a) $\frac{6.02\times 10^{23}}{22.4}$ (b) 6.02×10^{23}
(c) 22.4×10^{22} (d) 1000

18. An ore contains 1.34% of the mineral argentite, Ag_2S, by mass. How many gram of this ore would have to be processed in order to obtain 1.00 g of pure solid silver, Ag?
(a) 74.6 g (b) 85.7 g
(c) 107.9 g (d) 134.0 g

19. x g of Ag was dissolved in HNO_3 and the solution was treated with excess of NaCl when 2.87 g of AgCl was precipitated. The value of x is
(a) 1.08 g (b) 2.16 g (c) 2.70 g (d) 1.62 g

20. What weight of silver chloride will be precipitated when a solution containing 4.77 g of NaCl is added to a solution of 5.77 g of $AgNO_3$? ($Na = 23$, $Cl = 35.5$, $Ag = 108, N = 14$ and $O = 16$)
(a) 4.37 g (b) 4.87 g (c) 5.97 g (d) 3.87 g

21. 0.75 mole of a solid A_4 and 2 moles of $O_2(g)$ are heated in a sealed vessel, completely using up the reactants and produces only one compound. It is found that when the temperature is used to initial temperature, the contents of the vessel exhibit a pressure equal to $\frac{1}{2}$ of the original pressure. The formula of the product will be
(a) A_2O_3 (b) A_3O_8 (c) A_3O_4 (d) AO_2

22. A sample of a mixture of $CaCl_2$ and NaCl weighing 4.22 g was treated to precipitate all the Ca as $CaCO_3$. This $CaCO_3$ is then heated and quantitatively converted into 0.959g of CaO. Calculate the percentage of $CaCl_2$ in the mixture.
(Atomic mass of $Ca = 40, O = 16, C = 12$, and $Cl = 35.5$)
(a) 31.5% (b) 21.5% (c) 45.04% (d) 68.48%

More than One Correct Option

23. One of the statements of Dalton's atomic theory is given below:

"Compounds are formed when atoms of different elements combine in a fixed ratio."

Which of the following laws is not related to this statement? **[NCERT Exemplar]**
(a) Law of conservation of mass
(b) Law of definite proportions
(c) Law of multiple proportions
(d) Avogadro law

24. If 4 g of NaOH dissolves in 36 g of H_2O, calculate the mole fraction of component in the solution. Also, determine the molarity of the solution (Specific gravity of solution is 1 g mL^{-1}) **[NCERT Exemplar]**

(a) 0.9524, 2.5 M (b) 0.239, 1.5 M
(c) 0.0476, 2.5 M (d) 0.9524, 1.5 M

25. Which of the following pairs have the same number of atoms? **[NCERT Exemplar]**

(a) 16 g of $O_2(g)$ and 4 g of $H_2(g)$
(b) 16 g of O_2 and 44 g of CO_2
(c) 28 g of $N_2(g)$ and 32 g of O_2
(d) 12 g of C(*s*) and 23 g of Na(*s*)

26. Which of the following solutions have the same concentration? **[NCERT Exemplar]**

(a) 20 g of NaOH in 200 mL of solution
(b) 0.5 mol of KCl in 200 mL of solution
(c) 40 g of NaOH in 100 mL of solution
(d) 20 g of KOH in 200 mL of solution

27. 16 g of oxygen has same number of molecules as in **[NCERT Exemplar]**

(a) 16 g of CO (b) 28 g of N_2
(c) 14 g of N_2 (d) 1.0 g of H_2

Assertion and Reason

Directions (Q. No. 28 to 32) *Each of these questions contains two statements : Statement* I *(Assertion) and Statement* II *(Reason). Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c), (d) given below :*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

28. **Statement I** Weight of 1 molecule of O_2 = 32 u.

Statement II 1 g-molecule = 6.023×10^{23} molecules.

29. **Statement I** The empirical mass of ethene is half of its molecular mass.

Statement II The empirical formula represents the simplest whole number ratio of various atoms present in a compound. **[NCERT Exemplar]**

30. **Statement I** One atomic mas unit is defined as one twelfth of the mass of one carbon-12 atom.

Statement II Carbon-12 isotope is the most abundant isotope of carbon and has been chosen as standard. **[NCERT Exemplar]**

31. **Statement I** Significant figures for 0.200 is 3 where as for 200 it is 1.

Statement II Zero at the end or right of a number are significant provided they are not on the right side of the decimal point. **[NCERT Exemplar]**

32. **Statement I** Combustion of 16 g of methane gives 18 g of water.

Statement II In the combustion of methane, water is one of the products. **[NCERT Exemplar]**

Comprehension Based Questions

Directions (Q. Nos. 33 to 35) Mole is a unit which represents 6.02×10^{23} particles (atoms, molecules or ions etc.) irrespective of the nature. The number 6.023×10^{23} is called Avogadro's number and is represented by N_0. The calculation of the number is based on the Faraday's law of electrolysis. A mole also represents gram molecular mass (GMM) of the substance.

33. The number of moles of SO_2Cl_2 in 13.5 g is

(a) 0.25 (b) 1.5
(c) 0.4 (d) 0.1

34. How many atoms are present in a mole of H_2SO_4?

(a) $7\times 6.02\times 10^{23}$ (b) $1.5\times 6.02\times 10^{23}$
(c) 6.02×10^{23} (d) $2\times 6.02\times 10^{23}$

35. The number of potassium atoms in 2 moles of potassium ferricyanide is

(a) 36.13×10^{23} (b) 6.02×10^{23}
(c) 24.08×10^{23} (d) 2×10^{23}

Directions (Q. Nos. 36 to 38) The atomic mass of an atom (element) is not its actual mass. It is relative mass as compared with an atom of carbon taken as 12. It is expressed in amu (u). The actual mass of an atom means its mass in grams which is obtained by dividing the atomic mass of the element by Avogadro's number (6.02×10^{23}) because one gram atom contains Avogadro's number of atoms.

36. Which of the following has maximum mass?

(a) 0.1 moles of ammonia
(b) 1120 cc of carbon dioxide
(c) 0.1 g atom of carbon
(d) 6.02×10^{22} molecules of H_2 gas

37. The mass of one atom of hydrogen is approximately

(a) 1 g (b) 3.2×10^{-24} g
(c) 1.6×10^{-24} g (d) 0.5 g

38. 5.6 L of a gas at NTP are found to have a mass of 11 g. The molecular mass of the gas is

(a) 36 (b) 48
(c) 40 (d) 44

Previous Years' Questions

39. The mass of potassium dichromate crystals required to oxidise 750 cm^3 of 0.6 M Mohr's salt solution is (Given, molar mass : Potassium dichromate = 294, Mohr's salt = 392) [AIEEE 2011]

(a) 0.49 g (b) 0.45 g (c) 22.05 g (d) 2.2 g

40. The density (in g mL^{-1}) of a 3.60 M sulphuric acid solution that is 29% H_2SO_4 (molar mass = 98 g mol^{-1}) by mass will be [AIEEE 2007]

(a) 1.64 (b) 1.88
(c) 1.22 (d) 1.45

41. How many moles of magnesium phosphate, $Mg_3(PO_4)_2$ will contain 0.25 moles of oxygen atoms? [AIEEE 2006]

(a) 0.02 (b) 3.125×10^{-2}
(c) 1.25×10^{-2} (d) 2.5×10^{-2}

Answers

Round I

1. (a)	**2.** (b)	**3.** (c)	**4.** (d)	**5.** (d)	**6.** (b)	**7.** (a)	**8.** (a)	**9.** (c)	**10.** (c)
11. (c)	**12.** (b)	**13.** (a)	**14.** (d)	**15.** (b)	**16.** (d)	**17.** (c)	**18.** (b)	**19.** (c)	**20.** (c)
21. (a)	**22.** (a)	**23.** (d)	**24.** (b)	**25.** (c)	**26.** (d)	**27.** (d)	**28.** (c)	**29.** (d)	**30.** (a)
31. (c)	**32.** (c)	**33.** (d)	**34.** (d)	**35.** (a)	**36.** (b)	**37.** (b)	**38.** (a)	**39.** (c)	**40.** (b)
41. (c)	**42.** (c)	**43.** (b)	**44.** (d)	**45.** (c)	**46.** (a)	**47.** (c)	**48.** (d)	**49.** (a)	**50.** (d)
51. (b)	**52.** (d)	**53.** (a)	**54.** (a)	**55.** (b)	**56.** (b)	**57.** (c)	**58.** (b)	**59.** (c)	**60.** (c)
61. (b)	**62.** (a)	**63.** (c)	**64.** (b)	**65.** (c)	**66.** (b)	**67.** (d)	**68.** (a)	**69.** (b)	**70.** (c)
71. (d)									

Round II

1. (b)	**2.** (c)	**3.** (d)	**4.** (d)	**5.** (c)	**6.** (a)	**7.** (d)	**8.** (a)	**9.** (b)	**10.** (a)
11. (d)	**12.** (b)	**13.** (b)	**14.** (b)	**15.** (c)	**16.** (c)	**17.** (a)	**18.** (b)	**19.** (b)	**20.** (b)
21. (c)	**22.** (c)	**23.** (a,d)	**24.** (a,c)	**25.** (c,d)	**26.** (a,b)	**27.** (c,d)	**28.** (b)	**29.** (a)	**30.** (b)
31. (c)	**32.** (d)	**33.** (d)	**34.** (a)	**35.** (a)	**36.** (b)	**37.** (c)	**38.** (d)	**39.** (c)	**40.** (c)
41. (b)									

the Guidance

Round I

1. $JPa^{-1} = \dfrac{J}{Pa} = \dfrac{\text{work}}{\text{pressure}} = \dfrac{N\text{-}m}{N/m^2} = m^3$

3.
$$°F = \frac{9}{5} t° C + 32$$
$$200 - 32 = \frac{9}{5} t° C \Rightarrow \frac{9}{5} t° C = 168$$
$$t° C = \frac{168 \times 5}{9} = 93.3 °C$$

6. (a) $28.7 pm \times \dfrac{10^{-12} m}{1 pm} = 2.87 \times 10^{-11} m$

(b) $15.15 \mu s \times \dfrac{10^{-6} s}{1 \mu s} = 1.515 \times 10^{-5} s$

(c) $25365 mg \times \dfrac{1 g}{1000 mg} \times \dfrac{1 kg}{1000 g} = 2.5365 \times 10^{-2} kg$

7. (a) In multiplication and division, the least precise term 0.112 has 3 significant figures. Hence, the answer should not have more than three significant figures.

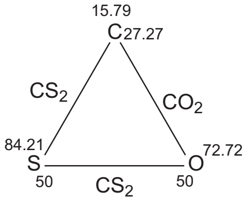
(b) In multiplication, 5 is the exact number and the other number has 4 significant figures. Hence, the answer should have 4 significant figures.

(c) In addition (or in subtraction), the answer cannot have more digits to the decimal point than either of the original members. Hence, the answer should have 4 significant figures.

11. The properties of a compound are quite different from the properties of constituent elements.

13. According to the law of conservation of mass,
Total mass of reactants = total mass of products
Amount of Fe_2O_3 is decided by limiting reagent.

14. In CS_2



C : S mass ratio is 15.79 : 84.21

15.79 parts of carbon combine with sulphur = 84.21

$\therefore$ 27.27 parts of carbon will combine with

$$S = \frac{84.21}{15.79} \times 27.27 = 145.434$$

Hence, ratio of S : O is 145.434 : 72.73 *i.e.*, 2 : 1

In SO_2, the ratio of S : O is 1 : 1

Since, the ratio of S : O is a simple whole number ratio, therefore law of reciprocal proportions is proved.

15. According to law of conservation of mass,

mass of reactants = mass of products

$\therefore \quad 6.3 + 15.0 = 18.0 + x$ or $x = 21.3 - 18.0 = 3.3$ g

16. $\underset{2V}{2N_2(g)} + \underset{IV}{O_2(g)} \longrightarrow \underset{2V}{2N_2O(g)}$

$$\frac{45.4}{22.7} = 2 \quad \frac{22.7}{22.7} = 1 \quad \frac{45.4}{22.7} = 2$$

Hence, the ratio between the volumes of the reactants and the product in the given question is simple *i.e.*, 2:1:2, It proves the Gay- Lussac's law of gaseous volumes, which states that when gases combine or are produced in a chemical reaction, they do so in a simple ratio by volume provided all gases are at same temperature and pressure.

17. As ratio of masses of nitrogen per gram of hydrogen in hydrazine and $NH_3 = 1\frac{1}{2} : 1 = \frac{3}{2} : 1$ or $3 : 2$

i.e., the law of multiple proportions.

18. To prepare 20 g zinc sulphate crystals, zinc required

$$= \frac{22.65}{100} \times 20 = 4.53 \text{ g}$$

19. $\text{Molarity} = \dfrac{\text{wt.} \times 1000}{\text{mol. wt.} \times \text{volume (mL)}} = \dfrac{5.85 \times 1000}{58.5 \times 500}$

$= 0.2 \text{ mol} L^{-1}$

20. $\because$ Mass of 22400 cm^3 CH_4 = 16 g

$\therefore \quad$ Mass of 112 cm^3 $CH_4 = \dfrac{16 \times 112}{22400} = 0.08$ g

21. $\text{Number of molecules} = \dfrac{\text{mass} \times N_A}{\text{molar mass}}$

22. $\text{Number of moles} = \dfrac{\text{weight}}{\text{molecular wt.}} = \dfrac{0.0018}{18} = 1 \times 10^{-4}$

[$\because$ 0.0018 mL = 0.0018 g]

$\therefore$ Number of water molecules $= 1 \times 10^{-4} \times 6.02 \times 10^{23}$

$= 6.023 \times 10^{19}$

24. $\text{Number of C atoms} = \dfrac{1 \times 10^{-3}}{12} \times N_A = 0.50 \times 10^{20}$

25. Mass of 1 atom of $^{12}C = \dfrac{\text{Atomic mass of C}}{\text{Avogadro's number}}$

$$= \frac{12 \text{ g}}{6.022 \times 10^{23}} = 1.9927 \times 10^{-23} \text{ g}$$

26. Molality, $m = \dfrac{\text{moles of solute}}{\text{mass of solvent (in kg)}}$

Mass of solvent (H_2O) = 500 g = 0.5 kg

$$\text{Moles of HCl} = \frac{18.25}{36.5} = 0.5$$

$$\therefore \qquad m = \frac{0.5}{0.5} = 1 \text{m}$$

27. $3F^- \equiv 1$ Formula unit (AlF_3)

3.0×10^{24} $F^- = 1 \times 10^{24}$ Formula units (AlF_3)

28. (a) 1g $Au = \dfrac{1}{197}$ mol-atoms of

$Au = \dfrac{1}{197} \times 6.022 \times 10^{23}$ atoms of Au

(b) 1g $Na = \dfrac{1}{23}$ mol-atoms of Na

$= \dfrac{1}{23} \times 6.022 \times 10^{23}$ atoms of Na

(c) 1 g $Li = \dfrac{1}{7}$ mol-atoms of Li

$= \dfrac{1}{7} \times 6.022 \times 10^{23}$ molecules of Li

(d) 1g $Cl_2 = \dfrac{1}{71}$ mole-molecules of $Cl_2 = \dfrac{1}{71}$

$\times 6.022 \times 10^{23}$ molecules of Cl_2

$= \dfrac{2}{71} \times 6.022 \times 10^{23}$ atoms of Cl

($\because$ 1 molecule of chlorine contains 2 atoms)

Therefore, 1 g of Li has largest number of atoms.

Note If a substance exists in atomic form, it contains mol-atoms and if a substance exists in molecular form, it contains mol-molecules.

30. Number of atoms in $N_2 = \dfrac{11.2 \times 10^{-3} \times 6.023 \times 10^{23} \times 2}{22.4}$

$= 6.023 \times 10^{20}$

Number of atoms in NO $= \dfrac{0.015 \times 2 \times 6.023 \times 10^{23}}{30}$

$= 6.023 \times 10^{20}$

31. In air

$$\text{molecular weight of } N_2 = \frac{28 \times 78}{100} = 21.84$$

$$\text{molecular weight of } O_2 = \frac{32 \times 21}{100} = 6.72$$

$$\text{molecular weight of Ar} = \frac{18 \times 0.9}{100} = 0.162$$

$$\text{molecular weight of } CO_2 = \frac{44 \times 0.1}{100} = 0.044$$

So, molecular weight of air = 21.84 + 6.72 + 0.162 + 0.044

= 28.766

32. Molecular mass of $CO_2 = 12 + 32 = 44$

$$44 \text{ g of } CO_2 \text{ has } 6.023 \times 10^{23} \text{ molecule}$$

$$0.2 \text{ g of } CO_2 \text{ has } \frac{6.023 \times 10^{23}}{44} \times 0.2$$

$$= 0.0273 \times 10^{23}$$

If 10^{21} molecules are removed then number of molecules

$$= 1.73 \times 10^{21}$$

$$\because \quad 6.023 \times 10^{23} \text{ molecules} = 1 \text{ mol}$$

$$\therefore \quad 1.73 \times 10^{21} \text{ molecules} = \frac{1}{6.023 \times 10^{23}} \times 1.73 \times 10^{21}$$

$$= 0.0028 \text{ mol}$$

33. 1 mole of H_2SO_4 gives 3 moles of ions or $3 \times 6.023 \times 10^{23}$ ions

$\therefore$ 0.1 mole of H_2SO_4 will give $0.1 \times 3 \times 6.023 \times 10^{23}$ ions

$$= 1.8 \times 10^{23} \text{ ions}$$

34. Atomic weight of the element

$$X = 6.643 \times 10^{-23} \times N_A = 40$$

$$\text{Number of moles of } X = \frac{20 \times 1000}{40} = 500$$

35. 3 molal solution of NaOH means 3 moles of NaOH are dissolved in 1 kg solvent. So, the mass of solution

= 1000 g solvent + 120 g NaOH = 1120 g solution

(Molar mass of NaOH = 23 + 16 + 1 = 40 g;

3 moles of NaOH = 3 × 40 = 120 g)

$$\text{Volume of solution} = \frac{\text{Mass of solution}}{\text{Density of solution}}$$

$$V = \frac{1120 \text{ g}}{1.110 \text{ g mL}^{-1}} = 1009 \text{ mL}$$

$$\text{Molarity} = \frac{\text{moles of solute} \times 1000}{\text{volume of solution (mL)}} = \frac{3 \times 1000}{1009} = 2.973 \text{ M}$$

36. Given, $d = 0.793 \text{ kg L}^{-1} = 0.793 \times 10^3 \text{ g L}^{-1}$

Molar mass of methanol,

$CH_3OH = (1 \times 12.01) + (4 \times 1.0079) + 16.00 = 32.0416 \approx 32$

$$\text{Molarity} = \frac{0.793 \times 10^3 \text{ g L}^{-1}}{32 \text{ g mol}^{-1}} = 24.781 \text{ mol}^{-1}$$

$$M_1 V_1 = M_2 V_2$$

$$24.781 \times V_1 = 0.25 \times 2.5$$

$$V_1 = \frac{0.25 \times 2.5}{24.781} = 0.02522 \text{ L} = 25.22 \text{ mL}$$

37. 15 ppm means 15 parts in one million (10^6) parts.

$$\text{Therefore, \% by mass} = \frac{15 \times 100}{10^6} = 1.5 \times 10^{-3}\%$$

Molar mass of $CHCl_3 = 12.01 + 1.0079 + (3 \times 35.45)$

$$M_{CHCl_3} = 119.367 \approx 119 \text{ g mol}^{-1}$$

1.5×10^{-3} % means 1.5×10^{-3} g chloroform is present in 100 g sample.

$$\text{Molarity, } M = \frac{w \times 1000}{m \times \text{ volume of sample}}$$

(For water, density = 1g cm^{-3}, so mass = volume)

$$M = \frac{1.5 \times 10^{-3} \times 1000}{119 \times 100} = 0.000126 = 1.26 \times 10^{-4} \text{ M}$$

38. (a) 1 mole of Ar = 6.022×10^{23} atoms.

$$52 \text{ moles of Ar} = 52 \times 6.022 \times 10^{23} \text{ atoms}$$

$$= 313.144 \times 10^{23} \text{ atoms}$$

$$= 3.131 \times 10^{25} \text{ atoms}$$

(b) 4 u of He = 1 He atom

$$\therefore \text{ 52 u of He} = \frac{52}{4} \text{ He atoms} = 13 \text{ He atoms}$$

(c) 1 mole atom of He = 4 g = 6.022×10^{23} atoms

$$52 \text{ g of He} = \frac{52 \times 6.022 \times 10^{23}}{4} \text{ atoms}$$

$$= 78.286 \times 10^{23} \text{ atoms}$$

$$= 7.8286 \times 10^{24} \text{ atoms}$$

39. 1 mole of $(NH_4)_3PO_4$ contains 12 moles of hydrogen atoms.

$\therefore$ 12 moles of hydrogen atoms $\equiv$ 1 mole of $(NH_4)_3PO_4$.

$$\therefore \quad 1 \text{ mole of hydrogen atom} = \frac{1}{12} \text{ mole of } (NH_4)_3PO_4$$

$$\therefore \quad 6.36 \text{ moles of hydrogen atom} = \frac{1}{12} \times 6.36$$

$$= \frac{6.36}{12} \text{ mole of } (NH_4)_3PO_4$$

1 mole of $(NH_4)_3PO_4$ = 4 moles of oxygen

$$\text{So,} \quad \frac{6.36}{12} \text{ mole of } (NH_4)_3PO_4 = \frac{4 \times 6.36}{12} = 2.12 \text{ mol}$$

40. $CuSO_4 \cdot 5H_2O$ has 1 mole of copper and 9 moles of oxygen atoms.

$$63.5 \text{ g Cu} \simeq 9 \times 16 \text{ g of oxygen}$$

$$8.64 \text{ g of oxygen} = \frac{63.5 \times 8.64}{9 \times 16} = 3.81 \text{ g}$$

41. Molecular weight of cortisone = 360.4

Molecular weight of 21 carbon atom = 21 × 12 = 252

$$\text{Percentage of carbon in cortisone} = \frac{252 \times 100}{360.4} = 69.9\%$$

43. $$\text{The mass of KI in 2g salt} = \frac{2 \times 1}{100} = 0.02 \text{ g}$$

$$= \frac{0.02}{39 + 127} \text{ mol}$$

$$= \frac{0.02}{166} \times 6.02 \times 10^{23} \text{ ions}$$

$$= 7.2 \times 10^{19} \text{ ions}$$

44. Mass of one molecule of water

$$= \frac{\text{mol. mass}}{N_0} = \frac{18}{6.02 \times 10^{23}} \text{ g}$$

$$\therefore \text{ Volume of 1 molecule of water} = \frac{\text{mass}}{\text{density}}$$

$$= \frac{18 \times 10^{-23}}{6.02 \times 1}$$

$$= 3 \times 10^{-23} \text{ mL}$$

46. $$\frac{\text{wt. of metal } X}{\text{wt. of metal } Y} = \frac{\text{Eq. wt. of metal } X}{\text{Eq. wt. of metal } Y}$$

$$\frac{w_1}{w_2} = \frac{E_1}{E_2} \text{ or } E_1 = \frac{w_1}{w_2} \times E_2$$

47. Empirical formula mass $= CH_2O$

$$= 12 + 2 \times 1 + 16 = 30$$

Molecular mass = 180

$$n = \frac{\text{molecular mass}}{\text{empirical formula mass}}$$

$$= \frac{180}{30} = 6$$

$\therefore$ Molecular formula $= n \times$ empirical formula

$$= CH_2O \times 6 = C_6H_{12}O_6$$

48. In a chemical reaction, coefficient represents mole of that substance.

$$X + 2Y \longrightarrow Z$$

This indicates 1 mole of X reacts with 2 moles of Y to form 1 mole of Z.

So, 5 moles of X will require 10 moles of Y. But we have taken only 9 moles of Y.

Hence, Y is in limiting quantity. Hence, we determine product from Y.

Thus, 5 moles of X react with 9 moles of Y to form 4 moles of Z.

49. Mass per cent of an element

$$= \frac{\text{Mass of that element in the compound} \times 100}{\text{Molar mass of the compound}}$$

Molar mass of $Na_2SO_4 = (2 \times 22.99) + 32.06 + (4 \times 16.00)$

$$= 142.04 \text{ g}$$

$$\text{Mass per cent of sodium} = \frac{45.98 \times 100}{142.04} = 32.37$$

50. $$\underset{3 \text{ mol}}{3BaCl_2} + \underset{2 \text{ mol}}{2Na_3PO_4} \longrightarrow \underset{1 \text{ mol}}{Ba_3(PO_4)_2} + 6NaCl$$

Here, Na_3PO_4 is the limiting reactant.

2 moles of Na_3PO_4 gives 1 mole of $Ba_3(PO_4)_2$

So, 0.2 mole of Na_3PO_4 will give 0.1 mole of $Ba_3(PO_4)_2$.

52. $$\underset{276 \text{ g}}{Ag_2CO_3} \xrightarrow{\Delta} \underset{216 \text{ g}}{2Ag} + CO_2 + \frac{1}{2}O_2$$

As 276 g of Ag_2CO_3 will give = 216 g of Ag

$$\text{So, } \quad 2.76 \text{ g of } Ag_2CO_3 \text{ will give} = \frac{2.76 \times 216}{276} = 2.16 \text{ g}$$

53. Ratio of atoms

$$C : H : N : O :: \frac{20.0}{12} : \frac{6.66}{1} : \frac{47.33}{14} : \frac{26.01}{16}$$

$$= 1.67 : 6.66 : 3.38 : 1.63$$

$$= 1 : 4 : 2 : 1$$

Empirical formula $= CH_4N_2O$

Empirical formula mass = 60 g

Molar mass $= 60 \text{g mol}^{-1}$

$\therefore$ Molecular formula $= CH_4N_2O$

54. Average molar mass of

$$Ar = \sum f_i \times A_i = (0.00337 \times 35.96755)$$

$$+ (0.00063 \times 37.96272) + (0.99600 \times 39.9624)$$

$$= 0.121 + 0.024 + 39.803 = 39.948 \text{ g mol}^{-1}$$

55. $$\underset{2 \text{ mol}}{MnO_2} + \underset{4 \text{ mol}}{4HCl} \longrightarrow MnCl_2 + 2H_2O + \underset{\substack{1 \text{ mol} \\ 22.4 \text{ L}}}{Cl_2}$$

But the yield is 11.2.

$$\therefore \quad \text{Percentage yield} = \frac{11.2}{22.4} \times 100 = 50\%$$

56. $$A + B_2 \longrightarrow AB_2$$

(a) According to the above reaction, 1 atom of A reacts with 1 molecule of B.
$\therefore$ 200 atoms of A will react with 200 molecules of B. In this case, B is the limiting reagent, so A is in excess.

(b) According to the above reaction, 1 mole of A reacts with 1 mole of B.
$\therefore$ 2 moles of A will react with 2 moles of B. In this case, A is the limiting reagent, so B is in excess.

(c) No limiting reagent.

(d) 2.5 moles of B requires only 2.5 moles of A to react. So, B is the limiting reagent and A is in excess.

57. H_2O is the limiting reagent for the given equation.

$\because$ 6 moles H_2O produces $Fe(OH)_3$ = 4 mol

$$\therefore 2 \text{ moles } H_2O \text{ will produce } Fe(OH)_3 = \frac{4 \times 2}{6} = 1.34 \text{ mol}$$

58. (i) Calculation for mass of HCl in 25 mL of 0.75 M HCl

$$\text{Molarity} = \frac{w \times 1000}{m \times \text{vol (mL)}}$$

$$0.75 = \frac{w \times 1000}{36.5 \times 25}$$

(Molar mass of HCl = 1 + 35.5 = 36.5 g/mol)

$$w = 0.75 \times 36.5 \times 25 / 1000 = 0.6844 \text{ g}$$

(b) Calculation for required mass of $CaCO_3$ to react completely with 0.6844 g HCl

$$\underset{100 \text{ g}}{CaCO_3(s)} + \underset{2 \times 36.5 = 73 \text{ g}}{2HCl(aq)} \longrightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

According to balanced chemical equation,

73 g HCl completely reacts with 100 g $CaCO_3$

1 g HCl completely reacts with $\frac{100}{73}$ g $CaCO_3$

$\therefore$ 0.6844 g HCl will completely reacts with

$$\frac{100 \times 0.6844}{73} = 0.9375 \text{ g}$$

59. Mass of 1 atom $= 1.8 \times 10^{-22}$ g

Mass of 6.02×10^{23} atoms

$$= 6.02 \times 10^{23} \times 1.8 \times 10^{-22} \text{ g}$$
$$= 6.02 \times 1.8 \times 10 \text{ g}$$
$$= 108.36 \text{ g}$$

$\therefore$ Atomic mass of element $= 108.36$

60.

Element	Symbol	%by mass	Atomic mass	Relative number of moles of element	Simple molar ratio	Simple whole number molar ratio
Iron	Fe	69.9	55.85	$\frac{69.9}{55.85} = 1.25$	$\frac{1.25}{1.25} = 1$	$1 \times 2 = 2$
Oxygen	O	30.1	16.00	$\frac{30.1}{16.00} = 1.88$	$\frac{1.88}{1.25} = 1.5$	$1.5 \times 2 = 3$

$\therefore$ Empirical formula $= Fe_2O_3$

Empirical formula mass of

$$Fe_2O_3 = (2 \times 55.85) + (3 \times 16.00)$$
$$= 159.7 \text{ g mol}^{-1}$$
$$n = \frac{\text{molar mass}}{\text{empirical formula mass}}$$
$$= \frac{159.8}{159.7} = 1$$

Hence, molecular formula is same as empirical formula; Fe_2O_3.

61. In first oxide,

Mass of arsenic $= 65.2$

Mass of oxygen $= 34.8$

$\therefore$ Eq. mass of arsenic $= \frac{65.2}{34.8} \times 8 = 14.99$

In second oxide,

Mass of arsenic $= 75.7$ g

Mass of oxygen $= 24.3$ g

$\therefore$ Equivalent mass of arsenic $= \frac{75.7}{24.3} \times 8 = 24.92$

Equivalent mass of arsenic : Equivalent mass of arsenic
(oxide I) (oxide II)

14.99 : 24.92

or 3 : 5

62. Eq. mass of copper chloride $= 99$

Eq. mass of chlorine $= 35.5$

$\therefore$ Eq. mass of copper $= 99 - 35.5 = 63.5$

$\therefore$ Valency of copper $= \frac{\text{at. mass of copper}}{\text{eq. mass of copper}} = 1$

$\therefore$ Formula of copper chloride is CuCl.

63. For minimum molecular mass, there must be one S atom per insulin molecule.

If 3.4 g S is present, the molecular mass $= 100$

$\therefore$ If 32 g S is present, the molecular mass $= \frac{100 \times 32}{3.4}$

$= 941.176$

64.

	Oxide I	Oxide II
Metal, *M*	50%	40%
Oxygen, O	50%	60%

As first oxide is MO_2

Let atomic mass of $M = x$

$$\therefore \quad \% \text{ O} = \frac{32}{x + 32} \times 100$$

or $\quad \frac{50}{100} = \frac{32}{x + 32}$ or $0.5 = \frac{32}{x + 32}$

or $\quad 0.5x + 16 = 32$

$$0.5x = 16$$
$$x = 32$$

$\therefore$ At. mass of metal $M = 32$

Let formula of second oxide is M_2O_n

$$\% M = \frac{2x}{2x + 16n} \times 100 = \frac{64}{64 + 16n} \times 100$$
$$\frac{40}{100} = \frac{64}{64 + 16n}$$

or $\quad \frac{100}{40} = \frac{64 + 16n}{64}$

$$2.5 = 1 + 0.25n$$
$$n = \frac{1.5}{0.25} = 6$$

Therefore, formula of second oxide $= M_2O_6$

or $= MO_3$

65. $\underset{4 \times 36.5}{4HCl(aq)} + \underset{87 \text{ g}}{MnO_2(s)} \longrightarrow 2H_2O(l) + MnCl_2(aq) + Cl_2(g)$

According to the balanced chemical equation,

87 g of MnO_2 react with 4×36.5 g HCl

5 g of MnO_2 will react with $\frac{4 \times 36.5 \times 5}{87} = 8.39$ g HCl

Note Amounts of one reactant required to react a particular amount of another reactant can be determined by using stoichiometric calculations.

66. $\underset{2V}{2H_2(g)} + \underset{1V}{O_2} \longrightarrow \underset{2V}{2H_2O(g)}$

According to Gay-Lussac's law of gaseous volume, 2 volumes of dihydrogen react with 1 volume of O_2 to produce 2 volumes of water vapour. Therefore, 10 volumes of dihydrogen on reaction with 5 volumes of dioxygen will produce 10 volumes of water vapour.

67. In 100 tons of Fe_2O_3, pure Fe_2O_3

$$= 100 - \frac{100 \times 20}{100}$$

$$= 80 \text{ tons}$$

$$\underset{\substack{2 \times 56 + 48 \\ 160}}{Fe_2O_3} + 3H_2 \longrightarrow \underset{\substack{2 \times 56 \\ 2 \times 56}}{2Fe} + 3H_2O$$

$\because$ 160 g Fe_2O_3 gives $Fe = 2 \times 56$ g

$\therefore$ 80 tons Fe_2O_3 will give $Fe = \dfrac{2 \times 56 \times 80}{160}$

$= 56$ tons

69. By the equation

$$\begin{array}{lccc} & Zn & + \; I_2 \longrightarrow & ZnI_2 \\ \text{Initial moles} & \frac{x}{65} & \frac{x}{254} & 0 \end{array}$$

(If x be the wt. of Zn and I_2 each initially)

$$\begin{array}{lccc} \text{No. of moles at the end of reaction} & \left(\frac{x}{65} - \frac{x}{254}\right) & 0 & \frac{x}{254} \end{array}$$

So, fraction of Zn unreacted $= \dfrac{\frac{x}{65} - \frac{x}{254}}{\frac{x}{65}} = 0.74$

Round II

1.

Combination	Mass of *A* (g)	Mass of *B* (g)
AB	2	5
AB_2	2	10
A_2B	4	5
A_2B_3	4	15

Mass of *B* which is combined with fixed mass of *A* (say 1 g) will be 2.5 g, 5 g, 1.25 g and 3.75 g. They are in the ratio 2 : 4 : 1:3 which is simple whole number ratio. Hence, the law of multiple proportions is applicable.

2. Nitrogen shows variable valency and thus, have variable equivalent weight.

3. Molecular mass of $(CHCOO)_2Fe = 170$

$\therefore$ In 100 g $(CHCOO)_2Fe$, iron present $= \dfrac{56}{170} \times 100$ mg

$= 32.9$ mg

Since, this quantity of Fe is present in 400 mg of capsule,

$\therefore$ % of Fe in capsule $= \dfrac{32.9}{400} \times 100 = 8.2\%$

4. For water, 1 g = 1 mL ($\because$ *d* for water = 1)

$\therefore$ 18 g = 18 mL

18 mL water $= 6.02 \times 10^{23}$ molecules $= N_A$ molecules

$\because$ In 1000 mL, number of water molecules $= \dfrac{N_A \times 1000}{18}$

$= 55.55\, N_A$

5. In 100 g haemoglobin, mass of iron = 0.33 g

$\therefore$ In 67200 g haemoglobin, mass of iron $= \dfrac{67200 \times 0.33}{100}$

$= 672 \times 0.33$ g

$\therefore$ The number of Fe atoms in one Hb molecule

$$= \frac{672 \times 0.33}{56}$$

$= 4$

6. In 12 g carbon, mass of C-14 isotope $= 12 \times \dfrac{2}{100} = 0.24$ g

$\therefore$ Number of C-14 atoms in 12 g of C $= \dfrac{0.24}{14} \times 6.02 \times 10^{23}$

$= 1.032 \times 10^{22}$

7. In 1 L air, volume of $O_2 = 210$ cc

$\because$ $22400 \text{ cm}^3 = 1$ mol

$\therefore$ $210 \text{ cm}^3 = \dfrac{210}{22400} = 0.0093$ mol

8. Let the per cent abundance of lighter isotope is x.

$\therefore$ Atomic mass, $z = \dfrac{x(z-1) + (100 - x)(z + 2)}{x + 100 - x}$

$3x = 200$ or $x = 66.6\%$

9. (CO_2 and (O)) This is an example of law of multiple proportion.

10. Mass of hydrogen $= \dfrac{0.7}{22.4} \times 2 = \dfrac{14}{224}$ g $= 0.0625$ g

$\because$ 0.0625 g of hydrogen is displaced by x g metal.

$\therefore$ 1 g of hydrogen is displaced by $\dfrac{x}{0.0625}$ g of metal

$\Rightarrow$ $\dfrac{x}{0.0625} = 28$

Eq. mass of metal, $x = 28 \times 0.0625 = 1.75$ g

11. $\dfrac{\text{Wt. of metal hydroxide}}{\text{Wt. of metal oxide}} = \dfrac{\text{Eq. wt. of metal + Eq. wt. of } OH^-}{\text{Eq. wt. of metal + Eq. wt. of } O_2^{2-}}$

$\Rightarrow$ $\dfrac{1.520}{0.995} = \dfrac{E + 17}{E + 8}$

On solving, $E = 9.0$

12. $\underset{208\text{ g}}{BaCl_2} + \underset{98\text{ g}}{H_2SO_4} \longrightarrow \underset{233\text{ g}}{BaSO_4} + 2HCl$

100 mL of 20.8% $BaCl_2$ solution contains 20.8 g $BaCl_2$

50 mL of 9.8% H_2SO_4 solution contains 4.9 g H_2SO_4

Here, H_2SO_4 is the limiting reactant.

$\because$ 98 g H_2SO_4 gives $BaSO_4 = 233$ g

$\therefore$ 4.9 g H_2SO_4 will give $BaSO_4 = \dfrac{233 \times 4.9}{98}$

$= 11.65$ g

13. Molar mass of $CaCO_3 = 40 + 12 + 3 \times 16 = 100 \text{ g mol}^{-1}$

Moles of $CaCO_3$ in 1000 g,

$$n_{CaCO_3} = \frac{\text{Mass (g)}}{\text{Molar mass}}$$

$$n_{CaCO_3} = \frac{1000 \text{ g}}{100 \text{ g mol}^{-1}} = 10 \text{ mol}$$

$$\text{Molarity} = \frac{\text{Moles of solute (HCl)} \times 1000}{\text{Volume of solution}}$$

$$0.76 = \frac{n_{HCl} \times 1000}{250}$$

$$n_{HCl} = \frac{0.76 \times 250}{1000}\ 0.19 \text{ mol}$$

$$\underset{1\text{ mol}}{CaCO_3(s)} + \underset{2\text{ mol}}{2HCl(aq)} \longrightarrow CaCl_2(aq) + CO_2\,(g) + H_2O(l)$$

According to the equation,

1 mole of $CaCO_3$ reacts with 2 moles of HCl

$\therefore$ 10 moles of $CaCO_3$ will react with $\dfrac{10 \times 2}{1} = 20$ moles of HCl.

But we have only 0.19 moles HCl, so HCl is the limiting reagent and it limits the yield of $CaCl_2$.

2 moles of HCl, produces 1 mole of $CaCl_2$.

0.19 mole of HCl will produce $\dfrac{1 \times 0.19}{2} = 0.095$mol $CaCl_2$.

Molar mass of $CaCl_2 = 40 + (2 \times 35.5) = 111 \text{ g mol}^{-1}$

$\therefore$ 0.095 mole of $CaCl_2 = 0.095 \times 111 = 10.54$ g

14. Since, 1g hydrogen combines with 80 g bromine, the equivalent weight of bromine $= 80$

$\because$ 4 g bromine combines with Ca $= 1$ g

$\therefore$ 80 g bromine will combine with Ca $= \dfrac{1 \times 80}{4} = 20$ g

$\therefore$ Eq. wt. of Ca is 20 g.

15. $(NH_4)_2SO_4 \longrightarrow 2NH_3 + H_2O + SO_3$

$2NH_3 + 2HCl \longrightarrow 2NH_4Cl$

$$\underset{132\text{ g}}{(NH_4)_2SO_4} \equiv 2NH_3 \equiv \underset{73\text{ g}}{2HCl}$$

$$73 \text{ g HCl} \equiv 132 \text{ g } (NH_4)_2SO_4$$

$$292 \text{ g HCl} \equiv \frac{132 \times 292}{73} \text{ g } (NH_4)_2SO_4$$

$$= 528 \text{ g } (NH_4)_2SO_4$$

16. $\underset{264\text{ g}}{2(NH_4)_2HPO_4} \equiv \underset{142\text{ g}}{P_2O_5}$

$$\text{Percentage of } P_2O_5 = \frac{\text{wt. of } P_2O_5}{\text{wt. of salt}} \times 100$$

$$= \frac{142}{264} \times 100 = 53.78\%$$

17. Partial pressure of oxygen $= \dfrac{2}{1 + 4 + 2} \times 2660$

$= 760$ mm

Thus, 1 L oxygen gas is present at 0°C and 760 mm pressure.

$\therefore$ Number of oxygen molecules $= \dfrac{6.023 \times 10^{23}}{22.4}$

18. $\underset{248\text{ g}}{Ag_2S} \equiv \underset{2 \times 108\text{ g}}{2Ag}$

2×108 g Ag is obtained from $Ag_2S = 248$ g

1 g Ag will be obtained from $Ag_2S = \dfrac{248 \times 1}{2 \times 108}$

$= \dfrac{248}{216}$ g

But, the ore contains only 1.34% Ag_2S.

Thus, 1 g Ag is obtained from ore $= \dfrac{248}{216} \times \dfrac{100}{1.34}$ g

$= 85.68$ g

19. $2Ag + 2HNO_3 \longrightarrow 2AgNO_3 + H_2$

$2AgNO_3 + 2NaCl \longrightarrow 2AgCl + NaNO_3$

$$\underset{143.5\text{ g}}{AgCl} \equiv \underset{170\text{ g}}{AgNO_3} \equiv \underset{108\text{ g}}{Ag}$$

$\because$ 143.5g AgCl is obtained from Ag $= 108$ g

$\therefore$ 2.87 g AgCl is obtained from Ag $= \dfrac{108 \times 2.87}{143.5}$

$= 2.16$ g

20. According to the equation,

$$NaCl + AgNO_3 \longrightarrow NaNO_3 + AgCl$$

$$\text{Number of moles of NaCl} = \frac{4.77}{58.5} = 0.08154$$

$$\text{Number of moles of } AgNO_3 = \frac{5.77}{170} = 0.03394$$

Thus, $AgNO_3$ is the limiting reagent in the reaction.

Now, applying POAC for Ag (as Ag atoms are conserved in the reaction)

Moles of Ag in $AgNO_3$ = moles of Ag in AgCl

or $1 \times$ moles of $AgNO_3 = 1 \times$ moles of AgCl

or 0.03394×143.5 (for AgCl) $= 4.87$ g

21. As both the reactants are consumed completely, thus the ratio of stoichiometric coefficients would be 0.75 : 2 or 3 : 8.

So, $3A_4 + 8O_2 \longrightarrow$ Product

Now as final pressure is half of oxygen initially, thus the molecular formula will be A_3O_4 to balance the equation correctly, *i.e.*,

$$3A_4 + 8O_2 \longrightarrow 4A_3O_4$$

22. $\underset{111\text{ g}}{CaCl_2} + CO_3^{2-} \longrightarrow \underset{100\text{ g}}{CaCO_3} + 2Cl^-$

$$\underset{100\text{ g}}{CaCO_3} \xrightarrow{\Delta} \underset{56\text{ g}}{CaO} + CO_2$$

$\because$ 56 g CaO is obtained by the decomposition of

$$CaCO_3 = 100 \text{ g}$$

$\therefore$ 0.959 g CaO will be obtained by the decomposition of

$$CaCO_3 = \frac{100 \times 0.959}{56}$$

$$= 1.71 \text{ g}$$

Further,

$$100 \text{ g } CaCO_3 \equiv 111 \text{ g } CaCl_2$$

$$1.71 \text{ g } CaCO_3 = \frac{111 \times 1.71}{100}$$

$$= 1.89 \text{ g } CaCl_2$$

$$\text{Percentage of } CaCl_2 \text{ in the mixture} = \frac{1.89}{4.22} \times 100$$

$$= 44.78$$

$$\approx 45\%$$

23. Law of conservation of mass and Avogadro's law are not related to the given statement.

24. Number of moles of NaOH,

$$n_{NaOH} = \frac{4}{40} = 0.1 \text{mol} \left\{ n = \frac{\text{mass (g)}}{\text{molar mass (g mol}^{-1})} \right\}$$

$$\text{Similarly, } n_{H_2O} = \frac{36}{18} = 2 \text{ mol}$$

Mole fraction of NaOH,

$$x_{NaOH} = \frac{\text{moles of NaOH}}{\text{moles of NaOH} + \text{moles of } H_2O}$$

$$x_{NaOH} = \frac{0.1}{0.1 + 2} = 0.0476$$

$$\text{Similarly, } \quad x_{H_2O} = \frac{n_{H_2O}}{n_{NaOH} + n_{H_2O}} = \frac{2}{0.1 + 2} = 0.9524$$

Total mass of solution = mass of solute + mass of solvent = 4 + 36 = 40 g

$$\text{Volume of solution } = \frac{\text{mass of solution}}{\text{sp. gravity}} = \frac{40 \text{ g}}{1 \text{ g mL}^{-1}} = 40 \text{mL}$$

$$\text{Molarity} = \frac{\text{moles of solute} \times 1000}{\text{volume of solution (mL)}}$$

$$= \frac{0.1 \times 1000}{40} = 2.5 \text{ M}$$

25. (c) Number of atoms in 28 g of $N_2 = \frac{28}{28} \times N_A \times 2$

$$= 2 N_A$$

Number of atoms in 32 g of $O_2 = \frac{32}{32} \times N_A \times 2$

$$= 2 N_A$$

(d) 12 g of C (*s*) contains atoms = $\frac{12}{12} \times N_A \times 1$

$$= N_A$$

No. of atoms in 23 g of Na = $\frac{23}{23} \times N_A \times 1 = N_A$

26. (a) Molarity $M = \frac{\text{wt. of NaOH} \times 1000}{\text{mol. wt. of NaOH} \times V \text{ (mL)}}$

$$= \frac{20 \times 1000}{40 \times 200} = 2.5 \text{ M}$$

(b) Molarity, $M = \frac{0.5 \times 1000}{200} = 2.5$ M

(c) $M = \frac{40 \times 1000}{40 \times 100} = 10$ M

(d) $M = \frac{20 \times 1000}{56 \times 200} = 1.785 M$

Thus, 20 g NaOH in 200 mL of solution and 0.5 mole of KCl in 200 mL have the same concentration.

27. Number of molecules = $\frac{\text{mass}}{\text{molar mass}} \times N_A$

Number of molecules, in 16 g oxygen = $\frac{16}{32} \times N_A$

$$= \frac{N_A}{2}$$

in 16 g of CO = $\frac{16}{28} \times N_A = \frac{N_A}{1.75}$

in 28 g of $N_2 = \frac{28}{28} \times N_A = N_A$

in 14g of $N_2 = \frac{14}{28} \times N_A = \frac{N_A}{2}$

in 1 g of $H_2 = \frac{1}{2} N_A = \frac{N_A}{2}$

28. Gram molecular weight is the weight of N_A molecules in gram.

29. The molecular formula of ethene is C_2H_4 and its empirical formula is CH_2.

Thus, empirical formula ×2 = molecular formula.

30. Both the statements are correct but statement II is not the correct explanation of statement I.

31. 0.200 contains 3 while 200 contains only one SF as zero at the end or right of a number are significant provided they are on the right side of the decimal point.

32.
$$\underset{\substack{1 \text{ mol} \\ =16 \text{ g}}}{CH_4} + 2O_2 \longrightarrow CO_2 + \underset{\substack{2 \text{ mol} \\ =36 \text{ g}}}{2H_2O}$$

33. Mol. mass of $SO_2Cl_2 = 32 + 32 + 71 = 135$

$$13.5 \text{ g } SO_2Cl_2 = 0.1 \text{ mol}$$

34. 1 mol of $H_2SO_4 = 6.02 \times 10^{23}$ molecules

$$= 7 \times 6.02 \times 10^{23} \text{ atoms}$$

35. 2 moles of $K_3[Fe(CN)_6] = 2 \times 6.02 \times 10^{23}$ molecules

$$= 3 \times 2 \times 6.02 \times 10^{23} \text{ atoms of K}$$

$$= 36.13 \times 10^{23} \text{ atoms of K.}$$

36. 0.1 g-atom of C = 1.2 g

0.1 mol of NH_3 = 1.7 g

6.022×10^{22} molecules of H_2 = 0.2 g

$$1120 \text{ cc of } CO_2 = \frac{44}{22400} \times 1120 = 2.2 \text{ g}$$

37. $$\text{Mass of 1 atom of H} = \frac{1}{6.02 \times 10^{23}} \text{ g}$$

$$= 1.6 \times 10^{-24} \text{ g}$$

38. $\because$ 5.6 L of a gas at NTP have mass = 11 g

$$\therefore \text{ 22.4 L of gas at NTP have mass} = \frac{11 \text{ g}}{5.6} \times 22.4$$

$$= 44 \text{ g}$$

39. Mohr's salt is $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$

Only oxidizable part is Fe^{2+}

$$[Fe^{2+} \longrightarrow Fe^{3+} + e^-] \times 6$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

Millimoles of Fe^{2+} = $750 \times 0.6 = 450$

$$\text{Moles of } Fe^{2+} = \frac{450}{1000} = 0.450 \text{ mol}$$

$$6 \text{ mol } Fe^{2+} \equiv 1 \text{mol } Cr_2O_7^{2-}$$

$$\therefore 0.450 \text{ mol } Fe^{2+} \equiv \frac{0.450}{6}$$

$$= 0.075 \text{ mol } Cr_2O_7^{2-}$$

$$= 0.075 \times 294 \text{ g}$$

$$= 22.05 \text{ g}$$

40. $$\text{Molarity} = \frac{10 \times \text{density} \times \text{wt. of solute}}{\text{mol. wt. of the solute}}$$

$$\therefore \text{ Density} = \frac{3.60 \times 98}{10 \times 29} = 1.21 \text{g mL}^{-1}$$

41. In $Mg_3(PO_4)_2$ molecule,

8 moles of O-atom are contained by 1 mole $Mg_3(PO_4)_2$

Hence, 0.25 mole of O atom are contained by

$$Mg_3(PO_4)_2 = \frac{1}{8} \times 0.25$$

$$= 3.125 \times 10^{-2}$$

2 States of Matter

Gaseous and Liquid States

JEE Main MILESTONE

- Different States of Matter
- Gaseous state
- Gas Laws
- Kinetic Theory of Gases
- Molecular Velocities
- Ideal and Real Gases
- van der Waal's
- Liquefaction of Gases
- Joule-Thomson Effect
- Liquid State

2.1 Different States of Matter

Solids, liquids and gases are three general states of matter which show difference in the several characteristics.

Table 2.1 **Characteristics of Different States of Matter**

S. No.	Solids	Liquids	Gases
1.	They are rigid, have a definite shape and a definite volume.	They are not rigid, shape is not definite but have a definite volume.	They are not rigid, have neither definite shape nor volume.
2.	The position of molecules are almost fixed. They can only vibrate to and fro about their mean position.	The position of molecules are not fixed, they can slide over one another but cannot escape the boundary in normal conditions.	The positions of molecules are not fixed at all. They can move freely and cannot be confined to definite boundary.
3.	Molecules are closely packed.	Molecules are closely packed.	Molecules are wide apart.
4.	Molecules are associated with minimum energy due to motion.	Molecules are associated with intermediate energy due to motion.	Molecules are associated with maximum energy.
5.	The intermolecular forces are very strong.	The intermolecular forces are weak.	The intermolecular forces are very weak.

Anything that occupies space and has weight is called matter or substance. Almost all substances exist in three states under appropriate conditions of temperature and pressure. The physical state of a substance is largely determined by temperature and pressure considerations.

Forces Responsible for Solid, Liquid and Gaseous States of Matter

There are following two factors which determine the physical state of matter. These are

(a) Thermal Agitation

Due to kinetic energy of the particles, the atoms (or molecules) of a matter are in a state of continuous vibration and agitation. This behaviour of them is called **thermal agitation.** An increase in temperature, increases the kinetic energy thus, results in increased randomness or disorder. A decrease in temperature, results in decrease of kinetic energy, thus the frequency of collisions and disorder reduce.

(b) Cohesive Forces

The cohesive forces can be **coulombic forces** or **van der Waals' forces,** depending on the type of molecules involved. van der Waals' forces are very short lived intermolecular attractive forces which are believed to exist between all kinds of molecules when they are sufficiently close to each other.

These forces are of following types

(i) **Dipole-dipole interactions** These are seen between polar molecules with permanent polarity in them. When polar molecules are brought nearer to each other, they orient themselves in such a way that positive end of one dipole attracts the negative end of other dipole and *vice-versa* as :

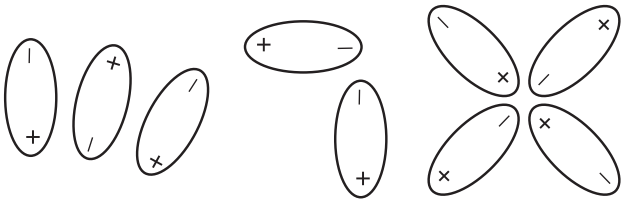


Fig. 2.1 Illustration of dipole-dipole interaction

These forces are strongest of all van der Waals' forces and are called **keesom** forces. The intensity of these forces is generally hampered by an increase in temperature.

(ii) **Ion-induced dipole interactions** Polar molecules are attracted towards ions and this interaction between ion and dipoles is called **ion-dipole interactions.** Ions however, can attract neutral molecules also and have the ability of causing polarity in them. Such interactions are called **ion-induced** dipole interactions.

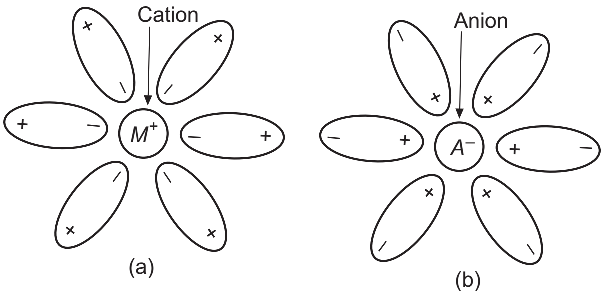


Fig. 2.2 Ion-dipole interaction **(a)** Cation (M^+) attracts the negative end of dipole **(b)** Anion (A^-) attracts the positive end

(iii) **Dipole-induced dipole interactions** When a dipole comes near the non-polar molecule, it can induce polarity in non-polar molecule resulting to **dipole-induced dipole interactions** which can be seen as

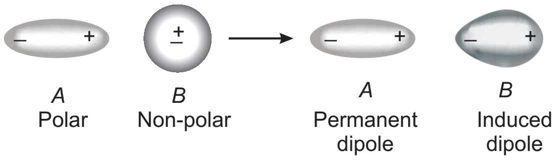


Fig. 2.3 Dipole-induced dipole interaction

(iv) **Instantaneous dipole-induced dipole interactions** Even non-polar molecules in themselves are polarised temporarily due to displacement of electron cloud with respect to nucleus (instantaneously). Such a instantaneous polar dipole when interact with non-polar molecule, the result is seen in the form of instantaneous dipole-induced dipole interaction which can be seen as

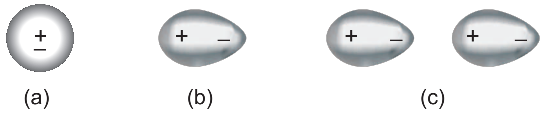


Fig. 2.4 Instantaneous dipole-induced dipole interaction :

(a) Non-polar molecule with a positive centre surrounded by a symmetrical negative electron cloud.

(b) The displacement of electron cloud makes the non-polar molecule temporarily polar.

(c) Temporarily polar molecules polarises the neighbouring molecule and creates in it the induced dipole.

Hence, the state of a matter is decided as follows

(i) In a solid, the cohesive forces predominate the effect of thermal agitation. Consequently, the particles are held together in rigid, highly-oriented and close-packed structure.

(ii) In a liquid, the cohesive forces are no longer strong enough, however, these are still sufficient, so that particles cannot escape each other's environment, they have sufficient mobility.

(iii) In a gas, the thermal agitation dominates the effect of cohesive forces, thus the gas molecules acquire the unrestricted and independent mobility in the vapour state.

Caution Points

(i) *The constituent particles of a gas undergo all types of motion, that is translational, rotational and vibrational. Liquid molecules possess translational and vibrational. While solid particles possess only vibrational motion.*

(ii) *The temperature and pressure at which all the three states of a substance can exist together in equilibrium is called triple point. e.g., ice, liquid water and water vapours can coexist (i.e., ice* $\rightleftharpoons$ water $\rightleftharpoons$ vapour) *at* 0.0098°C *and* 4.58 *mm.*

2.2 Gaseous State

It is the most disordered state of matter. In this state, matter neither have fixed volume nor fixed shape. It takes the shape and volume of the container. In which it is placed.

Characteristic Properties of Gases

Gases exhibit following characteristic properties

(a) **Expansibility** Gases expand indefinitely and fill any vessel, no matter how large, in which these are placed.

(b) **Compressibility** Gases are readily compressible. A large amount may be compressed into a small space by applying pressure.

(c) **Diffusion** Gases intermix freely with one another or move from one place to other without any difficulty.

(d) **Homogeneity** Pure gases or their mixtures are all homogeneous in composition.

(e) **Density** Gases possess very low density. The density of gas when compared to that of hydrogen is termed as **relative density.**

(f) **Gases exert pressure** Due to collision of molecules on the walls of container, gases exert certain amount of pressure, which obviously increases due to increase in temperature.

(g) **Kinetic energy** Gaseous molecules move very rapidly in all directions in a random manner, *i.e.,* gases have highest kinetic energy.

Measurable Properties of Gases

The characteristics of gases are described fully in terms of four parameters *i.e.,* pressure (p), volume (V), temperature (T) and mass or mole, which are termed as measurable properties.

(a) Mass

It is expressed in gram or kg and is equal to the difference in masses of empty vessel and vessel containing gas.

(b) Volume

It is equal to the volume of the container and is expressed in terms of litre (L), millilitre (mL), cubic centimetre (cm^3), cubic metre (m^3) or cubic decimetre (dm^3).

$$1 \text{ L} = 1000 \text{ mL} = 1000 \text{ cm}^3 = 1 \text{dm}^3$$

$$1 \text{ m}^3 = 10^3 \text{dm}^3 = 10^6 \text{cm}^3 = 10^6 \text{mL} = 10^3 \text{L}$$

(c) Pressure

It is defined as force divided by the area to which the force is applied.

$$\text{Pressure} = \frac{\text{force}}{\text{area}}$$

The greater the force acting on a given area, the greater the pressure. The origin of the force exerted by a gas is the continuous collisions of the molecules against the walls of the container. The collisions are so numerous that they exert an effectively steady force, which is experienced as a steady pressure.

The units of pressure are atm, mm Hg, torr etc.

1 atm = 76 cm of Hg = 760 mm of Hg = 760 torr

$$1 \text{ atm} = 101.325 \text{ kPa} = 101325 \text{ Pa} = 101.325 \text{ Nm}^{-2}$$

$$= 1.01325 \text{ bar}$$

$$1 \text{ bar} = 10^5 \text{ Pa} = 0.987 \text{ atm.}$$

$$\text{Atmospheric pressure} \quad p = hdg.$$

where, ***h*** is the height of the mercury column supported by the barometer, ***d*** is the density of mercury and ***g*** acceleration due to gravity.

(The pressure is obtained in pascal when h, d and g are expressed in SI unit.)

Pressure is measured by using a **manometer** which is a simple device with a horizontal arm and a U-tube carrying mercury or any other suitable liquid.

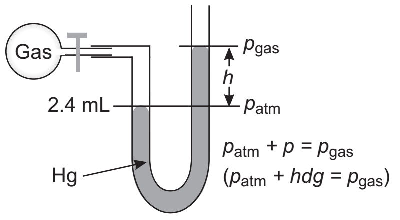


Fig. 2.5 An open arm manometer

However, atmospheric pressure is measured by **barometer.**

There are two types of manometers

(i) closed end and

(ii) open end manometer

Closed end manometer is normally used to measure pressure below atmospheric pressure whereas open end manometer is used to measure pressure above atmospheric pressure.

In an open end manometer

(i) If the level of Hg in the two limbs is same, the gas pressure (p_{gas}) = atmospheric pressure (p_{atm})

(ii) If the level of Hg is higher in the longer limb $p_{gas} = p_{atm} + p_h$

(iii) If the level of Hg is higher in the shorter limb,

$$p_{gas} = p_{atm} - p_h$$

where, p_h = difference in the Hg levels in the two columns of density (d) of a gas.

In case of close end manometer,

$$p_{gas} = p_h$$

Sample Problem 1 *How high a column of air would be necessary to cause the barometer to read 76 cm Hg if the atmosphere were of uniform density 1.7 kg/m^3? (density of mercury is 13.6×10^3 kg/m^3)*

(a) 13.6×10^3 (b) 6.08×10^5

(c) 7.62×10^4 (d) 1.7×10^3

Interpret (b) At a place where barometer uses air and mercury, pressure is same

$$p = h_1 d_1 g = h_2 d_2 g$$

$$\underset{\text{(mercury)}}{h_1 d_1} = \underset{\text{(air)}}{h_2 d_2}$$

$$76 \times 13.6 \times 10^3 = h_2 \times 1.7$$

$$h_2 = 6.08 \times 10^5 \text{ cm}$$

(d) Temperature

It is measured in terms of hotness or coldness. The measurement is based on the expansion of certain material (mostly it is mercury) with increasing temperature. It is measured in celsius scale or absolute scale (Kelvin scale). Celsius scale was earlier known as the **centigrade scale.**

Note

(i) **Standard temperature and pressure** (STP or NTP) mean 273.15 K (0°C) temperature and 1 bar (*i.e.*, exactly 10^5 pascal) pressure. At STP, molar volume of an ideal gas is 22.71098 L mol^{-1}.

(ii) The standard temperature for gas measurements (0°C or 273.15 K) is not the same as that usually assumed for thermodynamic measurements (25°C or 298 K is said to be SATP condition or Standard Ambient Temperature and Pressure).

2.3 Gas Laws

Gases exhibit dependency on temperature, pressure, volume and mass. The inter-relationship of these factors can be analysed through gas laws, which are

Boyle's Law (by Robert Boyle-1662)

According to this law, "At a given temperature, the volume of a given mass of a gas is inversely proportional to its pressure,"

i.e., $V \propto \frac{1}{p}$ or $pV = \text{constant}$, (the value of the constant depends on the amount of gas and temperature.)

or $$p_1V_1 = p_2V_2$$

(If temperature T remains constant, the process is called **isothermal process.**)

Alternatively, Boyle's law can also be stated as follows: "Temperature remaining constant, the product of pressure and volume of a given mass of a gas is constant".

We know that,

$$\text{mass, } m = \text{volume } (V) \times \text{density } (d)$$

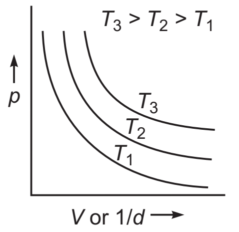
or $$d = \frac{m}{V}$$

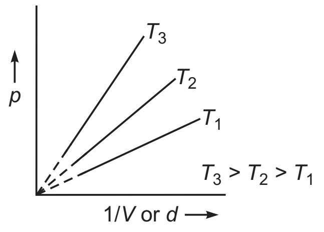
Therefore, at constant temperature and mass,

$$d \propto \frac{1}{V} \propto p \qquad \left(\because p \propto \frac{1}{V}\right)$$

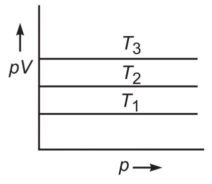
Thus, $$\frac{d_1}{d_2} = \frac{p_1}{p_2} = \frac{V_2}{V_1}$$

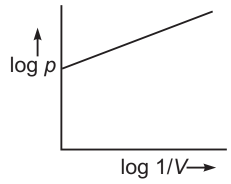
Graph between p and V at constant temperature is called **isotherm** and is an equilateral hyperbola. By plotting p *versus* $\frac{1}{V}$, this hyperbola is converted to a straight line. Other types of isotherm are also shown below



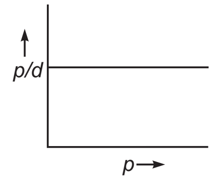


Similarly, the relationship between pV vs p and log p vs log $\frac{1}{V}$ looks like





and the plot of p *vs* p/d is



Practical Importance of Boyle's Law

The Boyle's law expresses in quantities an important experimental fact that gases are compressible. For example, air at the sea level is denser because it is compressed by the mass of air above it. However, density and pressure decrease with an increase in altitude.

The atmospheric pressure at Mount Everest is only about 0.5 atm. The decrease in pressure at high altitudes causes altitude sickness (sluggish feeling, headache, etc.,) due to a decrease in the oxygen intake in each breath.

The inside of jet airplanes, which normally fly at a height of about 10000m, is specially maintained at normal pressure. The planes are also equipped with emergency oxygen supply in case the pressure falls.

Sample **Problem 2** *A vessel of 120 mL capacity contains a certain amount of gas at 35°C and 1.2 bar pressure. The gas is transferred to another vessel of volume 180 mL at 35°C. What would be its pressure?* **[NCERT]**

(a) 0.6 *bar* (b) 1.2 *bar* (c) 0.8 *bar* (d) 0.4 *bar*

Interpret (c) $p_1 = 1.2$ bar, $p_2 = ?$, $V_1 = 120$ mL, $V_2 = 180$ mL

From Boyle's law, $p_1V_1 = p_2V_2$

$$p_2 = \frac{p_1V_1}{V_2} = \frac{1.2 \text{ bar} \times 120 \text{ mL}}{180 \text{ mL}}$$

$$p_2 = 0.8 \text{ bar.}$$

Charles' Law (by Jacques Charles'-1787)

According to this law, "At a constant pressure, the volume of a given mass of a gas is directly proportional to its absolute temperature." (The constant pressure process is referred to as **isobaric process**).

$V \propto T$ or $\frac{V}{T}$ = constant (the value of the constant depends upon the amount of gas and pressure.)

or $$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

At constant pressure and mass, density of a gas is inversely proportional to its absolute temperature.

$$d \propto \frac{1}{T} \propto \frac{1}{V}$$

Thus, $$\frac{d_1}{d_2} = \frac{T_2}{T_1} = \frac{V_2}{V_1}$$

Charles' obtained experimentally that at constant pressure, for 1°C increment/decrement in temperature of a gas, the volume increase/ decrease by a fraction of $\frac{1}{273}$.

Hence, if V_0 be the volume of a gas at 0°C and it is recorded to be V at t° C then

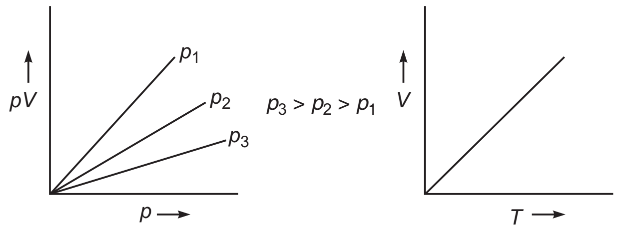
$$V = V_0 + \frac{1}{273} t\, V_0 = V_0\left(1 + \frac{t}{273}\right) = V_0\left(\frac{273 + t}{273}\right) = \frac{V_0}{273} T$$

At this stage, we define a new scale of temperature such that t°C on the new scale is given by $T = 273.15 + t$ and 0°C is given by $T_0 = 273.15$. This new temperature scale is called the *Kelvin temperature scale or absolute temperature scale*.

The volume of the gas at $-t$° C is given by $V_{-t} = V_0\left(1 - \frac{t}{273}\right)$

Thus, a decrease in temperature results in a decrease in the volume of the gas, and ultimately the volume becomes zero at −273° C. It means that any further lowering of temperature is impossible because it will correspond to negative volume, which is meaningless. Hence, an important conclusion can be drawn from the above discussion that the lowest possible temperature is −273° C. *This lowest possible temperature at which all gases are supposed to occupy zero volume is called absolute zero.* A scale of temperature based upon this choice of zero is called absolute scale of temperature.

The relationship can be shown graphically as



These curves are known as *isobars* or isoplestics and is always a straight line.

Practical Importance of Charles' Law

The use of hot air balloons in sports and for meteorological observations is an interesting application of Charles' law. According to Charles' law, gases expand on heating. Since the mass of a gas is unchanged, larger volume corresponds to lower density. Thus, hot air is less dense than cold air. This causes hot air balloons to rise by displacing cooler air of the atmosphere.

Sample **Problem 3** *It is desired to increase the volume of 80 cm^3 of a gas by 20% without changing pressure. To what temperature the gas be heated if its initial temperature is 25°C?*

(a) 35.6°C (b) 84.6°C
(c) 630.6°C (d) 35°C

Interpret (b) The desired increase in the volume of gas is

20% of 80 cm^3 $= \frac{80}{100} \times 20 = 16$ cm^3

Thus, the final volume of the gas is $80 + 16 = 96$ cm^3

Now, $V_1 = 80$ cm^3, $V_2 = 96$ cm^3

$T_1 = 25°$ C = 298 K, $T_2 = ?$

Applying Charles' law, we get

$$\frac{V_1}{T_2} = \frac{V_2}{T_2}$$

$$T_2 = \frac{V_2T_2}{V_1} = \frac{96 \text{ cm}^3 \times 298 \text{ K}}{80 \text{ cm}^3} = 357.6\text{K}$$

$$= 357.6 - 273 = 84.6° \text{ C}$$

Sample **Problem 4** *If V_0 is the volume of the given mass of a gas at 273 K and pressure p, then according to Charles' law the volume of the same mass of gas at 10°C and pressure, p will be*

(a) $V_0 + \frac{10}{273}$ (b) $10V_0$

(c) $\frac{283}{273} \cdot V_0$ (d) $\frac{[V_0 + 10]}{273}$

Interpret (c) From Charles' law,

$$\frac{V_1}{V_2} = \frac{T_1}{T_2}$$

$$\frac{V_0}{V} = \frac{273}{273 + 10}$$

$$V = \frac{283}{273} V_0$$

Gay-Lussac's Law (Pressure-Temperature Equation) (by Joseph Gay-Lussac-1802)

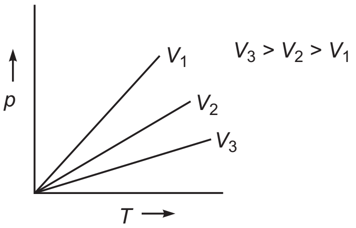
According to this law, "At a constant volume, the pressure of a given mass of a gas is directly proportional to its absolute temperature".

(If volume V remains constant, the process is called *isochoric process*.)

i.e., $$p \propto T \quad \text{or} \quad \frac{p}{T} = \text{constant}$$

or $$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

The relationship between p and T can be seen as



These curves are called *isochores*.

Sample **Problem 5** *The pressure exerted by 12 g of an ideal gas at temperature t°C in a vessel of V L is one atmosphere. When the temperature is increased by 10°C at the same volume, the pressure increases by 10%. The value of temperature t is*

(a) 173°C (b) 173 K
(c) 100°C (d) 100 K

Interpret (c) From Gay-Lussac's law,

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

$$\frac{1}{t + 273} = \frac{1.1}{t + 283}$$

$$t + 283 = 1.1t + 300.3$$

$$0.1t = -17.3$$

$$t = -173 \text{ K}$$

$$t = 273 - 173 = 100° \text{ C}$$

Avogadro's Law

According to this law, "Equal volumes of all gases at the same temperature and pressure contain the same number of molecules."

or

"At a given temperature and pressure, the volume of any gas is directly proportional to the number of moles of gas."

If p and T remain constant,

$$V \propto n \quad \text{or} \quad \frac{V}{n} = \text{constant}$$

or $$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

where, n = the number of moles, *i.e.*, $n = \frac{m}{M}$,

m = mass of substance in grams,
M = molecular mass of substance.

One mole of any gas contains the same number of molecules (6.023×10^{23}) and by this law, must occupy the same volume at a given temperature and pressure. The volume of one mole of a gas is called *molar volume*, V_m which is 22.4 L mol^{-1} at STP or NTP.

Sample **Problem 6** *Total number of electrons in 1.4 g dinitrogen gas is*

(a) 4.2×10^{23} (b) 6.02×10^{23}
(c) 3.01×10^{23} (d) 8.4×10^{24}

Interpret (a) $$1.4 \text{ g } N_2 = \frac{1.4}{28} \text{ mol } N_2$$

$$1 \text{ mole } N_2 \text{ contains } 14 \times 6.02 \times 10^{23} \text{ electrons}$$

$$\frac{1.4}{28} \text{ mole } N_2 \text{ will contain } \frac{14 \times 6.023 \times 10^{23} \times 1.4}{28}$$

$$= 4.2 \times 10^{23} \text{ electrons}$$

Ideal Gas Equation

From Boyle's law and Charles' law, we have

$$\frac{pV}{T} = \text{constant} \qquad \text{...(i)}$$

For 1 mole,

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2} \qquad \text{...(ii)}$$

This relation is known as *gas equation*.

From equation (i), *the value of constant depends on the amount of gas and the units in which pressure and volume are measured.*

If the amount of gas taken is 1 mole, the constant is represented by 'R'. So, for 1 mole of gas, the gas equation is

$$\frac{pV}{T} = R \quad \text{or} \quad pV = RT$$

For 'n' moles of gas, the equation is written as

$$pV = nRT = \frac{m}{M} RT$$

This is called *ideal gas equation*. This equation is obeyed by isothermal and adiabatic processes, where, R is called *universal gas constant*.

$$\text{Units of } R = \frac{\text{(energy unit)}}{\text{(mol)(temperature unit)}}$$

$$R = 8.314 \text{ J/mol-K} = 0.08205 \text{ L-atm/mol-K}$$
$$= 1.99 \text{ cal/mol-K} = 5.189 \times 10^{19} \text{ eV mol}^{-1} \text{ K}^{-1}.$$

Gas constant, R for a single molecule is called *Boltzmann constant* (K).

$$K = \frac{R}{N} = \frac{8.314 \times 10^{7}}{6.023 \times 10^{23}}$$
$$= 1.38 \times 10^{-16} \text{ erg mol}^{-1} \text{ degree}^{-1}$$
$$= 1.38 \times 10^{-23} \text{ J mol}^{-1} \text{ degree}^{-1}$$

Again from $pV = nRT$

$$pV = \frac{m}{M} RT$$
$$\frac{m}{V} = \frac{pM}{RT}$$
$$\because \quad \frac{m}{V} = d \text{ (density)}$$
$$\text{So,} \quad d = \frac{pM}{RT}$$

M and R are constant for a particular gas, so for two or more different temperatures and pressure,

$$\frac{d_1T_1}{p_1} = \frac{d_2T_2}{p_2} = \text{constant}$$

Sample **Problem 7** *Pressure of a mixture of 4 g of* O_2 *and 2 g of* H_2 *confined in a bulb of 1 L at 0°C is*

(a) 25 *atm* (b) 45 *atm*
(c) 15 *atm* (d) 31 *atm*

Interpret (a) Number of moles of $O_2 = \frac{4}{32} = 0.125$

$$\text{Number of moles of } H_2 = \frac{2}{2} = 1$$

$$\text{Total number of moles} = 1 + 0.125 = 1.125$$

$$p = \frac{nRT}{V}$$
$$= \frac{1.125 \times 0.082 \times 273}{1}$$
$$= 25.184 \text{ atm}$$

Sample **Problem 8** *Pressure of 1 g of an ideal gas A at 27°C is found to be 2 bar. When 2 g of another ideal gas B is introduced in the same flask at same temperature, the pressure becomes 3 bar. Find a relationship between their molecular masses.*

(a) $M_A = 2\,M_B$ (b) $M_B = 2\,M_A$
(c) $M_A = \frac{M_B}{4}$ (d) $M_B = 6\,M_A$

Interpret (c) $pV = nRT$

For A gas, $p_AV = n_ART$ ...(i)

Similarly for B gas, $p_BV = n_BRT$ ...(ii)

(V is same because the gases are taken in the same flask)

Number of moles of A gas; $n_A = \frac{1}{M_A}$

(M_A = molar mass of gas A)

Number of moles of B gas; $n_B = \frac{2}{M_B}$

(M_B = molar mass of gas B)

Pressure of gas A, $p_A = 2$ bar

Total pressure, $p_{\text{total}} = p_A + p_B = 3$ bar

Pressure of gas B, $p_B = p_{\text{total}} - p_A = 3 - 2 = 1$ bar

V, R and T are same for both the gases.

Hence, from Eqs. (i) and (ii),

$$\frac{p_A}{p_B} = \frac{n_A}{n_B} = \frac{1 \times M_B}{M_A \times 2}$$
$$\frac{M_B}{M_A} = \frac{2p_A}{p_B}$$
$$\frac{M_B}{M_A} = \frac{2 \times 2}{1}$$
$$M_B = 4M_A$$

Dalton's Law of Partial Pressure

According to this law, "If two or more gases, which do not react chemically, are enclosed in a vessel, the total pressure exerted by the gaseous mixture is the sum of partial pressures exerted by the constituent gases"

If $p_1, p_2 \ldots\ldots\ldots, p_n$ be partial pressures of 'n' gases present in a vessel, then total pressure

$$p_{\text{total}} = p_1 + p_2 + \ldots\ldots\ldots + p_n$$

(Partial pressure is the pressure, which each gas will individually exert if present alone in the vessel.)

Let two gases are enclosed in a container of volume V and their numbers of moles be n_1 and n_2. If their partial pressures be measured at temperature T, then

$$p_1V = n_1RT \Rightarrow \frac{RT}{V} = \frac{p_1}{n_1}$$

The total pressure of the gas mixture will be given by

$$p_{\text{total}} V = (n_1 + n_2)\, RT$$

We then get

$$p_1 = \frac{n_1}{n_1 + n_2}\, p_{\text{total}} = \chi_1 p_{\text{total}},$$

$$p_2 = \frac{n_2}{n_1 + n_2}\, p_{\text{total}} = \chi_2 p_{\text{total}}$$

where, $\chi_1 = \frac{n_1}{n_1 + n_2}$ is the mole fraction of the one gas

and $\chi_2 = \frac{n_2}{n_1 + n_2}$ is the mole fraction for other gas.

Application of Dalton's Law

Important applications of Dalton's law are as follows

(i) It is used to calculate mole fraction of gas as

$$\text{Mole fraction of a gas } (X) = \frac{\text{partial pressure of gas } (p)}{\text{total pressure } (p)}$$

(ii) It is used to calculate percentage of a gas in mixture as

$$\% \text{ of gas in mixture} = \frac{\text{partial pressure of gas } (p_1)}{\text{total pressure } (p)} \times 100$$

(iii) It is used to calculate pressure of gas collected over water. If a gas is collected over water, water vapour is mixed with the collected gas. Hence, the corrected pressure of the gas must be used, as given below :

$$p_{\text{Gas (dry)}} = p_{\text{Total (moist gas)}} - p_{\text{water vapour}}$$

(iv) It is also used to calculate relative humidity (R_{H}) at a given temperature as

$$R_{\text{H}} = \frac{\text{partial pressure of water in air}}{\text{vapour pressure of water}}$$

Limitations of Dalton's Law

This law is applicable only when the component gases in the mixture do not react with each other. *e.g.*, $N_2 + O_2, CO + CO_2, N_2 + Cl_2, CO + N_2$.

But this law is not applicable to gases which combine chemically. *e.g.*, $H_2 + Cl_2, CO + Cl_2, Cl_2 + NH_3 +$ HBr and HCl $+ NO + O_2$, etc.

Sample Problem 9 *A mixture of dihydrogen and dioxygen at one bar pressure contains 20% by weight of dihydrogen. Calculate the partial pressure of dihydrogen.* **[NCERT]**

(a) 0.8 (b) 0.4 (c) 0.6 (d) 0.2

Interpret (a) A mixture of H_2 and O_2 contains 20% by weight of H_2 means

$H_2 = 20$ g and $O_2 = 80$ g

$$\text{Moles of hydrogen, } n_{H_2} = \frac{20}{2} = 10 \text{ mol}$$

$$\text{Moles of oxygen, } n_{O_2} = \frac{80}{32} = 2.5 \text{ mol}$$

Mole fraction of hydrogen,

$$x_{H_2} = \frac{n_{H_2}}{n_{H_2} + n_{O_2}} = \frac{10}{10 + 2.5} = 0.8$$

$$\text{Partial pressure of } H_2, p_{H_2} = p_{\text{total}} \times X_{H_2}$$

$$p_{H_2} = 1 \text{ bar} \times 0.8$$

$$p_{H_2} = 0.8 \text{ bar}$$

Sample Problem 10 *1500 mL flask contains 400 mg O_2 and 60 mg H_2 at 100°C. What is the total pressure in the flask?*

(a) 0.66 atm (b) 0.867 atm
(c) 8.67 atm (d) 13.47 atm

Interpret (c) Number of moles of $O_2 = \frac{w}{m} = \frac{400 \times 10^{-3}}{32}$

$$= 0.0125$$

$$\text{Number of moles of } H_2 = \frac{w}{m} = \frac{60 \times 10^{-3}}{2} = 0.03$$

From $pV = nRT$,

$$\text{Partial pressure of } O_2 = \frac{0.0125 \times 0.0821 \times 373}{1500 \times 10^{-3}} = 0.255 \text{ atm}$$

$$\text{Partial pressure of } H_2 = \frac{0.03 \times 0.0821 \times 373}{1500 \times 10^{-3}} = 0.612 \text{ atm}$$

$$\text{Total pressure} = 0.255 + 0.612 = 0.867 \text{ atm}$$

Amagat Law of Partial Volume

According to this law, "When two or more gases, which do not react chemically are kept in a closed vessel, the total volume exerted by the mixture is equal to the sum of the partial volumes of individual gases".

Thus,

$$V_{\text{Total}} = V_1 + V_2 + V_3 + \dots$$

Sample Problem 11 *Two gas bulbs A and B are connected by a tube having a stopcock. Bulb A has a volume of 100 mL and contains hydrogen. After opening the gas from A to the evacuated bulb B, the pressure falls down to 40%. The volume of B (in mL) must be*

(a) 75 (b) 150
(c) 200 (d) 250

Interpret (b) From Dalton's partial pressure law,

$$p_A V_A + p_B V_B = p_{\text{total}} V_{(A+B)}$$

Let $p_A = 100$ atm

$p_B = 0$

$p_{\text{total}} = 40$ atm

$$\therefore \quad 100 \times 100 + 0 \times V_2 = 40\,(100 + V_2)$$

$$V_2 = 250 - 100 = 150 \text{ mL}$$

Graham's Law of Diffusion (or Effusion)

According to this law, "If a gas is allowed to escape from its container through a small hole into vacuum, the process is called *effusion.* On the other hand *diffusion*, is the passage of gas through a porous partition".

"Rate of diffusion", is defined as the volume, which diffuses in unit time,

$$\text{Rate of diffusion} = \frac{\text{volume of the gas diffused}}{\text{time taken for diffusion}}$$

The relationship between rates of diffusion of various gases can be given by *Graham's law of diffusion* (effusion) which states that :

"The **rates of effusion** (diffusion) of non-reactive gases under similar conditions of temperature and pressure are inversely proportional to the square roots of their densities."

$$\text{Rate of diffusion} \propto \frac{1}{\sqrt{d}} \propto \sqrt{\frac{1}{M}}$$

$$[\because \text{Molar mass} = 2 \times \text{vapour density}]$$

If r_1 and r_2 are the rates of diffusion of two gases of molecular weights M_1 and M_2 and their densities are d_1 and d_2 respectively then

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

If equal volume V of two gases diffuse or effuse in t_1 and t_2 second respectively, then

$$\frac{r_1}{r_2} = \frac{\frac{V}{t_1}}{\frac{V}{t_2}} = \frac{t_2}{t_1} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

When p is not constant,

then $\quad r \propto p$

or $\quad \dfrac{r_1}{r_2} = \dfrac{p_1}{p_2}\sqrt{\dfrac{M_2}{M_1}} \qquad \left(\because\ r \propto \dfrac{p}{\sqrt{M}}\right)$

If the volumes and moles of two gases are V_1, V_2 and n_1, n_2 respectively then, $\frac{r_1}{r_2} = \frac{n_1 t_2}{n_2 t_1} = \frac{V_1 t_2}{V_2 t_1}$.

When a gas at a pressure p and temperature T is separated from vacuum by a small hole, the rate of escape of its molecules is equal to the rate at which they strike the area of the hole.

Therefore, for a hole of area A_0,

$$\text{rate of effusion} = \frac{pA_0}{(2pMKT)^{1/2}}$$

$$= \frac{pA_0 N_A}{(2pMRT)^{1/2}}.$$

Applications of Graham's law

Graham's law is applicable

1. to determine vapour densities and molecular weights of gases.
2. to prepare Ausell's marsh gas indicator which is used in mines.

Caution Point *The gas with highest rate of diffusion in hydrogen.*

Sample **Problem 12** *Calculate the relative rates of diffusion of* $^{235}UF_6$ *and* $^{238}UF_6$ *in the gaseous state.*

(Atomic mass of $F = 19$*).*

(a) 0.9915 : 1.0000 (b) 0.9957 : 1.0000

(c) 1.0043 : 1.0000 (d) 1.0086 : 1.0000

Interpret (c) Molecular mass of $^{235}UF_6 = 235 + 6 \times 19 = 349$

Molecular mass of $^{238}UF_6 = 238 + 6 \times 19 = 352$

From Graham's law of diffusion,

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

$$= \sqrt{\frac{352}{349}} = 1.0043$$

$$\therefore \qquad r_1 : r_2 = 1.0043 : 1$$

Sample **Problem 13** *At what temperature, the rate of effusion of* N_2 *would be* 1.625 *times that of* SO_2 *at* 50°C*?*

(a) 373 K (b) 273 K

(c) 473 K (d) 127 K

Interpret (a)

$$\frac{r_{N_2}}{r_{SO_2}} = \sqrt{\frac{T_{N_2}}{T_{SO_2}} \cdot \frac{M_{SO_2}}{M_{N_2}}}$$

$$\frac{1.625}{1} = \sqrt{\frac{T_{N_2}}{323} \times \frac{64}{28}}$$

$$T_{N_2} = \frac{(1.625)^2 \times 323 \times 28}{64}$$

$$= 373\text{ K}$$

Check Point 1

1. In terms of Charles' law, explain why –273°C is the lowest possible temperature?
2. If the number of moles of a gas were doubled and the pressure and temperature remained the same, what would happen to the volume?
3. Why is Dalton's law of partial pressure not applicable to a mixture of HCl and NH_3 gas?
4. Both propane and carbon dioxide diffuse at the same rate under identical conditions. Explain, why?

2.4 Kinetic Theory of Gases

The molecular details regarding gases can be visualised with the help of *kinetic molecular theory of gases* which is based on following assumptions

1. A gas consists of extremely small discrete particles, called the molecules, dispersed throughout the container.
2. Molecules are so small and so far apart that the actual volume of the molecules is negligible as compared to the total volume of gas.
3. Gas molecules are in constant random motion with high velocities. They move in straight lines with uniform speed and change directions on collision with other molecules or with the walls of container.
4. The intermolecular forces are negligible. Thus, the gas molecules can move freely, independent of each other.
5. All collisions are perfectly elastic, hence there is no loss of kinetic energy during the collision. However, there may be redistribution of energy during such a collision.
6. The effect of gravity on the motion of the molecules is negligible in comparison to the effect of collision.
7. The pressure of a gas is caused by the hits recorded by molecules on the walls of the container.

   $\because$ Pressure $\propto$ Number of collisions per unit time per unit area by the molecules on the wall of the container.
8. At a particular instance, different molecules in a sample have different speeds and hence, different kinetic energies. However, the average kinetic energy of the molecules is assumed to be directly proportional to the absolute temperature.

   Kinetic energy $\propto$ absolute temperature

Kinetic Gas Equation

On the basis of postulates of kinetic theory of gases, the following gas equation was derived

$$pV = \frac{1}{3} mnv_{\text{rms}}^2$$

where, p = pressure exerted by the gas

V = volume of the gas

m = average mass of each molecule

n = number of molecules

v_{rms} = root mean square velocity of the gas.

Calculation of kinetic energy, According to kinetic gas equation

$$pV = \frac{1}{3} mnv_{\text{rms}}^2$$

But $\quad pV = RT$

and, for 1 mole of a gas, $n = N$ (Avogadro's number)

$$\therefore \quad RT = \frac{1}{3} mNv_{\text{rms}}^2 = \frac{1}{3} Mv_{\text{rms}}^2 \qquad (\because\ m \times N = M)$$

$$= \frac{2}{3} \cdot \frac{1}{2} Mv_{\text{rms}}^2 = \frac{2}{3} \cdot \text{KE} \qquad \left[\because\ E = \frac{1}{2} mv^2\right]$$

$$\therefore \quad \text{KE} = \frac{3}{2} RT$$

Average kinetic energy per molecule

$$= \frac{\text{average kinetic energy per mole}}{N}$$

$$= \frac{3}{2} \frac{RT}{N} = \frac{3}{2} \cdot \frac{R}{N} \cdot T = \frac{3}{2} kT$$

where, $k = \frac{R}{N}$ = constant and is known as **Boltzmann constant**. Its numerical value is 1.38×10^{-23} J/mol-K.

Maxwell generalisation From $\text{KE} = \frac{3}{2} RT \Rightarrow \text{KE} \propto T$

$$\text{KE} = \frac{1}{2} mv_{\text{rms}}^2 \Rightarrow \text{KE} \propto v^2{}_{\text{rms}}$$

It gives, $\quad v_{\text{rms}}^2 \propto T$ or $v_{\text{rms}} \propto \sqrt{T}$

Hence, molecular velocity of a gas is directly proportional to the square root of the absolute temperature. When $T = 0$, $v_{\text{rms}} = 0$. Hence, at absolute zero temperature, all molecular motion ceases and total kinetic energy of the molecules is zero.

Above relations shows that KE of a gas is independent of nature, pressure and volume of the gas, but depends on the temperature. This is known as *Maxwell generalisation*.

***Sample* Problem 14** *At what temperature is the kinetic energy of a gas molecule becomes half of its value at 327°C?*

(*a*) 27 *K* (*b*) 27°C (*c*) 927 *K* (*d*) 927°C

Interpret (*b*) From kinetic energy, $E = \frac{3}{2} RT$, we have

$$\frac{E_1}{E_2} = \frac{\frac{3}{2} RT_1}{\frac{3}{2} RT_2} \Rightarrow \frac{1}{\frac{1}{2}} = \frac{600}{T_2}$$

$$T_2 = 300\ \text{K} = 27°\ \text{C}$$

2.5 Molecular Velocities

Different kinds of velocities of molecules can be calculated. These are

Average Velocity ($\overline{V}$)

It is the arithmetic mean of the various speeds of the molecules.

Let there be 'N' molecules of gas having velocities $v_1, v_2 \ldots\ldots, v_N$.

Then, average velocity, $\bar{v}(\text{or } v_{av}) = \dfrac{v_1 + v_2 + \ldots.. + v_N}{N}$

Maxwell established that $v_{av} = \sqrt{\dfrac{8RT}{\pi M}} = \sqrt{\dfrac{8KT}{\pi M}}$

Root Mean Square Velocity (u or v_{rms})

It is the square root of the mean of the squares of the velocity of a larger number of molecules of the same gas.

$$u = \sqrt{\frac{v_1^2 + v_2^2 + \ldots + v_N^2}{N}}$$

From the kinetic gas equation, we find that

$$u = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3KT}{M}} = \sqrt{\frac{3p}{d}}$$

For the same gas at two different temperatures, the ratio of RMS velocity will be $\dfrac{u_1}{u_2} = \sqrt{\dfrac{T_1}{T_2}}$

For two different gases at the same temperature, the ratio of RMS velocities will be $\dfrac{u_1}{u_2} = \sqrt{\dfrac{M_2}{M_1}}$

Caution Point *The gas with high RMS velocity with have high rate of diffusion while the gas with high molecular weight will have low RMS velocity.*

Most Probable Velocity (v_p)

It is the velocity, which the largest number of molecules possess.

$$v_p = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2pV}{M}} = \sqrt{\frac{2p}{d}}$$

Caution Point *With increase in temperature, most probable velocity increases but fraction possessing it decreases.*

Relation between different molecular velocities

$$v_p : v_{\text{av}} : u = \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}}$$

$$= \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3} = 1 : 1.128 : 1.224$$

Therefore, $v_p < \bar{v} < u$.

We also get, $v_p = 0.816\,u, \bar{v} = 0.9213\,u$ or $u = 1.085 \times \bar{v}$

Sample **Problem 15** *The ratio of most probable velocity to that of average velocity is*

(a) $\dfrac{\sqrt{\pi}}{2}$ (b) $\dfrac{2}{\pi}$ (c) $\dfrac{2}{\sqrt{\pi}}$ (d) $\dfrac{\pi}{2}$

Interpret (a) $\dfrac{V_p}{V_{\text{av}}} = \dfrac{\sqrt{\dfrac{2RT}{M}}}{\sqrt{\dfrac{8RT}{\pi M}}} = \dfrac{\sqrt{\pi}}{2}$

Sample **Problem 16** *The ratio between the root mean square velocity of* H_2 *at 50 K and that of* O_2 *at 800 K is*

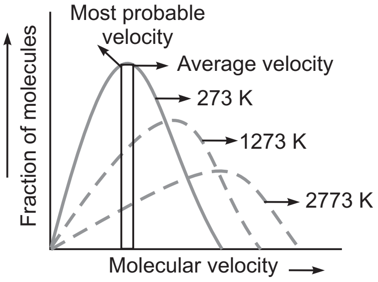
(a) 1 (b) 4 (c) 2 (d) 1/4

Interpret (a) $\dfrac{v_{H_2}}{v_{O_2}} = \sqrt{\dfrac{T_{H_2}}{T_{O_2}} \cdot \dfrac{M_{O_2}}{M_{H_2}}} = \sqrt{\dfrac{50}{2} \cdot \dfrac{32}{800}} = 1$

Maxwell's Distribution of Molecular Speeds (Velocities)

Maxwell and Boltzmann proposed that gas molecules are always in rapid random motion colliding with each other and with the walls of container. Because of such collisions, their velocities change. A fraction of molecules have a particular molecular velocity at a time. James Clark Maxwell calculated the distribution of velocity among fraction of total number of molecules, on the basis of probability.

The distribution of velocities of different gas molecules may be shown by the following curve.



From the curve it may be concluded that

(i) Only a small fraction of molecules have either very low or very high velocity.
(ii) Curve becomes flat when temperature is raised *i.e.,* distribution around average velocity becomes wider. Average molecular velocity increases with rise in temperature.
(iii) Most of the molecules have velocity close to most probable velocity, represented by the top of the curve.
(iv) At higher temperature, greater number of molecules have high velocity, while few molecules have lower velocity.

2.6 Ideal and Real Gases

The gas which obeys gas laws is called an **ideal gas,** while others are **real gases.** Real gases obey the gas laws under moderate conditions of temperature and pressure. *At very low temperature and high pressure, the real gases show considerable deviation from the ideal gas behaviour* (*i.e.*, ideal gas laws).

Table 2.2 **Differences Between Ideal and Real Gases**

S. No.	Ideal Gas	S. No.	Real Gas
1.	An ideal gas obeys all the gas laws at all temperatures and pressures.	1.	A real gas obeys gas laws only at very low pressures and high temperatures.
2.	The volume of molecules is negligible as compared to the total volume of the gas.	2.	The volume of molecules is not negligible.
3.	Attractive forces among the molecules do not exist.	3.	Attractive forces among the molecules do not exist particularly at high pressures and low temperatures.
4.	It obeys the equation of state $pV = nRT$.	4.	It satisfies the van der Waals' equation $\left(p + \frac{a_{n^2}}{V^2}\right)(V - nb) = nRT$
5.	It is hypothetical.	5.	All existing gases are real.

Cause of Deviation from Ideal Behaviour

The ideal gas laws were derived from following two assumptions of kinetic theory of gases which did not hold good in all conditions

(i) The intermolecular forces of attraction between gaseous molecules is negligible.

(ii) The volume occupied by the gas molecules is negligible in comparison to the total volume of the gas.

(a) Evidence for Molecular Attraction

If assumption (i) is correct, the gas will never liquefy. However, we know that gases do liquefy when cooled and compressed. The molecules of gases have weak van der Waals' forces of attraction. This is also supported by the fact that when a compressed gas is passed through a porous plug of silk or cotton in adiabatic conditions, the emerging gas is found to be cooler than the entering gas (**Joule-Thomson effect**). This is because on expansion some work has to be done against the internal forces of attraction, which requires energy. This energy comes from the system itself.

(b) Evidence for Molecular Volume

The molecules of a gas, however, do occupy a certain volume as can be seen from the fact that gases can be liquefied and solidified at a low temperature and high pressure. In the solid state, however, there is a considerable resistance to any further attempt at compression. It is, therefore, apparent that the molecules of a gas must have an appreciable volume, which is probably of the same order as that occupied by the same number of molecules in the solid state.

Compressibilty Factor : Explanation Deviation from Ideal Behaviour

The deviation of gases from ideal behaviour can be understood better by evaluating the effect of pressure and temperature on *compressibility factor* (Z) *i.e.,* $Z = \frac{pV}{RT}$, for one mole of gas. *When*

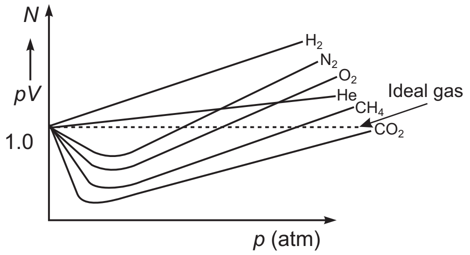
(i) $Z = 1$, the gas is ideal at all temperatures and pressures.

(ii) $Z > 1$, the gas is less compressible than expected from ideal behaviour and shows *positive deviation*, usually at high pressure, *i.e.,* $pV > RT$.

(iii) $Z < 1$, the gas is more compressible than expected from ideal behaviour and shows *negative deviation*, usually at low pressure, *i.e.,* $pV < RT$.

The extent of deviation at any given temperature depends upon the nature of the gas. For example, CO_2 and N_2 are more compressible at low pressures and show negative deviation, but they are less compressible at high pressures and show positive deviation.

Variation of Z with pressure for different gases is shown in the following graph drawn at a constant temperature (300 K).



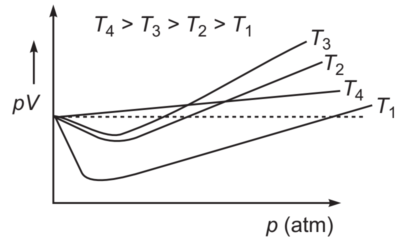
Variation of Z with pressure for different gases

It may be noted from the figure that the value of Z is approximately 1 at very low pressure (up to 10 atm). For H_2 and He the value of Z is always greater than 1 while the value first decreases and then increases for other gases.

Above graph shows the regions where two effects (attraction forces and size) predominate. For hydrogen at 0°C, the molecular attractive forces are weak and the size effect dominates its behaviour. For N_2 at 0°C, the attractive forces are large enough to cause negative deviation $\left(Z\left(= \frac{pV}{nRT}\right) < 1\right)$ up to about 150 atm, beyond which the size effect dominates $(Z < 1)$. For CO_2, intermolecular attraction is large even at 40°C. In N_2 and CO_2, the two effects compensate each other at 150 atm and 600 atm respectively and thus $Z = 1$.

At very low pressure, gas molecules are widely separated and both these effects become negligible. At high temperatures, molecules have greater kinetic energy, and attractive forces are smaller and the behaviour of gases is close to the ideal gas behaviour.

The variation of Z with temperature is shown in the following graph



Variation of Z with temperature

It may be noted that at high temperature, the curve approaches more and more to the ideal nature. **The temperature at which $\frac{pV}{RT}$ is unity for a gas up to appreciable range of pressure is called Boyle's temperature (T_b).**

$$\text{Boyle's temperature } (T_b) = \frac{a}{bR} = \frac{1}{2} T_i$$

Where a and b are van der Waals' constant and T_i is called *inversion temperature*.

Easily liquefiable gas has high T_b (T_b for $O_2 = 40$ K). The gases, which are difficult to liquefy have low T_b (T_b for H_2 23 K).

Caution Points

1. *The gases having low critical temperature are called permanent gases. While gases above critical temperature and under high pressure are known as supercritical fluids.*
2. *Ideal gases do not show any cooling or heating on adiabitic expansion becomes there are no intermolecular forces of attraction present in them.*

2.7 van der Waals' Equation

To rectify the errors caused by ignoring the intermolecular forces of attraction and the volume occupied by molecules, **Johannes van der Waals'** proposed following equation, which is valid for real gases upto a large range of temperature and pressure

$$\left(p + \frac{n^2a}{V^2}\right)(V - nb) = RT$$

where, a and b are constants and are called correction terms for pressure and volume.

Constant 'a' is a indirect measure of magnitude of attractive forces between the molecules. **Greater is the value of 'a', more easily the gas can be liquefied.**

Unit of a are at $mL^2\ mol^{-2}$ or atm. $m^6\ mol^{-2}$ or $Nm^4\ mol^{-2}$.

The constant b is introduced to correct that portion of gas which is not compressible. It is also called **excluded volume** or **co-volume.** If closest distance of approach of two molecules be $2r$, (r is the radius of one molecule), the excluded volume for two molecules is

$$\left(\frac{4}{3}\right) \pi (2r)^3 = 8\left(\frac{4}{3}\pi r^3\right) = 8 \times \text{volume of one molecule}$$

Hence, for one molecule the excluded volume, $b = 4 \times \left(\frac{4}{3}\pi r^3\right)$

For N molecules,

$$b = N \times \text{total volume of one molecule, or } b = 4N\left(\frac{4}{3}\pi r^3\right)$$

b is measured in cm^3/mol or $L\ mol^{-1}$ or $m^3\ mol^{-1}$.

Significance of van der Waals' Constants

Since an easily liquefiable gas has greater intermolecular attraction, hence the value of 'a' is a measure of the intermolecular attraction. In other words, we can say that the value of 'a' indicates the strength of van der Waals' forces. Thus, for high value of 'a', the ease with which a gas can be liquefied will be high. The easily liquefiable gases (like SO_2, NH_3, H_2S, CO_2 etc.) have high value of 'a' than the permanent gases (such as H_2, N_2, O_2, etc).

The constant value of 'b' for any gas indicates that the gas molecules are incompressible.

Sample Problem 17 *N_2 molecule is spherical with radius 100 pm. The value of van der Waals' constant b and the actual volume of the gas at STP are respectively*

(a) $1.0 \times 10^{-2}, 2.2 \times 10^3$ (b) $1.0 \times 10^{-3}, 2.2 \times 10^4$

(c) $1.0 \times 10^{-2}, 2.2 \times 10^4$ (d) $1.0 \times 10^{-3}, 2.2 \times 10^3$

Interpret (c) $100\ \text{pm} = 100 \times 10^{-12}\ \text{m} = 1 \times 10^{-8}\ \text{cm}$

(i) Volume of N_A molecules, $V = \frac{4}{3}\pi r^3 N_A$

$$= \frac{4}{3} \times \frac{22}{7} \times (1 \times 10^{-8})^3 \times 6.022 \times 10^{23}$$

$$= 2.52\ \text{cm}^3 = 2.52 \times 10^{-3}\ \text{dm}^3\ \text{mol}^{-1}$$

$$b = 4V = 4 \times 2.52 \times 10^{-3}\ \text{dm}^3\ \text{mol}^{-1}$$

$$= 10.08 \times 10^{-3}\ \text{dm}^3\ \text{mol}^{-1}$$

Actual volume = volume at STP – volume occupied by molecules mol^{-1}

$$= 22400 - 2.52 = 22.397.48\ \text{cm}^3$$

Sample Problem 18 *The Boyle's law can't be used to calculate the volume of a real gas from its initial state to final state during adiabatic expansion because*

(*a*) *temperature increases*
(*b*) *pressure decreases*
(*c*) *pressure remains the same*
(*d*) *temperature decreases*

Interpret (*d*) No, we cannot use Boyle's law to calculate volume during adiabatic expansion because temperature is lowered during adiabatic expansion, *i.e.*, temperature does not remain constant, which violates Boyle's law.

Sample Problem 19 *Two van der Waals' gases have the same value of b but different values of a. Which of these will occupy greater volume under identical conditions? If the gases have the same value of a but different values of b, which of them will be more compressible?*

Interpret When two gases have the same value of *b* but different values of *a*, the gas having a larger value of *a* will occupy lesser volume. This is because the gas with a larger value of *a* will have larger foces of attraction and hence, lesser distance between its molecules.

When two gases have the same value of *a* but different values of *b*, the smaller the value of *b*, the larger the compressibility because the gas with the smaller value of *b* will occupy lesser volume and hence, will be more compressible.

Sample Problem 20 *The compression factor (compressibility factor) for* 1 *mole of a van der Waals' gas at* 0°*C and* 100 *atm pressure is found to be* 0.5. *Assuming that the volume of a gas molecule is negligible, the value of van der Waals' constant 'a' is*

(*a*) $0.253\ L^2 mol^{-2}$ *atm*
(*b*) $0.53\ L^2 mol^{-2}$ *atm*
(*c*) $1.251 L^2 mol^{-2}$ *atm*
(*d*) $1.83\ L^2 mol^{-2}$ *atm*

Interpret (*c*) From, $Z = \frac{pV}{nRT}$

$$0.5 = \frac{100 \times V}{1 \times 0.0821 \times 273}$$

$$V = 0.112 \text{ L}$$

Now from van der Waals' equation,

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

$$\left\{100 + \frac{a}{(0.112)^2}\right\}(0.112 - 0) = 0.0821 \times 273$$

$$\left(100 + \frac{a}{0.0125}\right) \times (0.112) = 22.4133$$

$$100 + \frac{a}{0.0125} = 200.1187$$

$$\frac{a}{0.0125} = 100.1187$$

$$a = 100.1187 \times 0.0125$$

$$= 1.2515 \text{ L}^2 \text{ mol}^{-2} \text{ atm}$$

Sample Problem 21 *For real gases the relation between p,V and T is given by van der Waals' equation* $\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$ *where, 'a' and 'b' are van der Waals' constants, 'nb' is approximately equal to the total volume of the molecules of a gas, 'a' is the measure of magnitude of intermolecular attraction.*

(i) Arrange the following gases in the increasing order of 'b'.

O_2, CO_2, H_2, He

(*a*) $O_2 < CO_2 < He < H_2$
(*b*) $He < H_2 < O_2 < CO_2$
(*c*) $H_2 < He < CO_2 < O_2$
(*d*) $H_2 < He < O_2 < CO_2$

(ii) Arrange the following gases in the decreasing order of magnitude of 'a'. [**NCERT**]

CH_4, O_2, H_2

(*a*) $CH_4 > O_2 > H_2$
(*b*) $CH_4 > H_2 > O_2$
(*c*) $H_2 > CH_4 > O_2$
(*d*) $O_2 > CH_4 > H_2$

Interpret (i) (*d*) Molar volume occupied by the gas molecules is proportional to the size of molecules and van der Waals' constant '*b*' represents molar volume of the gas molecules. Hence, value of '*b*' increases in the following order

$$H_2 < He < O_2 < CO_2$$

(ii) (*a*) van der Waals' constant '*a*' is the measure of magnitude of intermolecular attraction. The magnitude of intermolecular attractions increases with increase in size of electron cloud in a molecule. Hence, for the given gases, magnitude of '*a*' decreases in the following order

$$CH_4 > O_2 > H_2$$

Greater the size of electron cloud, greater is the polarisability of the molecule and greater is the dispersion forces or London forces.

Hot Spot

VAN DER Waals' Equation at Different Conditions

Although the chapter is not very important for JEE Main examination but the questions if asked may be based on this topic as it is some what more important than the others topics of this chapter. The level of questions vary from easy to average.

(a) When Pressure is Low

At low pressure, volume V is very large and hence, the correction term b (a constant of small value) can be neglected in comparison to very large value of V. Hence, it can be neglected from van der Waals' equation for 1 mole of gas, *i.e.,*

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

$$\left(p + \frac{a}{V^2}\right)V = RT$$

$$pV + \frac{a}{V} = RT$$

$$pV = RT - \frac{a}{V} \text{ or } \frac{pV}{RT} = 1 - \frac{a}{VRT}$$

or $$Z = 1 - \frac{a}{VRT} = \frac{pV}{RT}$$

where, Z is compressibility factor.

At extremely low pressure At extremely low pressure, V is very large, therefore, the value of $\frac{a}{V}$ is very small and hence, can be neglected. Thus,

$$pV = RT$$

This explains why the real gases behaviour ideally at extremely low pressure.

(b) When Pressure is High

At high pressure, volume V is quite small and hence, the term b cannot be neglected in comparison to V. Again, as the term $\frac{a}{V^2}$ is quite large but it is so small in comparison to high pressure p that it can be neglected. Thus, the van der Waals' equation may be written as

$$p(V - b) = RT$$

$$pV = RT + pb$$

or $$\frac{pV}{RT} = 1 + \frac{pb}{RT} \text{ or } Z = 1 + \frac{pb}{RT}$$

(c) When Temperature is High

At any given pressure, if the temperature is extremely high, V is very large and hence, the terms $\frac{a}{V^2}$ and b can be neglected. Thus, the van der Waals' equation reduces to

$$pV = RT$$

This explains why the real gases behave like ideal gas at high temperature.

(d) When Temperature is Low

At low temperature both p and V are small, hence both pressure and volume corrections are appreciable, so that the deviations are more pronounced.

Merits of van der Waals' Equation

(i) This equation explains behaviour of real gases upto moderately high pressure.

(ii) This equation represents the trend of the isotherms representing the variation of pV with p for various gases.

(iii) With the help of this equation, values of Boyle's temperature, critical constants and inversion temperatures may be calculated in terms of 'a' and 'b'.

(iv) This equation is also helpful in obtaining a 'reduced equation of state' which being a general equation of state has the advantage that a single curve can be obtained for all gases when the equation is graphically represented by plotting the variables.

Limitations of van der Waals' Equation

(i) Although van der Waals' equation is much more accurate than the ideal gas equation, appreciable deviation at too low temperatures and pressures have been observed.

(ii) The values of van der Waals' constant 'a' and 'b' do not remain constant over the entire ranges of temperature and pressure.

Hence, van der Waals' equation is valid only over specific range of temperature and pressure.

2.8 Liquefaction of Gases

A gas can be liquefied when its temperature is below critical temperature, *i.e.*, by cooling or compressing it.

As a gas is compressed at a given temperature, the intermolecular distance decreases and intermolecular forces come into effect. The motion and hence, kinetic energy of the molecules gradually decreases and the gas is said to be undergoing *liquefaction*. During liquefaction, the pressure remains constant. The process of liquefaction spreads over a definite time interval.

Gases which have high critical temperatures (such as CO_2, SO_2, NH_3, Cl_2 etc.) can be liquefied by applying a suitable pressure alone. Permanent gases (such as H_2, N_2, O_2 etc.) cannot be liquefied by the action of pressure and cooling.

A gas can be liquefied by "lowering the temperature" or "increasing the pressure".

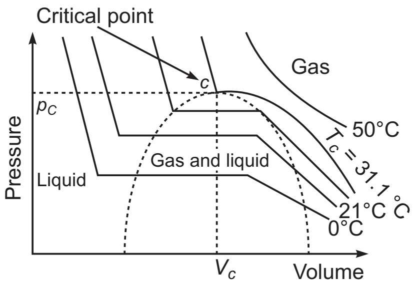


Fig. 2.6 Isotherms of CO_2 at different temperatures

Methods of Liquefaction of Gases

Two modern methods of cooling the gas to or below their T_c and hence of liquefaction of gases are Linde's method and Claude's method.

(a) Linde's Method

This process is based upon Joule-Thomson effect which states that "When a gas is allowed to expand adiabatically from a region of high pressure to a region of extremely low pressure, it is accompanied by cooling."

(b) Claude's Method

This process is based upon the principle that when a gas expands adiabatically against an external pressure (as a piston in an engine), it does some external work. Since work is done by the molecules at the cost of their kinetic energy, the temperature of the gas falls causing cooling.

Caution Point Adiabatic demagnetisation is also used to liquefy a gas.

Uses of Liquefied Gases

Liquefied gases compressed under a high pressure are of great importance in industries such as

(i) Liquid ammonia and liquid sulphur dioxide are used as refrigerants.
(ii) Liquid carbon dioxide finds use in soda fountains.
(iii) Liquid chlorine is used for bleaching and disinfectant purposes.
(iv) Liquid air is an important source of oxygen in rockets, jet-propelled planes and bombs.
(v) Compressed oxygen is used for welding purposes.
(vi) Compressed helium is used in airships.

Critical State

A state for every substance at which its vapour and liquid states are indistinguishable is known as *critical state*.

At this state, following conditions are achieved

Critical Temperature

There is a temperature below which the gas can be liquefied but above it the gas defies liquefaction. This temperature is called critical temperature (T_c).

It is given by,

$$T_c = \frac{8a}{27Rb}$$

Critical Pressure

The critical pressure (p_c) is the minimum pressure required to liquefy the gas at its critical temperature. It is given by, $p_c = \dfrac{a}{27b^2}$

Critical Volume

The critical volume (V_c) is the volume occupied by a mole of the gas at the critical temperature and critical pressure. It is given by $V_c = 3b$

From the above, the critical compressibility factor (Z_c) is given by

$$Z_c = \frac{p_c V_c}{RT_c} = \frac{3}{8} = 0.375$$

All the gases behaves as a van der Waals' gas if its critical compressibility factor (Z_c) is equal to 0.375.

Sample Problem 22 *The value of critical temperature, T_c and critical pressure, p_c for some gases are given, which of the gases can be liquefied at 100 K and 50 atm?*

Gases	A	B	C	D
p_c (atm)	2.2	14	35	45
T_c (K)	5.1	33	127	140

(a) *D only* (b) *A only*
(c) *A and B* (d) *C and D*

Interpret (c) For liquefaction, the critical temperature, T_c must be less than 100 K.

The gases *A* and *B* have low values of critical temperature, thus these can be liquefied at 100 K.

2.9 Joule-Thomson Effect

According to Joule-Thomson, when a real gas is allowed to expand adiabatically through a porous plug or a fine hole into a region of low pressure, it is accompanied by cooling (except for hydrogen and helium which get warmed up)."

Cooling takes place because some work is done to overcome the intermolecular forces of attraction. As a result, the internal energy decreases and so does the temperature.

Ideal gases do not show any cooling or heating because there are no intermolecular forces of attraction, *i.e.,* they do not show Joule-Thomson effect.

During Joule-Thomson effect, enthalpy of the system remains constant.

Joule-Thomson coefficient, $\mu = \left(\frac{\partial T}{\partial p}\right)_H$.

For cooling, $\mu = +$ ve (because dt and dp will be $-$ve)

For heating, $\mu = -$ ve (because $dt = +$ ve, $dp = -$ ve)

For no heating or cooling, $\mu = 0$ (because $dT = 0$).

Check Point 2

1. What is the significance of different values of Boyle's temperature, T_b ?
2. On comparing the values of the van der Waals' constants for NH_3 and N_2, the value of '*a*' is larger for NH_3 but that of '*b*' is larger for N_2. Why?
3. Explain why ideal gases do not show any cooling or heating?

2.10 Liquid State

It is the state of matter in which the molecules are held close to each other and execute random motion through intervening spaces. Most of the physical properties of liquids are controlled by the strengths of intermolecular attractive forces.

On the basis of kinetic molecular theory of liquids, liquids may be described as

(i) A liquid is made up of molecules.

(ii) Molecules of a liquid are closely packed.

(iii) There are appreciable cohesive forces between the molecules.

(iv) The molecules are in constant random motion and slide upon one another.

(v) Liquids are virtually incompressible.There are very slight changes in volume with change in temperature or pressure. This is due to strong forces of attraction and very small free space available in liquids.

(vi) The average kinetic energy of the molecules in liquid is proportional to its Kelvin temperature.

(vii) Normal boiling point (T_b) of the liquid is nearly two-thirds of its critical temperature (T_c) when both are expressed on the absolute scale. This is called **Guldberg's rule.**

$$T_b = \frac{2}{3} T_c$$

(viii) For non-associated liquids which do not have too high boiling points, the ratio of the heat of vaporisation (in joules) to the normal boiling point of the liquid on the absolute scale is approximately equal to 88. *i.e.,* $\frac{\Delta H_v}{T_{bp}} \approx 88 \text{ J K}^{-1} \text{ mol}^{-1}$ or 21 cal K^{-1} mol^{-1}. The above statement is called *Trouton's rule.*

The liquids exhibit following characteristic properties

1. Shape and Volume

The liquid state is intermediate in character between the complete molecular randomness (in gases) and the orderly arrangement of molecules (in crystalline solids). In liquids, the molecules are moving sufficiently slow for the intermolecular forces of attraction to hold them together in a **definite volume.**

However, the molecular motion is too rapid for the attraction force to fix the molecules into definite positions of a crystal lattice. *Hence a liquid retains its volume but not its shape*. The liquid therefore, flows to assume the shape of the container in which it is placed.

2. Density

The molecules in a liquid are closely packed, thus their densities are many times more than the vapours. However, the density is low as compared to solids. An increase in temperature increases the volume of most liquids slightly and consequently decreases the liquid density.

3. Evaporation

The process of change of liquids into vapour at any temperature below the boilng point is termed as *evaporation*. Like gases, the liquids too have a distribution of kinetic energy ranging from very low values to very high values. As a result of this, the highly energetic fractions of molecules at the surface overcome the intermolecular attraction and escape as vapour.

Kinetic energy of a given molecule of a liquid is continuously changing as it colloids with other molecules, but at any given instance some of the molecules of total collection, have relatively high energies and some have relatively low energies. The molecules with kinetic energies sufficiently high to overcome the attractive forces of surrounding molecules, can escape from the liquid and enter the gas phase.

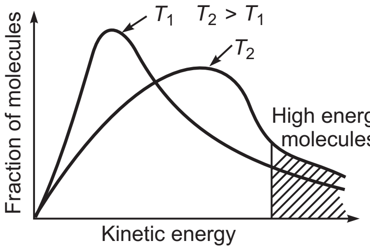


Fig. 2.7 Kinetic energy distribution in liquids

The loss of a number of high energy molecules causes the average kinetic energy of the molecules remaining in liquid to fall and temperature of liquids falls proportionately.

The rate of evaporation increases as the temperature is raised, since the average kinetic energy of molecules increases.

Heat of Vaporisation and Condensation

The evaporation of a liquid involves the loss of energy by the liquid, thus the temperature of the remaining liquid would fall. The heat required to evaporate a unit mass of a given liquid at constant temperature is called the *heat of vaporisation.*

The value of heat of vaporisation generally **decreases with increase in temperature reaching zero at the critical temperature.** The heat of vaporisation depends on the strength of intermolecular forces.

The reverse of evaporation is **condensation.** The heat corresponding to this process is called the **heat of condensation** and is numerically equal to heat of evaporation.

Molar Heat of Vaporisation (ΔH_v)

When a liquid and its vapour are in equilibrium, the temperature of vapour and the temperature of liquid are same. Hence, molecules in each phase have same kinetic energy, however the two phases differ in total internal energy.

When the liquid is converted into gas, energy must be supplied to separated the molecules. Thus, the energy of the gas phase is higher than that of the liquid phase by the amount of this difference. Also the volume of a gas is considerably larger than the volume of the liquid from which it is derived hence, energy must be supplied to do the work to make room for the vapour by pushing back the atmosphere.

The heat of vaporisation includes both, the energy required to overcome intermolecular cohesive forces and the energy needed to expand the vapour.

The molar heat of vaporisation (ΔH_v) decreases with increase in temperature and $\Delta H_v = 0$ at critical temperature. At the critical temperature, all the molecules have sufficient energy to vaporise.

4. Vapour Pressure

The process by which molecules of liquids go into the gaseous state (vapour) is called *vaporisation* or **evaporation.** The reverse process whereby gas molecules become liquid molecules is called **condensation.**

There is a dynamic equilibrium estabilished between the liquid and the vapour at a given temperature.

$$\text{Liquid} \rightleftharpoons \text{Vapour}$$

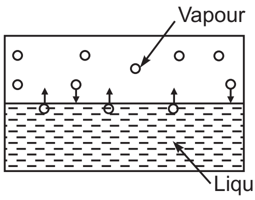


Fig. 2.8 Equilibrium between liquid and gaseous state

The pressure exerted by the vapours in equilibrium with liquid at a fixed temperature is called *vapour pressure*.

The vapour pressure of liquids depends on the type of intermolecular forces operating among the molecules *e.g.*, ethanol will have higher vapour pressure than water at a given temperature, as ethanol has a weaker hydrogen bonding than water.

Assuming vapour to be acting as an ideal gas, the pressure of the vapour at a given temperature 'T' is given by

$$pV = nRT$$

$$p = \frac{n}{V} RT = CRT$$

where 'C' is concentration of vapour (in mol/L). Variation of vapour pressure with temperature is also given by *Clausius Clapeyron equation* as

$$\log_{10} \frac{p_2}{p_1} = \frac{\Delta H_{\text{vap}}}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

The vapour pressure increases with rise in temperature. This is so because at higher temperature more molecules in liquids will have the larger kinetic energy and will break away from the liquid surface.

Caution Point *Since evaporation is a surface phenomenon, the increase in surface area increases the rate of evaporation/vapour pressure.*

Sample **Problem 23** *Two vessels have different base area. They are filled with water to the same height. If the amount of water in one be 4 times that in the other, then the ratio of pressure on their bottoms will be*

(*a*) 4 : 1
(*b*) 1 : 1
(*c*) 8 : 1
(*d*) 16 : 1

Interpret (*b*) Pressure depends only on the height of liquid column.

5. Boiling Point

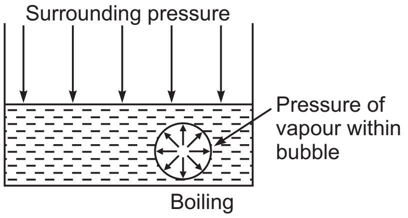


Fig. 2.9 Boiling of a liquid

When a liquid is heated, tiny bubbles are formed in it throughout the volume. These rise to the surface and burst. The liquid is said to be *boiling* and the temperature at which it happens is called the *boiling point* of the liquid.

The pressure within the bubble is equal to the vapour pressure of the liquid at that temperature. When the vapour pressure of the liquid is equal to the external pressure acting on the surface of the liquid, the bubbles increases in size and burst. Hence, *the boiling point is the temperature at which the vapour pressure becomes equal to the surrounding pressure.*

The boiling point of a liquid can be lowered by reducing the external pressure and can be increased by raising the external pressure.

The domestic pressure cookers work on this principle. The pressure inside the pressure cooker is maintained above one atmosphere and the liquid contained then would boil at a higher temperature than 100° C thus, the food is cooked in a shorter time.

Sample **Problem 24** *A person living in Shimla observed that cooking food without using pressure cooker takes more time. The reason for this observation is that at high attitude.*

[**NCERT** Exemplar]

(*a*) *pressure increases* (*b*) *temperature decreses*
(*c*) *pressure decreases* (*d*) *temperature increases*

Interpret (*c*) Food takes more time to cook that means its vapour pressure becomes equal to atomspheric pressure at a lower temperature. That is at high altitude, pressure is lower or pressure decreases (as $p \propto T$ at constant v and n)

6. Surface Tension

A molecule in the interior of a liquid is attracted equally in all directions by the molecules around it. However, a molecule on the surface of a liquid is attracted only sideways and towards the interior. The liquid surface is, therefore, under tension and tends to contract to the smallest possible area in order to have the minimum number of molecules at the surface. The surface acts like a stretched membrane. The force acting along the surface of a liquid at right angle to any line per unit length is called *surface tension.*

$$\text{Surface tension, } Y = \frac{\text{work } (W)}{\text{change in area } (\Delta A)} = \frac{\text{Force } (F)}{\text{Length } (L)}$$

In order to increase the surface area, force must be exerted to overcome the surface tension. The work (energy) required to expand the surface of a liquid by unit area may also be defined as *surface tension.*

Unit of surface tension is N/m.

Effects of Surface Tension

(i) Due to surface tension a liquid tends to have a minimum surface area. For a given volume of a liquid, sphere has the minimum surface area. Therefore, **the small drops of liquids are spherical.**

(ii) Due to surface tension, liquids rise or fall in capillary tubes.

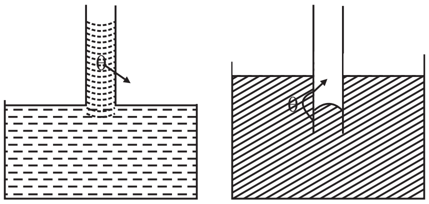


Fig. 2.10 Rise of liquid in capillary tube

The height of liquids in column rise in the capillary is given by

$$h = \frac{2T \cos\theta}{r\rho g}$$

where, r = radius of capillary,
ρ = the density of liquid,
T = the surface tension and
θ = contact angle.

(iii) Cleaning action of soap and detergents is due to lowering of interfacial tension between water and greasy substances.

(iv) Efficiency of toothpaste, nasal jellies and mouth washed depends, in part, on the fact that they contain substances, which can lower surface tensions.

Characteristics of Surface Tension

Important characteristics of surface tension are

(i) It decreases with rise in temperature up to the critical temperature of the liquid at which there is no distinction. Variation of Y with temperature is given by **Evtvos equation.**

$$Y\left(\frac{M}{d}\right)^{2/3} = K(t_c - t)$$

where, M = molar mass, d = density,
t = temperature in °C
t_c = critical temperature

(ii) Addition of a surface active agent (*e.g.,* soap) decreases surface tension.

(iii) Surface tension is different for different liquids due to different intermolecular forces.

(iv) It results in rise and fall of liquid in capillary tube. This is called **capillary action.** Adhesive forces between liquid and walls of tube tend to increase surface area of liquid. The surface tension tends to reduce area, thereby pulling the liquid up in tube. The liquid climbs until the adhesive and cohesive forces are balanced by force of gravity.

- (i) If adhesive forces are stronger than cohesive forces → **meniscus acquires U-shape.**
- (ii) If cohesive forces are stronger than adhesive forces → **meniscus is convex.**

Sample Problem 25 *A liquid of density* $850\,kg/m^3$ *having a surface tension of* 0.055 *N/m, will rise how far in a glass capillary of* 1.40 *mm inside diameter?*

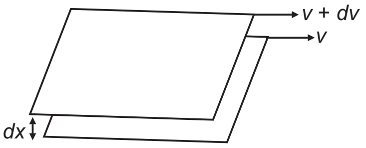
(a) 21 *mm* (b) 32 *mm* (c) 19 *mm* (d) 24 *mm*

Interpret (c) $h = \dfrac{2Y}{rgd} = \dfrac{2 \times 0.055}{0.70 \times 10^{-3} \times 850 \times 9.8}$

$= 0.019\ \text{m} = 19\ \text{mm}$

7. Viscosity and Fluidity

Different liquids flow at different rates, *e.g.*, glycerine and honey flow very slowly while ether and water flow rapidly. The property of liquid, which determines their rate of flow is called *viscosity* of the liquid. A liquid may be considered to be consisting of molecular layer arranged one over the other. The friction forces between the layers (the van der Waals' force of intermolecular attraction) offer resistance to flow of liquids when a shearing force is applied. *Viscosity of a liquid is a measure of its frictional resistance.*



Consider a liquid flowing on a glass surface. The molecular layer in contact with the stationary surface has zero velocity. The successive layers above it move with increasingly higher velocities.

Consider two adjacent layers of a liquid, separated by a distance dx, moving with velocities 'v' and $v + dv$. The force of friction (F) resisting the relative motion of two layers is proportional to the area 'A' of the layer and the velocity gradient $\left(\dfrac{dv}{dx}\right)$, *i.e.*,

$$F \propto A\,\frac{dv}{dx} \quad \text{or} \quad F = \eta\,A\,\frac{dv}{dx} \quad \text{or} \quad \eta = \frac{F}{A}\,\frac{dx}{dv}$$

Where, η is the proportionality constant known as *coefficient of viscosity*, which is constant for a given liquid at a given temperature.

$$\left(\frac{dv}{dx}\right) = \text{velocity gradient.}$$

The coefficient of viscosity (η) *may be defined as the force of resistance per unit area which will maintain unit velocity gradient between two liquid layers.*

With increase in temperature, viscosity of a liquid decreases as the rise in temperature results in increase in kinetic energy of molecules, thus the interlayer friction is reduced.

Units of viscosity $\eta = \dfrac{F}{A}\,\dfrac{dx}{dv} = \text{mass / length - time}$

In CGS system, unit of η is g/cm-s, this is called **poise.**

$$1\ \text{poise} = \frac{1}{10}\ \text{kg/m-s}$$

Viscosity (η) of a liquid decreases with rise in temperature. Variation of η with temperature, T is given by

$$\log_{10}\eta = \log_{10} A + \frac{E_a}{2.303\,RT}$$

The reciprocal of viscosity is called **fluidity** denoted by ϕ.

$$\phi = \frac{1}{\eta}$$

Effects of Viscosity

(i) Lubricating oils are graded according to their viscosity. For good quality of all weather lubricants **long chain coiling polymers** are added to the oil, which uncoil on increasing the temperature thus viscosity of oil also increases.

(ii) In **arteriosclerosis,** the arterial walls contract and get hardened resulting in decrease of the diameter of capillaries, which then offer resistance to the flow of blood due to its viscosity. This result in a condition of high blood pressure and strain on the heart.

(iii) In fever, an increased circulation of blood is needed. Rise of body temperature decreases the viscosity of blood by about **3% per degree kelvin**. Lowering of viscosity result in a more flow of blood without any extra strain on the heart.

(iv) In case of **asphyxia,** concentration of carbon dioxide in blood increases. This result in swelling of the corpuscles thereby increasing the viscosity of the blood.

Check Point 3

1. Water menisus in a glass tube is concave while that of mercury is convex, why?
2. Why does the boiling point of liquid rise on increasing pressure?
3. All other factors being equal, which will cool to room temperature faster, a closed container of water of 100°C or an open container of water at 100°C?
4. Why are drops of liquids spherical in nature?

WORKED OUT

Examples

Example 1 1.22 *g of a gas measured over water at* 15°C *and a pressure of* 775 *mm of mercury occupied* 900 *mL. Calculate the volume of dry gas at NTP (vapour pressure of water at* 15°C *is* 14 *mm).*

(a) 372.21 *mL* (b) 854.24 *mL*
(c) 869.96 *mL* (d) 917.76 *mL*

Solution (*b*) Pressure of dry gas = Pressure of moist gas − Vapour pressure of water

$$= 775 - 14 = 761 \text{ mm}$$

From,
$$\underset{\text{(initial)}}{\frac{p_1V_1}{T_1}} = \underset{\text{(NTP)}}{\frac{p_2V_2}{T_2}}$$

So,
$$V_2 = \frac{p_1V_1T_2}{T_1\,p_2} = \frac{761 \times 900 \times 273}{288 \times 760}$$

$$= 854.24 \text{ mL}$$

Example 2 *An open flask contains air at* 27°C. *The temperature at which it should be heated so that 1/3rd of air measured at* 27°C *escapes out will be*

(a) 450°*C* (b) 200°*C* (c) 177°*C* (d) −73°*C*

Solution (c) Let the initial number of moles of air at 27°C (300 K) be *n*

Number of moles of air left when the air is heated to the temperature $T\text{ K} = n - \frac{n}{3} = \frac{2n}{3}$

At constant pressure and constant volume,

$$n_1T_1 = n_2T_2$$

or
$$n \times 300 = \frac{2n}{3} \times T$$

or
$$T = 450 \text{ K} = (450 - 273) = 177°\text{ C}$$

Example 3 3.7 *g of a gas at* 25°C *occupied the same volume as* 0.184 *g of hydrogen at* 17°C *and at the same pressure. The molecular mass of the gas is*

(a) 0.024 (b) 39.14
(c) 41.33 (d) 59.14

Solution (c) For hydrogen,

$$w = 0.184 \text{ g},\ T = 17 + 273 = 290 \text{ K},\ M = 2$$

From
$$pV = \frac{w}{M}RT = \frac{0.184}{2} \times R \times 290 \qquad \text{...(i)}$$

For unknown gas,

$$w = 3.7 \text{ g},\ T = 25 + 273 = 298 \text{ K},\ M = ?$$

$$pV = \frac{3.7}{M} \times R \times 298 \qquad \text{...(ii)}$$

From Eqs. (i) and (ii)

$$\frac{3.7}{M} \times R \times 298 = \frac{0.184}{2} \times R \times 290$$

or
$$M = \frac{3.7 \times 298 \times 2}{0.184 \times 290} = 41.33$$

Example 4 *What percentage of a sample of nitrogen must be allowed to escape if its temperature, pressure and volume are changed from* 220°C, 3.0 *atm and* 1.65 *L to* 110°C, 0.7 *atm and* 1.0 *L respectively?*

(a) 18.13% (b) 34%
(c) 62% (d) 81.77%

Solution (*d*) From $pV = \frac{w}{m}RT$

$$w = \frac{pVm}{RT}$$

$$\text{Mass of gas before escaping} = \frac{3.0 \times 1.65 \times 28}{0.0821 \times 493} = 3.42 \text{ g}$$

$$\text{Mass of gas after escaping} = \frac{0.7 \times 1.0 \times 28}{0.0821 \times 383} = 0.62 \text{ g}$$

Percentage of nitrogen allowed to escape

$$= \frac{(3.42 - 0.62)}{3.42} \times 100 = 81.77\%$$

Example 5 *At* 27°C, *hydrogen is leaked through a tiny hole into a vessel for* 20 *min. Another unknown gas at the same temperature and pressure as that of hydrogen leaked through the same hole for* 20 *min. After the effusion of the gases the mixture exerts a pressure of* 6 *atm. The hydrogen content of the mixture is* 0.7 *mol. If the volume of the container is* 3 *L, the molecular mass of the unknown gas is*

(a) 2 (b) 10.33 (c) 103 (d) 1033

Solution (*d*) Let p_{H_2} and p_{un} be the partial pressures of hydrogen and unknown gas respectively and *w* be the number of moles of unknown gas.

From $$pV = nRT$$

$$p_{H_2} = \frac{0.7}{3} \times 0.0821 \times 300$$

$$p_{un} = \frac{w}{3} \times 0.0821 \times 300$$

Adding both,

$$p_{H_2} + p_{un} = \left(\frac{1}{3}\right) \times 0.0821 \times 300 \; (0.7 + w) = 6$$

$$6 = 8.21(0.7 + w)$$

$$0.7 + w = 0.7308$$

$$w = 0.0308 \text{ mol}$$

From Graham's law of diffusion,

$$\frac{\frac{0.7}{20}}{\frac{0.0308}{20}} = \sqrt{\frac{M}{2}} \quad \text{or} \quad M = 1033 \text{ g mol}^{-1}$$

Example 6 *The ratio of velocities of diffusion of gases A and B is* 1 : 4. *If the ratio of their masses present in the mixture is* 2 : 3, *the ratio of their mole fractions is*

(*a*) 1 : 4 (*b*) 1 : 24 (*c*) 4 : 1 (*d*) 24 : 3

Solution (*b*) $\frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}} = \frac{1}{4}$ or $\frac{M_B}{M_A} = \frac{1}{16}$

Let W_A and W_B be the masses of A and B respectively,

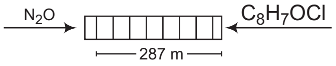
$$\text{Mole fraction of } A = \frac{\frac{W_A}{M_A}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}}$$

$$\text{Mole fraction of } B = \frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}}$$

$$\text{Ratio of mole fractions of } A \text{ and } B = \frac{W_A}{M_A} \times \frac{M_B}{W_B}$$

or
$$\frac{W_A}{W_B} \times \frac{M_B}{M_A} = \frac{2}{3} \times \frac{1}{16} = \frac{1}{24}$$

Example 7 *A cinema hall has equidistant rows 1 m apart. The length of the cinema hall is 287 m and it has 287 rows. From one side of the cinema hall, laughing gas* (N_2O) *is released and from the other side, tear gas* ($C_6H_5COCH_2Cl$) *is released. In which rows, spectators will be laughing and weeping simultaneously?*



(*a*) 187th *from* N_2O *and* 100th *row from* $C_6H_5COCH_2Cl$

(*b*) 100th *row from tear gas and* 187th *from* N_2O

(*c*) 287 *from* N_2O *and* 287 *from* $C_6H_5COCH_2Cl$

(*d*) 100th *row from both*

Solution (*a*) Molar mass of

$$C_8H_7OCl = 8 \times 12 + 7 \times 1 + 16 + 35.5 = 154.5 \text{ g}$$

Molar weight of $N_2O = 2 \times 14 + 16 = 44\ g$

According to Graham's law of diffusion.

$$\frac{r_{N_2O}}{r_{C_8H_7OCl}} = \sqrt{\frac{M_{C_8H_7OCl}}{M_{N_2O}}} = \sqrt{\frac{154.5}{44}} = \sqrt{3.5} = 1.87 : 1$$

$$d_{N_2O} = \frac{1.87}{2.87} \times 287 = 187^{th} \text{ row from } N_2O \text{ side}$$

$$d_{C_8H_7OCl} = \frac{1.0}{2.87} \times 287 = 100^{th} \text{ row tear from gas side.}$$

Therefore, the spectator from the side of N_2O in the 187th row will be laughing and weeping simultaneously. Alternatively, the spectator from the side of tear gas in the 100th row will be laughing and weeping simultaneously.

Example 8 *A gas bulb of* 1 *mL capacity contains* 2.0×10^{21} *molecules of nitrogen exerting a pressure of* $7.57 \times 10^3\ Nm^{-2}$. *The root mean square speed of the gas molecules is*

(*a*) 274 ms^{-1} (*b*) 494 ms^{-1}

(*c*) 690 ms^{-1} (*d*) 988 ms^{-1}

Solution (*b*) Number of moles of the gas $= \frac{2.0 \times 10^{21}}{6.023 \times 10^{23}}$ mol

$$= 3.32 \times 10^{-3} \text{ mol}$$

From, $pV = nRT$

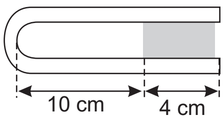
$$T = \frac{pV}{nR} = \frac{7.57 \times 10^3 \times 10^{-3}}{3.32 \times 10^{-3} \times 8.314} = 274.25 \text{ K}$$

$\because$ Root mean square speed, $v_{rms} = \sqrt{\frac{3RT}{M}}$

$$\therefore \quad v_{rms} = \sqrt{\frac{3 \times 8.314 \times 274.25}{28 \times 10^{-3}}}$$

$$= 494.26 \text{ ms}^{-1}$$

Example 9 *A 10.0 cm gas column is trapped by a column of* Hg *4 cm long in capillary tube of uniform bore. The tube is held horizontally in a room at 1 atm. Length of the air column when the tube is held vertically with the open end up is*



(*a*) 3.50 *cm* (*b*) 9.95 *cm* (*c*) 6.20 *cm* (*d*) 4.80 *cm*

Solution (*b*) If A is the area of cross section of the tube, then

$$V_1 = 10\ A \text{ cm}^3$$

$V_2 = ?, p_1 = 760$ mm Hg, $p_2 = (760 + 4)$ mmHg

We know that,

$$p_1V_1 = p_2V_2$$

$$V_2 = \frac{760 \times 10A}{764} = 9.95\,A$$

$$\therefore \quad \text{Length of air column} = \frac{9.95\,A}{A} = 9.95 \text{ cm}$$

Start Practice for JEE Main

Round I (Topically Divided Problems)

Characteristics of Gases and Gas Laws

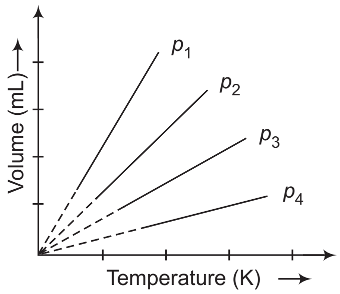
1. Physical properties of ice, water and steam are very different. What is the chemical composition of water in all the three states? **[NCERT Exemplar]**

(a) H_2O^{16}, H_2O^{18}, H_2O^{16} (b) H_2O, D_2O, T_2O
(c) D_2O, T_2O, H_2O (d) H_2O in all states

2. 300 mL of a gas at 27°C is cooled to –3°C at constant pressure, the final volume is

(a) 270 mL (b) 340 mL
(c) 150 mL (d) 240 mL

3. A plot of volume (V) *versus* temperature (T) for a gas at constant pressure is a straight line passing through the origin. The plots at different values of pressure are shown in the figure. Which of the following order of pressure is correct for this gas? **[NCERT Exemplar]**



(a) $p_1 > p_2 > p_3 > p_4$ (b) $p_1 = p_2 = p_3 = p_4$
(c) $p_1 < p_2 < p_3 < p_4$ (d) $p_1 < p_2 = p_3 < p_4$

4. If two moles of an ideal gas at 246 °C occupy a volume of 44.8 L, the pressure must be

(a) 4 atm (b) 2 atm
(c) 8 atm (d) 6 atm

5. 380 mL of a gas at 27°C, 800 mm of Hg weighs 0.455 g. The molecular weight of the gas is

(a) 46 (b) 38 (c) 28 (d) 24

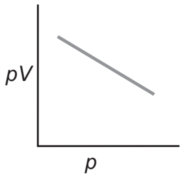
6. Dalton's law of partial pressure is not applicable to

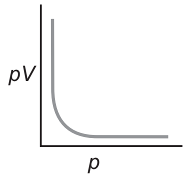
(a) H_2 and N_2 mixture (b) H_2 and Cl_2 mixture
(c) H_2 and CO_2 mixture (d) None of these

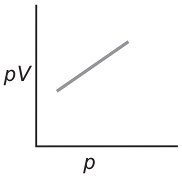
7. The density of neon will be highest at

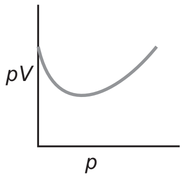
(a) STP (b) 0°C, 2 atm
(c) 273°C, 1 atm (d) 273°C, 2 atm

8. Which of the following is a Boyle's plot at very low pressure?

(a)


(b)


(c)


(d)


9. Which gas has the highest partial pressure in atmosphere?

(a) CO_2 (b) H_2O
(c) O_2 (d) N_2

10. The rates of diffusion of SO_2, CO_2, PCl_3 and SO_3 are in the following order

(a) $PCl_3 > SO_3 > SO_2 > CO_2$ (b) $CO_2 > SO_2 > PCl_3 > SO_3$
(c) $SO_2 > SO_3 > PCl_3 > CO_2$ (d) $CO_2 > SO_2 > SO_3 > PCl_3$

11. The pressure of a 1 : 4 mixture of dihydrogen and dioxygen enclosed in a vessel is one atmosphere. What would be the partial pressure of dioxygen? **[NCERT Exemplar]**

(a) 0.8×10^5 atm (b) $0.008\ Nm^{-2}$
(c) $8 \times 10^4\ Nm^{-2}$ (d) 0.25 atm

12. The equation of state corresponding to 8g of O_2 is

(a) $pV = 8RT$ (b) $pV = RT/4$
(c) $pV = RT$ (d) $pV = RT/2$

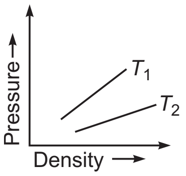
13. At 0°C, the density of a certain oxide of a gas at 2 bar is same as that of dinitrogen at 5 bar. What is the molecular mass of the oxide? **[NCERT]**

(a) 10 u (b) 20 u
(c) 40 u (d) 70 u

14. What will be the molar volume of nitrogen and argon at 273.15K and 1 atm? **[NCERT** Exemplar**]**

(a) 11.2, 22.4 respectively (b) 22.4, 22.4 respectively
(c) 11.2, 11.2 respectively (d) 22.4, 11.2 respectively

15. Figure shows graphs of pressure *versus* density for an ideal gas at two temperatures T_1 and T_2. Which is correct?



(a) $T_1 > T_2$ (b) $T_1 = T_2$
(c) $T_1 < T_2$ (d) None of these

16. The density of a gas A is twice that of a gas B at the same temperature. The molecular weight of gas B is thrice that of A. The ratio of the pressures acting on B and A will be

(a) $\frac{1}{6}$ (b) $\frac{7}{8}$
(c) $\frac{2}{5}$ (d) $\frac{1}{4}$

17. 1.0 L of N_2 and 7/8 L of O_2 at the same temperature and pressure were mixed together. What is the relation between the masses of the two gases in the mixture?

(a) $M_{N_2} = 3M_{O_2}$ (b) $M_{N_2} = 8M_{O_2}$
(c) $M_{N_2} = M_{O_2}$ (d) $M_{N_2} = 16M_{O_2}$

18. What will be the pressure of the gaseous mixture when 0.5 L of H_2 at 0.8 bar and 2.0 L of dioxygen at 0.7 bar are introduced in a 1L vessel at 27°C? **[NCERT]**

(a) 0.4 (b) 1.5
(c) 1.8 (d) None of these

19. 2.9 g of a gas at 95°C occupied the same volume as 0.184 g of dihydrogen at 17°C at the same pressure. What is the molar mass of the gas? **[NCERT]**

(a) 20 g mol^{-1} (b) 10 g mol^{-1}
(c) 40 g mol^{-1} (d) 80 g mol^{-1}

20. A gaseous mixture containing He, CH_4 and SO_2 was allowed to effuse through a fine hole then find what molar ratio of gases coming out initially? (Given mixture contains He, CH_4 and SO_2 in 1 : 2 : 3 mole ratio).

(a) $\sqrt{2} : \sqrt{2} : 3$ (b) 2 : 2 : 3
(c) 4 : 4 : 3 (d) 1 : 1 : 3

21. An open vessel at 27°C is heated until 3/8th of the air in it has been expelled. Assuming that the volume remains constant, calculate the temperature at which the vessel was heated.

(a) 307°C (b) 107°C
(c) 480°C (d) 207°C

22. A bottle of dry ammonia and one of dry hydrogen chloride are connected through a long tube. The stoppers at both ends of the tube are opened simultaneously. The white ammonium chloride ring first formed will be

(a) at the centre of the tube
(b) near the hydrogen chloride bottle
(c) near the ammonia bottle
(d) throughout the length of the tube

23. Two closed vessels of equal volume containing air at pressure p_1 and temperature T_1 are connected to each other through a narrow tube. If the temperature in one of the vessels is now maintained at T_1 and that in the other at T_2, what will be the pressure in the vessels?

(a) $\frac{2p_1T_1}{T_1 + T_2}$ (b) $\frac{T_1}{2p_1T_2}$
(c) $\frac{2p_1T_2}{T_1 + T_2}$ (d) $\frac{2p_1}{T_1 + T_2}$

24. Two different gases 'A' and 'B' are filled in separate containers of equal capacity under the same conditions of temperature and pressure. On increasing the pressure slightly the gas 'A' liquefies but gas B does not liquify even on applying high pressure untill it is cooled. This is because **[NCERT]**

(a) gas A is above critical temperature while gas B is below it
(b) gas B is above critical temperature while gas A is below it
(c) Both the gases are above critical temperature
(d) Both the gases are below critical temperature

25. Air at sea level is dense, this is a practical implementation of

(a) Boyle's law (b) Charles' law
(c) Avogadro's law (d) Dalton's law

26. Oxygen gas generated by the decomposition of potassium chlorate is collected. The volume of oxygen collected at 24°C and atmospheric pressure of 760 mm Hg is 128 mL. Calculate the mass of oxygen gas obtained. The pressure of the water vapour at 24°C is 22.4 mm Hg.

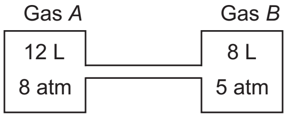
(a) 0.123 g (b) 0.163 g
(c) 0.352 g (d) 1.526 g

27. When a sample of gas is compressed at constant temperature from 15 atm to 60 atm, its volume changes from 76 cm^3 to 20.5 cm^3. Which of the following statements are possible explanations of this behaviour?

I. The gas behaves non-ideally.
II. The gas dimerises.
III. The gas is absorbed into the vessel walls.

(a) I, II and III (b) I and II only
(c) II and III only (d) Only I

28. Two vessels containing gases *A* and *B* are interconnected as shown in the figure. The stopper is opened, the gases are allowed to mix homogeneously. The partial pressures of *A* and *B* in the mixture will be, respectively



(a) 8 and 5 atm (b) 9.6 and 4 atm
(c) 4.8 and 2 atm (d) 6.4 and 4 atm

Kinetic Theory of Gases and Deviation from Ideal Behaviour

(Including Liquefaction of Gases)

29. A gas that follows Boyle's law, Charles' law and Avogadro's law is called an ideal gas. Under what conditions a real gas whould behave ideally?

[**NCERT** Exemplar, **NCERT**]

(a) High pressure and low temperature
(b) Low pressure and high temperature
(c) High pressure and high temperature
(d) Low pressure and low temperature

30. Based on kinetic theory of gases following laws can be proved

(a) Boyle's law
(b) Charles' law
(c) Avogadro's law
(d) All of the above

31. The pressure of a real gas is less than the pressure of an ideal gas because of

(a) increase in the number of collisions
(b) finite size of the molecules
(c) increase in the kinetic energy
(d) intermolecular forces

32. The average kinetic energy of an ideal gas per molecule in SI units at 25°C will be

(a) 6.17×10^{-21} kJ (b) 6.17×10^{-21} J
(c) 6.17×10^{-20} J (d) 7.16×10^{-20} J

33. Which one of the following statements is not true about the effect of an increase in temperature on the distribution of molecular speeds in a gas?

(a) The area under the distribution curve remains the same as under the lower temperature
(b) The distribution becomes broader
(c) The fraction of the molecules with the most probable speed increases
(d) The most probable speed increases

34. The pressure of 2 moles of ammonia at 27° when its volume is 5 L according to van der Waals' equation is (Given, $a = 4.17, b = 0.03711$)

(a) 10.33 atm (b) 9.33 atm
(c) 9.74 atm (d) 9.2 atm

35. If temperature of 1 mole of a gas is increased by 50°C, calculate the change in kinetic energy of the system.

(a) 623.25 J (b) 6.235 J
(c) 623.5 J (d) 6235.0 J

36. The liquefaction behaviour of temporary gases like CO_2 approaches that of permanent gases like N_2, O_2 etc., as we go to

(a) below critical temperature
(b) above critical temperature
(c) above absolute zero
(d) below absolute zero

37. At low pressure, the van der Waals' equation is reduced to

(a) $Z = \frac{pV_m}{RT} = 1 - \frac{ap}{RT}$ (b) $Z = \frac{pV_m}{RT} = 1 + \frac{b}{RT}p$
(c) $pV_m = RT$ (d) $Z = \frac{pV_m}{RT} = 1 - \frac{a}{RT}$

38. At what temperature the rms speed of hydrogen molecules is same as that of oxygen molecules at 1327°C?

(a) 173 K (b) 100 K (c) 400 K (d) 523 K

39. In a closed flask of 5 L, 1.0 g of H_2 is heated from 300 to 600 K. Which statement is not correct?

(a) Pressure of the gas increases
(b) The rate of collision increases
(c) The number of mole of gas increases
(d) The energy of gaseous molecules increases

40. The ratio of average speed of an oxygen molecule to the rms speed of a nitrogen molecule at the same temperature is

(a) $\left(\frac{3\pi}{7}\right)^{1/2}$ (b) $\left(\frac{7}{3\pi}\right)^{1/2}$

(c) $\left(\frac{3}{7\pi}\right)^{1/2}$ (d) $\left(\frac{7\pi}{3}\right)^{1/2}$

41. The rms speed of hydrogen is $\sqrt{7}$ times the rms speed of nitrogen. If T is the temperature of the gas, then

(a) $T_{H_2} = T_{N_2}$ (b) $T_{H_2} > T_{N_2}$

(c) $T_{H_2} < T_{N_2}$ (d) $T_{H_2} = \sqrt{7}T_{N_2}$

42. Which of the following is correct for critical temperature?

(a) It is the lowest temperature at which liquid and vapour can coexist

(b) Beyond the critical temperature, there is no distinction between the two phases and a gas cannot be liquefied by compression

(c) At critical temperature, the surface tension of the system is not zero

(d) At critical temperature, the gas and the liquid phases have different critical densities

43. According to kinetic theory of gases for a diatomic molecule

(a) the pressure exerted by the gas is proportional to the mean square speed of the molecules

(b) the pressure exerted by the gas is proportional to the root mean square speed of the molecules

(c) the root mean square speed is inversely proportional to the temperature

(d) the mean translational KE of the molecule is directly proportional to the absolute temperature

44. At lower temperatures, all gases except H_2 and He show

(a) negative deviation

(b) positive deviation

(c) positive and negative deviation

(d) None of the above

45. The most probable speed of 8 g of H_2 200 ms^{-1}. Average kinetic energy of H_2 gas is

(a) 240 J (b) 180 J (c) 320 J (d) 360 J

46. At what temperature will most probable speed of the molecules of the second number of alkyne series be the same as that of SO_2 at 527°C?

(a) 347°C (b) 227°C (c) 800°C (d) 254°C

47. A helium atom is two times heavier than a hydrogen molecule. At 298 K, the average kinetic energy of a helium atom is

(a) two times that of a hydrogen molecule

(b) four times that of a hydrogen molecule

(c) half that of a hydrogen molecule

(d) same as that of a hydrogen molecule

48. Positive deviation from ideal behaviour takes place because of

(a) molecular interaction between atoms and $pV/nRT > 1$

(b) molecular interaction between atoms and $pV/nRT < 1$

(c) finite size of atoms and $pV/nRT > 1$

(d) finite size of atoms and $pV/nRT < 1$

49. At STP, the order of root mean square velocities of molecules of H_2, N_2, O_2 and HBr is

(a) $H_2 > N_2 > O_2 > HBr$ (b) $HBr > O_2 > N_2 > H_2$

(c) $HBr > H_2 > O_2 > N_2$ (d) $N_2 > O_2 > H_2 > HBr$

50. The density of a gas filled electric lamp is 0.75 kg/m^3. After the lamp has been switched on, the pressure in it increases from 4×10^4 Pa to 9×10^4 Pa. What is increase in U_{rms}?

(a) 100 (b) 300 (c) 200 (d) 400

51. At low pressure, van der Waals' equation is reduced to $\left[p + \frac{a}{V^2}\right]V = RT$. The compressibility factor can be given as

(a) $1 + \frac{a}{RTV}$ (b) $1 - \frac{RTV}{a}$

(c) $1 + \frac{RTV}{a}$ (d) $1 - \frac{a}{RTV}$

52. The compressibility of a gas is less than unity as STP. Therefore,

(a) $V_m > 22.4$ L (b) $V_m < 22.4$ L

(c) $V_m = 11.2$ L (d) $V_m = 44.8$ L

53. The Joule-Thomson coefficient is zero at

(a) absolute temperature (b) critical temperature

(c) inversion temperature (d) below 0°C

Liquid State

54. The magnitude of surface tension of liquid depends on the attractive forces between the molecules, Arrange the following in increasing order of surface tension water, alcohol (C_2H_5OH) and hexane $[CH_3(CH_2)_4CH_3]$ **[NCERT]**

(a) water < alcohol < hexane

(b) hexane < alcohol < water

(c) alcohol < water < hexane

(d) hexane < water < alcohol

55. Clausius-Clapeyron equation is

(a) $\frac{d \log p}{dT} = \frac{\Delta H_{vap}}{2.303\ RT^2}$

(b) $\log p = \log A - \frac{\Delta H_{vap}}{2.303\ RT}$

(c) Both (a) and (b)

(d) None of the above

56. Following properties will decrease with increase in temperature except
(a) surface tension (b) viscosity
(c) density (d) vapour pressure

57. Which is true statement?
(a) All liquids have concave meniscus
(b) All liquids have convex meniscus
(c) Mercury has convex and other liquids have concave meniscus
(d) Mercury has concave and other liquids have convex meniscus

58. Surface tension of water is 73 dyne cm^{-1} at 20°C. If surface area is increased by 0.10 m^2, work done is
(a) 7.3 erg (b) 7.3×10^4 erg
(c) 73 J (d) 0.73 J

59. What is SI unit of viscosity coefficient (η)? **[NCERT Exemplar]**
(a) Pascal (b) Nsm^{-2} (c) km^{-2} s (d) Nm^{-2}

60. Which of the following property of water can be used to explain the spherical shape of rain droplets? **[NCERT Exemplar]**
(a) Viscosity (b) Surface tension
(c) Critical phenomena (d) Pressure

61. Evaporation and boiling differs
(a) evaporation is spontaneous at all temperatures while boiling is at constant temperature
(b) boiling is spontaneous at all temperatures while evaporation takes place at constant temperature
(c) both are spontaneous at all temperatures
(d) evaporation is exothermic while boiling is endothermic

62. If latent heat of vaporisation is L at boiling point T(K) then entropy of vaporisation is
(a) LT (b) LT^{-1}
(c) TL^{-1} (d) None of these

63. Select the correct statement(s).
(a) The standard boiling temperature is the temperature at which the vapour pressure of the substance is 1 bar
(b) The normal boiling temperature is the temperature at which the vapour pressure of the substance is 1 atm
(c) Substances for which $T > T_c$ and $p > p_c$ are called super critical fluids
(d) All of the above are correct statements

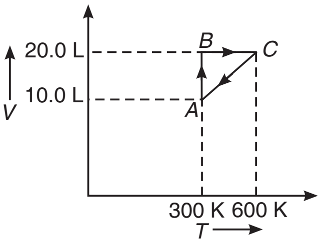
64. Select the incorrect statement.
(a) The properties of liquid crystals are intermediate between liquids and solids
(b) Surface tension of a liquid is maximum at critical temperature
(c) Viscosity decreases with increase in temperature
(d) CO_2 and H_2O show the unusual properties of supercritical fluids

Round II (Mixed Bag)

Only One Correct Option

1. The drain cleaner, Drainex contains small bits of aluminium which react with caustic soda to produce dihydrogen. What volume of dihydrogen at 20° C and 1 bar will be released when 0.15 g of aluminium reacts? **[NCERT]**
(a) 22400 mL (b) 203 mL
(c) 0.203 mL (d) 1120 mL

2. This graph expresses the various steps of the system containing 1 mole of gas. Which type of process, system has when it moves from C to A?



(a) Isochoric (b) Isobaric
(c) Isothermal (d) Cyclic

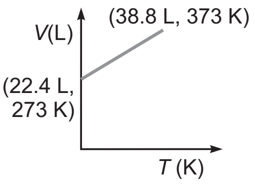
3.

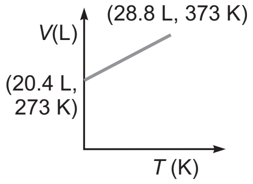
Gas	CO	CH_4	HCl	SO_2
Critical temp, T_c (K)	134	190	324	430

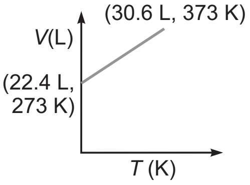
In the context of given values of critical temperature, the greater ease of liquefication is of
(a) SO_2 (b) HCl
(c) CH_4 (d) CO

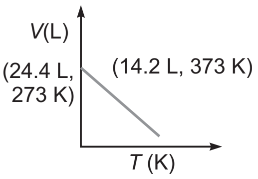
4. In two vessels of 1 L each at the same temperature, 1 g of H_2 and 1 g of CH_4 are taken. For these
(a) V_{rms} values will be same
(b) kinetic energy per mol will be same
(c) total kinetic energy will be same
(d) pressure will be same

5. Which one of the following volume (V)-temperature (T) plots represents the behaviour of one mole of an ideal gas at one atmospheric pressure?

(a) 

(b) 

(c) 

(d) 

6. The temperature at which nitrogen under 1.00 atm pressure has the same root mean square speed as that of carbon dioxide at STP, is

(a) 0°C (b) 27°C
(c) −99°C (d) −200°C

7. The molecular mass of each N_2 and CO is 28. If 0.5 L of N_2 at 27°C and 700 mm pressure contains n molecules, the number of molecules in 1.0 L of CO under identical conditions will be

(a) $\frac{n}{2}$ (b) n
(c) $2n$ (d) None of these

8. Gases X, Y, Z, P and Q have the van der Waals' constants a and b (in CGS units) as shown below.

	X	Y	Z	P	Q
a	6	6	20	0.05	30
b	0.025	0.15	0.1	0.02	0.2

The gas with the higher critical temperature is

(a) P (b) Q
(c) Y (d) X

9. Gases possess characteristic critical temperature which depends upon the magnitude of intermolecular forces between the particles. Following are the critical temperatures of some gases.

Gases	H_2	He	O_2	N_2
Critical temperature in Kelvin	33.2	5.3	154.3	126

From the above data what would be the order of liquefaction of these gases?

(Start writing the order from the gas liquefying first)

[NCERT Exemplar]

(a) H_2, He, O_2, N_2
(b) He, O_2, H_2, N_2
(c) N_2, O_2, He, H_2
(d) O_2, N_2, H_2, He

10. Pay load is defined as the difference between the mass of displaced air and the mass of the balloon. Calculate the pay load when a balloon of radius 10 m and mass 100 kg is filled with helium at 1.66 bar at 27°C. (Density of air = 1.2 kg m^{-3} and R = 0.083 bar dm^3 K^{-1} mol^{-1}) **[NCERT]**

(a) 1117.6 kg (b) 1217.46 kg
(c) 5028.57 kg (d) 3811.11 kg

11. A student forgot to add the reaction mixture to the round bottomed flask at 27°C but instead he/she placed the flask on the flame. After a lapse of time, he realized his mistake, and using a pyrometer he found the temperature of the flask was 477°C. What fraction of air would have been expelled out? **[NCERT]**

(a) 0.4 (b) 0.6
(c) 0.8 (d) 0.1

12. Which of the given sets of temperature and pressure will cause a gas to exhibit the greatest deviation from ideal gas behaviour?

(a) 100°C and 4 atm (b) 100°C and 2 atm
(c) −100°C and 4 atm (d) 0°C and 2 atm

13. By what ratio the average velocity of the molecule in a gas change when the temperature is raised from 50 to 200°C?

(a) $\frac{1.21}{1}$ (b) $\frac{1.46}{1}$
(c) $\frac{1.14}{1}$ (d) $\frac{4}{1}$

14. A spherical balloon of 21 cm diameter is to be filled with hydrogen at STP from a cylinder containing the gas at 20 atm and 27°C. If the cylinder can hold 2.82 L of water, the number of balloons that can be filled up is

(a) 5 (b) 2
(c) 10 (d) 12

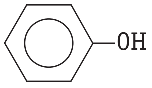
15. Calculate the total pressure in a 10.0 L cylinder which contains 0.4 g helium, 1.6 g oxygen and 1.4 g nitrogen at 27°C.

(a) 0.492 atm (b) 49.2 atm
(c) 4.92 atm (d) 0.0492 atm

16. The rate of effusion doesn't depend on

(a) the area of cross section of hole
(b) number of molecules per unit volume
(c) the average molecular speed
(d) size of the molecule

17. Which has maximum vapour pressure at a given temperature?

(a) $CH_3CH_2CH_2OH$ (b) 

(c) $CH_3—O—CH_3$ (d) CH_3COOH

18. A gas is heated in such a way so that its pressure and volume both becomes double. Again by lowering temperature, one fourth of initial number of moles of air has been taken in, to maintain the double volume and pressure. By what fraction, the temperature must have been raised finally?

(a) $\frac{1}{5}$ times (b) $\frac{4}{5}$ times
(c) $\frac{16}{5}$ times (d) $\frac{8}{5}$ times

19. Match the following gas laws in column I with the equation representing them in column II.

[NCERT Exemplar]

	Column I		Column II
(i)	Boyle's law	(A)	$V \propto n$ at constant T and p
(ii)	Charles' law	(B)	$p_{\text{Total}} = p_1 + p_2 + p_3 + ...$ at constant T, V
(iii)	Dalton's law	(C)	$\frac{pV}{T}$ = constant
(iv)	Avogadro's law	(D)	$V \propto T$ at constant n and p
		(E)	$p \propto \frac{1}{V}$ at constant n and T

Codes

(a) (i) E (ii) D (iii) B (iv) A (b) (i) A (ii) B (iii) C (iv) D
(c) (i) D (ii) C (iii) B (iv) A (d) (i) A (ii) E (iii) B (iv) D

20. Match the graphs between the following variables with their names. **[NCERT Exemplar]**

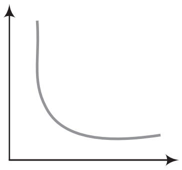
Graphs		Names	
(i)	Pressure *vs* temperature graph at constant molar volume.	(A)	Isotherms
(ii)	Pressure *vs* volume graph at constant temperature.	(B)	Constant temperature curve
(iii)	Volume *vs* temperature graph at constant pressure.	(C)	Isochores
		(D)	Isobars

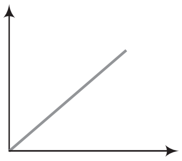
Codes

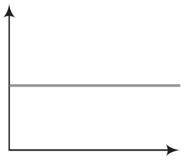
(a) (i) D (ii) A (iii) C (b) (i) A (ii) D (iii) C
(c) (i) C (ii) A (iii) D (d) (i) A (ii) C (iii) D

21. Match the following graphs of ideal gas with their coordinates **[NCERT Exemplar]**

Graphical representation *x* and *y* coordinates

(i)  (*A*) pV *vs* V

(ii)  (*B*) p *vs* V

(iii)  (*C*) p *vs* $\frac{1}{V}$

Codes

(a) (i) *A* (ii) *B* (iii) *C* (b) (i) *C* (ii) *B* (iii) *A*
(c) (i) *B* (ii) *A* (iii) *C* (d) (i) *B* (ii) *C* (iii) *A*

More than One Correct Option

22. If 1 g of each of the following gases are taken at STP, which of the gases will occupy (a) greatest volume and (b) smallest volume? **[NCERT Exemplar]**

(a) CO (b) H_2O (c) CH_4 (d) NO

23. Which of the following changes decrease the vapour pressure of water kept in a sealed vessel? **[NCERT Exemplar]**

(a) Decreasing the quantity of water
(b) Adding salt to water
(c) Decreasing the volume of the vessel to one-half
(d) Decreasing the temperature of water

24. With regard to the gaseous state of matter which of the following statements are correct? **[NCERT Exemplar]**

(a) Complete order of molecules
(b) Complete disorder of molecules
(c) Random motion of molecules
(d) Fixed position of molecules

25. Under which of the following two conditions applied together, a gas deviates most from the ideal behaviour? **[NCERT Exemplar]**

(a) Low pressure (b) High pressure
(c) Low temperature (d) High temperature

26. If the rms velocities of nitrogen and oxygen molecules are same at two different temperatures and same pressure then

(a) most probable velocity of molecules is also equal
(b) average speed of molecules is also same
(c) number of moles of each gas is also equal
(d) density of nitrogen and oxygen is also equal

27. Boyle's law may be expressed as

(a) $\left(\frac{dp}{dV}\right)_T = \frac{K}{V}$ (b) $\left(\frac{dp}{dV}\right)_T = -\frac{K}{V^2}$
(c) $\left(\frac{dp}{dV}\right)_T = \frac{K^2}{V}$ (d) $V \propto \frac{1}{p}$

28. Which of the following is/are true?

(a) Higher the value of a, weaker is intermolecular force of attraction

(b) At low pressure, $Z = 1 - \frac{a}{V_m RT}$, for ideal gas

(c) $\frac{V_1}{V_2} = \left(\frac{T_2}{T_1}\right)^{3/2}$, for reversible adiabatic expansion

(d) A gas can be liquefied below critical temperature at high pressure

Assertion and Reason

Directions (Q. Nos. 29 to 33) *Each of these questions contains two statements : Statement* I (*Assertion*) *and Statement* II (*Reason*)*. Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes* (*a*), (*b*), (*c*), (*d*) *given below*

(a) Statement I is true; Statement II is true; Statement II is a correct explanation for Statement I.

(b) Statement I is true; Statement II is true; Statement II is not a correct explanation for Statement I.

(c) Statement I is true; Statement II is false.

(d) Statement I is false; Statement II is true.

29. **Statement I** Three states of matter are the result of balance between intermolecular forces and thermal energy of the molecules.

Statement II Intermolecular forces tend to keep the molecules together but thermal energy of molecules tends to keep them apart. [NCERT Exemplar]

30. **Statement I** At constant temperature, pV vs V plot for real gases is not a straight line.

Statement II At high pressure all gases have $Z > 1$ but at intermediate pressure most gases have $Z < 1$.

[NCERT Exemplar]

31. **Statement I** At critical temperature liquid passes into gaseous state imperceptibly and continuously.

Statement II The density of liquid and gaseous phase is equal at critical temperture. [NCERT Exemplar]

32. **Statement I** Liquids tend to have maximum number of molecules at their surface.

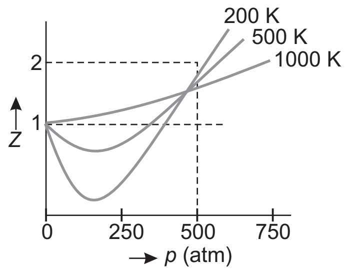
Statement II Small liquid drops have spherical shape. [NCERT Exemplar]

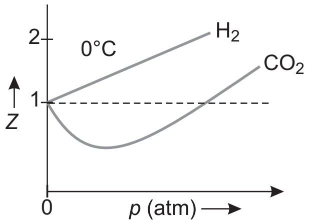
33. **Statement I** In van der Waals' equation of gases, the kinetic equation of gas is modified.

Statement II This modification is carried out with respect to actual volume of molecules and attractive forces between the gaseous molecules.

Comprehension Based Questions

Directions (Q. Nos. 34 to 36) Sketch shows the plot of Z *vs* p for a hypothetical gas for one mole at three distinct temperature.





Boyle's temperature is the temperature at which a gas shows ideal behaviour over a pressure range in the low pressure region.

Boyle's temperature (T_b) $= \frac{a}{Rb}$.

If a plot is obtained at temperature below Boyle's temperature then the curve will show negative deviation in low pressure region and positive deviation in the high pressure region. Near critical temperature, the curve is more likely as CO_2 and at the temperature above critical temperature, the curve is more like H_2 at 0°C.

34. For 500 K plot value of Z changes from 2 to 2.2 if pressure is varied from 1000 atm to 1200 atm (high pressure) then the value of $\frac{b}{RT}$ will be

(a) 10^{-4} atm^{-1}

(b) 10^{-3} atm^{-1}

(c) 10^{-5} atm^{-1}

(d) 0.10 atm^{-1}

35. As shown in the figure at 200 K and 500 atm, value of compressibility factor is 2. Then volume of the gas at this point will be

(a) 0.065 L

(b) 0.045 L

(c) 0.032 L

(d) 1.096 L

36. Which of the following is correct?

(a) $\frac{a}{b} = 1$ kcal mol^{-1}

(b) $\frac{a}{b} < 0.4$ kcal mol^{-1}

(c) $\frac{a}{b} > 0.4$ kcal mol^{-1}

(d) 2 kcal mol$^{-1} > \frac{a}{b} > 0.4$ kcal mol^{-1}

Directions (Q. Nos. 37 to 39) The pressure-volume relationship for gases helps to explain the mechanics of breathing. When we breathe in, the diaphragm is lowered and the chest wall is expanded, increasing the volume of the chest cavity. Boyle's law tells us that the pressure inside the cavity must decrease as outside air enters the lungs because it is at a higher pressure than the air in the chest cavity. When we breathe out, the diaphragm rises and the chest will contract decreasing the volume of chest cavity.

37. A 15.0 L cylinder of Ar gas is connected to an evacuated 235.0 L tank. If the final pressure is 750 mm Hg, what have been the original gas pressure in the cylinder?

(a) 76 atm (b) 12.56 atm

(c) 16.45 atm (d) 23 atm

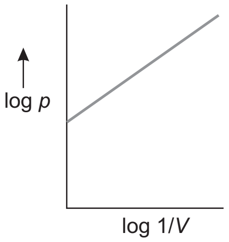
38. A balloon indoors where the temperature is 27°C has a volume of 2.00 L. What will be the volume of outdoors where the temperature is –23°C? Assuming pressure remains constant.

(a) 1.67 L (b) 2.23 L

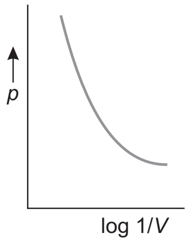
(c) 0.53 L (d) 1.26 L

39. Which of the following graphs is not according to Boyle's law?

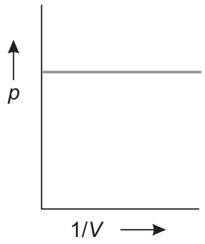
(a)



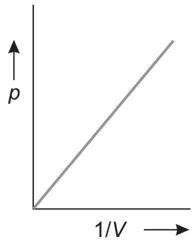
(b)



(c)



(d)



Previous Years' Questions

40. The molecular velocity of any gas is **[AIEEE 2011]**

(a) inversely proportional to the square root of temperature

(b) inversely proportional to absolute temperature

(c) directly proportional to square of temperature

(d) directly proportional to square root of temperature

41. a and b are van der Waals' constants for gases. Chlorine is more easily liquefied than ethane because **[AIEEE 2011]**

(a) a and b for Cl_2 > a and b for C_2H_6

(b) a and b for Cl_2 < a and b for C_2H_6

(c) a for Cl_2 > a for C_2H_6 but b for Cl_2 > b for C_2H_6

(d) a for Cl_2 > a for C_2H_6 but b for Cl_2 < b for C_2H_6

42. When r, p and M represent rate of diffusion, pressure and molecular mass, respectively, then the ratio of the rates of diffusion (r_A/r_B) of two gases A and B, is given as **[AIEEE 2011]**

(a) $(p_A/p_B)^{1/2}(M_A/M_B)$ (b) $(p_A/p_B)(M_B/M_A)^{1/2}$

(c) $(p_A/p_B)^{1/2}(M_B/M_A)$ (d) $(p_A/p_B)(M_A/M_B)^{1/2}$

43. If 10^{-4} dm^3 of water is introduced into a 1 dm^3 flask at 300 K, how many moles of water are in the vapour phase when equilibrium is established (Given vapour pressure of H_2O at 300K is 3170 Pa; $R = 8.314$ JK^{-1} mol^{-1}) **[AIEEE 2010]**

(a) 5.56×10^{-6} mol

(b) 1.53×10^{-2} mol

(c) 4.46×10^{-2} mol

(d) 1.27×10^{-3} mol

44. Equal masses of methane and oxygen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by oxygen is **[AIEEE 2007]**

(a) $\frac{2}{3}$ (b) $\frac{1}{3} \times \frac{273}{298}$

(c) $\frac{1}{3}$ (d) $\frac{1}{2}$

Answers

Round I

1. (d) **2.** (a) **3.** (c) **4.** (b) **5.** (c) **6.** (b) **7.** (b) **8.** (d) **9.** (b) **10.** (d)
11. (c) **12.** (b) **13.** (d) **14.** (b) **15.** (a) **16.** (a) **17.** (c) **18.** (c) **19.** (c) **20.** (c)
21. (d) **22.** (b) **23.** (a) **24.** (b) **25.** (a) **26.** (b) **27.** (d) **28.** (c) **29.** (b) **30.** (d)
31. (d) **32.** (b) **33.** (d) **34.** (b) **35.** (c) **36.** (b) **37.** (d) **38.** (b) **39.** (c) **40.** (b)
41. (b) **42.** (b) **43.** (d) **44.** (a) **45.** (a) **46.** (b) **47.** (d) **48.** (a) **49.** (a) **50.** (c)
51. (d) **52.** (b) **53.** (c) **54.** (b) **55.** (c) **56.** (d) **57.** (c) **58.** (b) **59.** (b) **60.** (b)
61. (a) **62.** (b) **63.** (d) **64.** (b)

Round II

1. (b) **2.** (b) **3.** (a) **4.** (b) **5.** (c) **6.** (c) **7.** (c) **8.** (d) **9.** (d) **10.** (d)
11. (b) **12.** (c) **13.** (c) **14.** (c) **15.** (a) **16.** (d) **17.** (c) **18.** (c) **19.** (a) **20.** (c)
21. (d) **22.** (c,d) **23.** (b,d) **24.** (b,c) **25.** (b,c) **26.** (a,b,d) **27.** (b,d) **28.** (b,c,d) **29.** (a) **30.** (b)
31. (a) **32.** (d) **33.** (a) **34.** (b) **35.** (a) **36.** (d) **37.** (c) **38.** (a) **39.** (c) **40.** (d)
41. (d) **42.** (b) **43.** (d) **44.** (c)

the Guidance

Round I

1. In different physical states, chemical composition of a substance remains the same *i.e.*, H_2O.

3.
$$p \propto \frac{1}{V} \propto T$$

Thus, $p_4 > p_3 > p_2 > p_1$

5.
$$pV = \frac{w}{M} RT$$
$$M = \frac{wRT}{pV}$$
$$= \frac{0.455 \times 0.0821 \times 300 \times 760 \times 1000}{800 \times 380}$$
$$= 28.0 \text{ g}$$

6. Dalton's law of partial pressure is not applicable to gases which react chemically and produce different number of moles of products than the reactants. Some gases which do not obey this law are
$SO_2 + Cl_2, CO + Cl_2, NO + O_2, NH_3 + HCl$ and $H_2 + Cl_2$

7. We know that density
$$d = \frac{pM}{RT}$$
$$d \propto \frac{1}{T}$$
and $$d \propto p$$
Thus, density of neon is maximum at 0°C and 2 atm.

9. We know that
$$p = n\frac{RT}{V} = \frac{w}{M}\,\frac{RT}{V}$$
As the M increases, partial pressure decreases. Thus, H_2O has the highest partial pressure.

10. Rate of diffusion is inversely proportional to the molecular weight *i.e.*,
$$r \propto \sqrt{\frac{1}{M}}$$
So, the order of rate of diffusion is
$$CO_2 > SO_2 > SO_3 > PCl_3$$

11. Partial pressure of O_2 = mole fraction of $O_2 \times$ total p
$$= \frac{4}{1+4} \times 1$$
$$= 0.8 \text{ atm} = 8 \times 10^4 \text{ Nm}^{-2}$$

12. Ideal gas equation
$$pV = nRT$$
$$pV = \frac{w}{M}RT = \frac{8}{32}RT$$
$$pV = \frac{RT}{4}$$

13. Density, $d = \frac{Mp}{RT}$

When T and d are same and R is constant,

then $p_1 M_1$ (gaseous oxide) $= p_2 M_2$ (nitrogen).

$2 \text{ bar} \times M_1 = 5 \text{ bar} \times 28 \text{ u}$

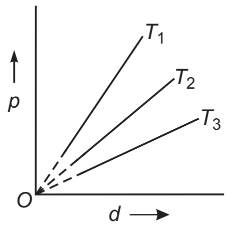
(Molar mass of $N_2 = 28$ u)

Molecular mass of unknown oxide,

$$M_1 = \frac{5 \text{ bar} \times 28}{2 \text{ bar}} = 70 \text{ u}$$

14. Every gas has 22.4 L molar volume at 273.15 K and 1 atm pressure (STP).

15. At constant temperature, density of a gas is directly proportional to its pressure and inversely proportional to its volume.



$T_3 > T_2 > T_1$

16.
$$\frac{d}{p} = \frac{M}{RT}$$

Let density of gas $B = d$

So, density of gas $A = 2d$

and molecular weight of $A = M$

So, molecular weight of $B = 3M$

Since R is a constant and T is same, so

$$p_A = \frac{d_A RT}{M_A} \text{ and } p_B = \frac{d_B RT}{M_B}$$

$$\frac{p_B}{p_A} = \frac{d_B}{d_A} \times \frac{M_A}{M_B} = \frac{d}{2d} \times \frac{M}{3M} = \frac{1}{6}$$

17. At constant temperature and pressure, the masses of two gases in a mixture are same, so

$$M_{N_2} = M_{O_2}$$

18.
$$pV = nRT$$

Moles of $H_2, n_{H_2} = \frac{pV}{RT} = \frac{0.8 \times 0.5}{RT} = \frac{0.40}{RT}$

Similarly, moles of O_2, $n_{O_2} = \frac{pV}{RT} = \frac{0.7 \times 2}{RT} = \frac{1.4}{RT}$

Total number of moles $= \frac{0.40}{RT} + \frac{1.4}{RT} = \frac{1.8}{RT}$

Total pressure, $p_{\text{total}} = \frac{nRT}{V} = \frac{1.8 \times RT}{RT \times 1} = 1.8$ atm

19.
$$pV = nRT$$

$$pV = \frac{\omega RT}{M}$$

Unknown gas; H_2 gas

$$p_1 V_1 = \frac{\omega_1 R T_1}{M_1};\ p_2 V_2 = \frac{\omega_2 R T_2}{M_2}$$

$$p_1 V_1 = p_2 V_2$$

Hence,
$$\frac{\omega_1 R T_1}{M_1} = \frac{\omega_2 R T_2}{M_2}$$

$$\frac{2.9 \text{ g} \times R \times 368 \text{ K}}{M_1} = \frac{0.184 \text{ g} \times R \times 290 \text{ K}}{2 \text{ g mol}^{-1}}$$

Molar mass of unknown gas,

$$M_1 = \frac{2.9 \text{ g} \times 368 \text{ K} \times 2 \text{ g mol}^{-1}}{0.184 \text{ g} \times 290 \text{ K}} = 40 \text{ g mol}^{-1}$$

20.
$$\frac{n'_{He}}{n'_{CH_4}} = \frac{1}{2}\sqrt{\frac{16}{4}} = \frac{1}{1}$$

$$\frac{n'_{He}}{n'_{SO_2}} = \frac{1}{3}\sqrt{\frac{64}{4}} = \frac{4}{3}$$

So, $n'_{He} : n'_{CH_4} : n'_{SO_2} = 4 : 4 : 3.$

21. According to Gay Lussac's law

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

If $\frac{3}{8}^{\text{th}}$ of the air is expelled out then remaining air $= \frac{5}{8}$

$$T_2 = \frac{(273 + 27) \times 8}{5} = \frac{2400}{5} = 480 \text{ K}$$

$$= 480 - 273 = 207° \text{ C}$$

22. According to Graham's law of diffusion,

$$r \propto \sqrt{\frac{1}{M}}$$

The rate of diffusion of ammonia ($M = 17$) is more than the HCl ($M = 36.5$), thus white ring forms near the hydrogen chloride bottle.

23.
$$\frac{p_1}{T_1} + \frac{p_1}{T_1} = \frac{p}{T_1} + \frac{p}{T_2}$$

$$\frac{2p_1}{T_1} = p\left(\frac{T_1 + T_2}{T_1 T_2}\right)$$

or
$$p = \frac{2p_1 T_2}{T_1 + T_2}$$

24. A gas cannot be liquefied above critical temperature. So, gas 'A' is below its critical temperature whereas gas 'B' is above its critical temperature.

25. $\frac{p_1}{d_1} = \frac{p_2}{d_2}$ (at a constant temperature)

This is the Boyle's law.

So, the case — "Air at sea level is dense" is studied under Boyle's law.

26. From the total pressure and the vapour pressure of water, we can calculate the partial pressure of O_2.

$$p_{O_2} = p_T - p_{H_2O} = 760 - 22.4 = 737.6 \text{ mm Hg}$$

From the ideal gas equation we write

$$\omega = \frac{pVM}{RT} = \frac{0.974 \times 0.128 \times 32.0}{0.0821 \times 297} = 0.163 \text{ g}$$

27. At constant temperature, for ideal gas,

$$p_1V_1 = p_2V_2$$

For the given sample,

$$15 \times 76 = 60 \times 20.5$$

$$\therefore \qquad p_1V_1 \neq p_2V_2$$

$\therefore$ The gas behaves non-ideally. However, the gas neither undergo dimerisation nor adsorbed into the vessel walls.

28. Moles of $A, n_A = \frac{p_AV_A}{RT} = \frac{8 \times 12}{RT} = \frac{96}{RT}$

Moles of $B, n_B = \frac{p_BV_B}{RT} = \frac{8 \times 5}{RT} = \frac{40}{RT}$

Total pressure $\times$ total volume $= (n_A + n_B) \times RT$

$$p \times (12 + 8) = \frac{1}{RT}(96 + 40)\,RT$$

$$p = 6.8$$

$\therefore$ Partial pressure of $A = p \times$ mole fraction of A

$$= 6.8 \times \left(\frac{96}{RT} \Big/ \frac{96 + 40}{RT}\right) = 4.8 \text{ atm}$$

$\therefore$ Partial pressure of $B = p \times$ mole fraction of B

$$= 6.8 \times \left(\frac{40}{RT} \Big/ \frac{96 + 40}{RT}\right) = 2 \text{ atm.}$$

30. On the basis of kinetic theory of gases

$$pV = \frac{1}{2} N_A m\bar{v}^2$$

and $$\frac{1}{2} m\bar{v}^2 = \frac{3}{2} KT$$

$$p = \frac{1}{3}\left(\frac{N}{V}\right) m\bar{v}^2$$

or $$p = \frac{2}{3}\left(\frac{N}{V}\right)\frac{1}{2} m\bar{v}^2$$

$$= \frac{2}{3}\left(\frac{N}{V}\right)\left(\frac{3}{2}\right) KT$$

or $$pV = nKT$$

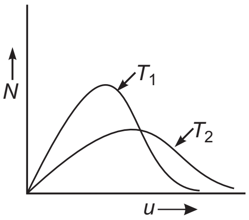
32. Average kinetic energy per molecule

$$= \frac{3}{2} KT$$

$$= \frac{3}{2} \times 1.38 \times 10^{-23} \times 300 \text{ J}$$

$$= 6.21 \times 10^{-21} \text{ J}$$

33. Distribution of molecules (N) with velocity (u) at two temperatures T_1 and $T_2 (T_2 > T_1)$ is shown below :



At both temperatures, distribution velocity first increases, reaches a maximum value and the decreases.

34. $\left(p + \frac{n^2a}{V^2}\right)(V - nb) = nRT$

$$p = \frac{nRT}{(V - nb)} - \frac{an^2}{V^2}$$

$$= \frac{2 \times 0.082 \times 300}{5 - 2 \times 0.03711} - \frac{4.17 \times 4}{25}$$

$$= 9.33 \text{ atm}$$

35. $\text{KE} = \frac{3}{2} RT$ for 1 mole of a gas

$$\Delta\text{KE} = \frac{3}{2} \times 8.314 \times (50 - 0)$$

$$= \frac{3}{2} \times 8.314 \times 50 = 623.55 \text{ J}$$

36. Gases for which intermolecular forces of attraction are small such as N_2, O_2 etc., have low value of T_c, thus liquefied above critical temperature.

37. van der Waals' equation (at low pressure),

$$\left[p + \frac{a}{V^2}\right](V - b) = RT$$

$$(V - b) \approx V$$

or $$pV = RT - \frac{a}{V}$$

or $$\frac{pV_m}{RT} = 1 - \frac{a}{RT} = Z$$

38. $$v_{H_2} = v_{O_2}$$

So, $$\sqrt{M_{O_2}T_{H_2}} = \sqrt{M_{H_2}T_{O_2}}$$

$$32 \times T_{H_2} = 2 \times 1600$$

$$T_{H_2} = \frac{2 \times 1600}{32} = 100 \text{ K}$$

40. $$u_{av} = \sqrt{\frac{8RT}{\pi M}} \quad \text{So, } u_{av\,(O_2)} = \sqrt{\frac{8RT}{\pi \times 32}}$$

$$u_{rms} = \sqrt{\frac{3RT}{M}} \quad \text{so} \quad u_{rms\,(N_2)} = \sqrt{\frac{3RT}{28}}$$

$$\frac{u_{av\,(O_2)}}{v_{rms\,(N_2)}} = \sqrt{\frac{8 \times 28}{\pi \times 32 \times 3}} = \sqrt{\frac{7}{3\pi}} = \left[\frac{7}{3\pi}\right]^{1/2}$$

41. We know that

$$u_{rms} = \sqrt{\frac{3RT}{M}}$$

$\because$ u_{rms} of hydrogen is more than the u_{rms} of nitrogen, thus its temperature is also greater than nitrogen.

45. $$200 = \sqrt{\frac{2RT}{2 \times 10^{-3}}} \text{ or } RT = 40$$

Average kinetic energy $= \frac{3}{2}nRT = \frac{3}{2} \times \frac{8}{2} \times 40 = 240$ J

46. Second member of alkyne series is C_3H_4. ($M = 40$)

$$\begin{array}{ccc} C_3H_4 & & SO_2 \\ \sqrt{\frac{2RT_1}{M_1}} & = & \sqrt{\frac{2RT_2}{M_2}} \end{array}$$

$$T_1 = T_2\left(\frac{M_1}{M_2}\right) = 800\left(\frac{40}{64}\right) \text{ K}$$

$$= 500 \text{ K } = 227°\text{C}$$

47. Kinetic energy $\left(= \frac{3}{2}RT\right)$ does not depends upon the atomic mass of the gases.

48. If $Z > 1$, the gas is less compressible than expected from ideal behaviour and shows positive deviation usually at high pressure, *i.e.*, $pV > RT$

49. We know that, $v_{\text{rms}} = \sqrt{\frac{3RT}{M}}$

So, as the molecular mass increases, rms speed decreases. Thus, the correct order of root mean square speed is

$$H_2 > N_2 > O_2 > HBr$$

50. $$u_1 = \sqrt{\frac{3p}{d}}$$

$$\therefore \quad \Delta u_{\text{rms}} = \sqrt{\frac{3}{d}} \times (\sqrt{p_2} - \sqrt{p_1})$$

$$= \sqrt{\frac{3}{0.75}} \times (300 - 200) = \sqrt{4} \times 100 = 200$$

51. $$\left[p + \frac{a}{V^2}\right]V = RT$$

$$pV + \frac{a}{V} = RT$$

$$\frac{pV}{RT} + \frac{a}{VRT} = 1$$

$$\frac{pV}{RT} = \left(1 - \frac{a}{VRT}\right) = Z.$$

52. The compressibility factor

$$Z = \frac{p \times 22.4}{RT} = 1 \qquad \text{(for ideal gas)}$$

$$Z = \frac{p \times Vm}{RT} < 1$$

$$\therefore \quad \frac{22.4}{V_m} > 1$$

$$\text{or} \quad V_m < 22.4$$

53. Joule-Thomson coefficient (μ) is zero at inversion temperature.

$$\text{Mathematically, } \mu = \left(\frac{\partial T}{\partial p}\right)_H$$

When, $\mu = 0$, the gas neither gets cooled down nor gets heated upon expansion.

54. In hexane, there are only London forces between the molecules. These forces are very weak. H—bonding is stronger in H_2O in comparison to C_2H_5OH. Hence, the increasing order of surface tension is

Hexane > alcohol > water

56. On increasing temperature, vaporisation increases. Hence, vapour pressure increases.

58. Work done = surface tension × increase in area

$$= 73 \times 0.10 = 73 \times 0.10 \times 10^4 = 7.3 \times 10^4 \text{ erg}$$

59. The SI unit of $\eta = \text{Nsm}^{-2}$

62. $$\Delta S = \frac{L}{T} = LT^{-1}$$

Round II

1. $$\underset{\substack{2 \times 27 \text{ g} \\ 0.15 \text{ g}}}{2\text{Al}} + 2\text{NaOH} + 2H_2O \longrightarrow 2\text{NaAlO}_2 + \underset{\substack{3 \text{ mol} \\ \frac{0.15 \times 3}{2 \times 27} = 0.00833 \text{ mol}}}{3H_2}$$

$$pV = nRT$$

$$V_{H_2} = \frac{0.00833 \text{ mol} \times 0.0821 \text{dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1} \times 293 \text{ K}}{1 \times 0.987 \text{ atm}}$$

$$(1\text{bar} = 0.987 \text{ atm})$$

$$V_{H_2} = 0.203 \text{ dm}^3$$

$$V_{H_2} = 203 \text{ mL}$$

Note Temperature must be in kelvin. If it is given in °C, convert it into K.

2. **At *A*** → temperature $= T$, volume $= V$, pressure $= p_1$

At C → temperature $= 2T$ volume $= 2V$, pressure $= p_2$

$$\frac{p_1V}{T} = \frac{p_2 \times 2V}{2T}$$

$p_1 = p_2$, *i.e.*, system is isobaric

3. Higher the critical temperature, greater will be the ease of liquefication.

4. $$\text{KE} = \frac{3}{2}kT$$

where, k is constant.

$$\text{KE} \propto T$$

Here, the temperature is same. Hence, for 1 g of H_2 and 1 g of CH_4 which are taken in two vessels of 1 L each at same temperature, the kinetic energy per mol will be the same.

5. *V-T* plot represents the behaviour of 1 mole of an ideal gas at 1 atm pressure.

Given, $T_1 = 273\text{ K},\ T_2 = 373\text{ K}$

According to Charles' law,

$$V \propto T$$

$$\frac{V_1}{V_2} = \frac{T_1}{T_2} = \frac{273}{373} = 0.73$$

When, $V_1 = 22.4, V_2 = 30.6$, because $\frac{V_1}{V_2} = 0.73.$

6. Let rms speed of nitrogen at *T*K be *u* and is equal to that of CO_2 at STP

$$u_{\text{rms}} = \sqrt{\frac{3RT}{28}} = \sqrt{\frac{3R \times 273}{44}}$$

$$T = \frac{273 \times 28}{44} = 173.73\text{ K} = -99.27^\circ\text{ C}$$

7. Molecular mass of $N_2 = 28, CO = 28$

Number of molecules of N_2

$(V = 0.5\text{ L}, T = 27^\circ\text{ C}, p = 700\text{ mm}) = n$

Number of molecules of N_2

$(V = 1\text{ L}, T = 27^\circ\text{ C}, p = 700\text{ mm}) = 2n$

8. Critical temperature, $T_c = \frac{8a}{27Rb}$

Greater is the value of $\left(\frac{a}{b}\right)$, more is the critical temperature of gas.

For, gas *X* $\frac{a}{b} = \frac{6}{0.025} = 240$

gas *Y*, $\frac{a}{b} = \frac{6}{0.150} = 40$

gas *Z*, $\frac{a}{b} = \frac{20}{0.1} = 200$

gas *P*, $\frac{a}{b} = \frac{0.05}{0.02} = 2.5$

gas *Q*, $\frac{a}{b} = \frac{30}{0.2} = 150$

Therefore, gas *X* will have the highest critical temperature.

9. A gas with higher critical temperature liquify first.

10. Radius, $R_{\text{balloon}} = 10\text{m}$

$$V_{\text{balloon}} = \frac{4}{3}\pi r^3 = \frac{4}{3} \times \frac{22}{7} \times (10)^3 = 4190.476\text{ m}^3$$

$$V_{\text{balloon}} = V_{\text{displaced air(by balloon)}}$$

$\therefore$ Mass of displaced air $= V_{\text{displaced air}} \times$ density of air

$$m_{\text{displaced air}} = 4190.476\text{ m}^3 \times 1.2\text{ kg m}^{-3}$$

$$m = 5028.57\text{ kg}$$

Mass of He filled in balloon, $w_{\text{He}} = \frac{pVM}{RT}$ $\left(pV = \frac{wRT}{M}\right)$

$$w_{\text{He}} = \frac{1.66\text{ bar} \times 4190.476 \times 10^3\text{ dm}^3 \times 4 \times 10^{-3}\text{ kg mol}^{-1}}{0.083\text{ bar dm}^3\text{ K}^{-1}\text{mol}^{-1} \times 300\text{ K}}$$

$$w_{\text{He}} = 1117.46\text{ kg}$$

Total mass of filled balloon, w_{balloon}

= mass of balloon + mass of He filled in the balloon

$$w_{\text{ balloon}} = 100\text{ kg} + 1117.46\text{ kg} = 1217.46\text{ kg}$$

Pay load = mass of displaced air – mass of balloon

= 5028.57 kg – 1217.46 kg = 3811.11 kg

11. Suppose volume of the air in flask $= V\text{ cm}^3$ at 27°C or300 K

$$V_1 = V\text{ cm}^3, V_2 = ?, T_1 = 300\text{ K}, T_2 = 750\text{ K}$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{V}{300} = \frac{V_2}{750} \text{ or } 300\ V_2 = 750\ V$$

$$V_2 = 2.5\ V$$

Volume expelled $= 2.5\ V - V = 1.5\ V$ (final volume)

Fraction of air expelled $= \frac{1.5\ V}{2.5\ V} = 0.6$

Alternatively, using $pV = nRT$

$$n \propto \frac{1}{T}$$

$$\frac{n_2}{n_1} = \frac{T_1}{T_2} = \frac{300}{750} \Rightarrow \frac{n_2}{n_1} = 0.4$$

$\therefore$ Fraction of air expelled = 0.6

12. Greatest deviation from ideal behaviour is exhibited by real gases at low temperature and high pressure.

13.

$$\frac{(v_{\text{av}})_1}{(v_{\text{av}})_2} = \sqrt{\frac{T_1}{T_2}}$$

Given, $T_1 = 150 + 273 = 423\text{K}$

$T_2 = 50 + 273 = 323\text{K}$

$$\therefore \quad \frac{(v_{\text{av}})_1}{(v_{\text{av}})_2} = \sqrt{\frac{T_1}{T_2}} = \sqrt{\frac{423}{323}} = \frac{1.14}{1}$$

14. Volume of balloon $= \frac{4}{3}\pi r^3$

$$= \frac{4}{3} \times \frac{22}{7} \times \left(\frac{21}{2}\right)^3 = 4851\text{ mL}$$

Volume of the cylinder containing gas

= 2.82 L = 2820 mL

Volume at STP, $= V_1 = \frac{p_2 V_2 T_1}{T_2 p_1} = 2820 \times \frac{273 \times 20}{300 \times 1}$

= 51324 mL

Volume of the gas that will remain in the cylinder after filling balloons is equal to the volume of cylinder, *i.e.,* 2820 mL.

Available hydrogen for filling = 51324 − 2820

= 48504 mL

Number of balloons $= \dfrac{48504}{4851} \approx 10$

15. Number of moles of helium $= \dfrac{0.4}{4} = 0.1$

Number of moles of oxygen $= \dfrac{1.6}{32} = 0.05$

Number of moles of nitrogen $= \dfrac{1.4}{28} = 0.05$

Total moles in the 10.0 L cylinder at 27°C

$= (0.1 + 0.05 + 0.05) = 0.2$ mol

$$p_T = \frac{nRT}{V} = \frac{0.2 \times 0.082 \times 300}{10} = 0.492 \text{ atm}$$

16. Effusion does not depend on size of the molecule.

17. CH_3OCH_3 lacks H-bonding, hence, it is most volatile, so it has maximum vapour pressure.

18. $p_1 = p; \quad V_1 = V; \quad p_2 = 2p; \quad V_2 = 2V$

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

$$\frac{pV}{T_1} = \frac{2p \times 2V}{T_2} \Rightarrow T_2 = 4T_1$$

When air has been taken in and p, V remain constant,

$$n_1 \cdot 4T_1 = n_2 \cdot T_2$$

$$n_1 = n \text{ and } n_2 = n + \frac{1}{4}n = \frac{5}{4}n$$

$$\therefore \qquad n \cdot 4T_1 = \frac{5}{4}n \cdot T_2 \Rightarrow T_2 = \frac{16}{5}T_1$$

19. Boyle's law, $p \propto \dfrac{1}{V}$ at constant T and n

Charles' law, $V \propto T$ at constant p and n

Dalton's law, $p_{\text{Total}} = p_1 + p_2 + p_3 + \ldots\ldots$ at constant T, V

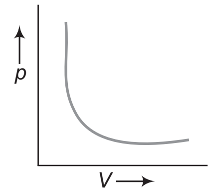
Avogadro's law, $V \propto n$ at constant T and p

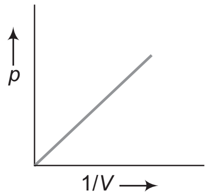
20. When molar volume is constant, the $p-T$ graph is called isochore.

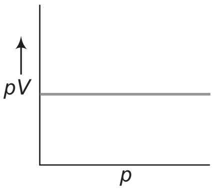
When temperature is constant, the p-V graph is called isotherm.

When pressure is constant, V-T graph is called isobar.

21.







22. Volume of 1mole of the gas = 22.4 L at STP

Volume occupied by 28 g CO (1mol CO) = 22.4L at STP

($\because$ Molar mass of CO $= 12 + 16 = 28 \text{ g mol}^{-1}$)

$\therefore$ Volume occupied by 1 g CO $= \dfrac{22.4}{28}$ L at STP

Similarly, volume occupied by 1 g $H_2O = \dfrac{22.4}{18}$ L at STP

($\because$ Molar mass of $H_2O = (2 \times 1) + 16 = 18 \text{ g mol}^{-1}$)

Volume occupied by 1 g $CH_4 = \dfrac{22.4}{16}$ L at STP

($\because$ Molar mass of $CH_4 = 12 + (4 \times 1) = 16 \text{ g mol}^{-1}$)

Volume occupied by 1 g NO $= \dfrac{22.4}{30}$ L at STP

($\because$ Molar mass of NO $= 14 + 16 = 30 \text{ g mol}^{-1}$)

Thus, 1 g CH_4 will occupy maximum volume and 1 g of NO will occupy minimum volume at STP.

23. When salt is added, less surface area is available for the solvent to vaporise and hence, solvent experience less pressure by vapours. Thus, vapour pressure decreases. Moreover, vapour pressure also decreases with decrease in temperature because kinetic energy of the molecules decreases.

24. In gaseous state, molecules are in a state of random motion *i.e.,* it is the state with higher disorder.

25. At high pressure and low temperature, a gas deviates most from the ideal behaviour.

26.

$$(v_{\text{rms}})_{N_2} = (v_{\text{rms}})_{O_2}$$

$$\sqrt{\frac{3RT_{N_2}}{M_{N_2}}} = \sqrt{\frac{3RT_{O_2}}{M_{O_2}}}$$

$$\frac{T_{N_2}}{M_{N_2}} = \frac{T_{O_2}}{M_{O_2}}$$

Then $v_{\text{av}} \left(\sqrt{\dfrac{8RT}{\pi m}}\right)$ and $v_{\text{mps}} \left(\sqrt{\dfrac{2RT}{M}}\right)$ is also same.

$$d_{N_2} = \frac{p_{N_2}M_{N_2}}{RT_{N_2}} \text{ and } d_{O_2} = \frac{p_{O_2}M_{N_2}}{RT_{O_2}}$$

if $\qquad p_{N_2} = p_{O_2}$ then $d_{N_2} = d_{O_2}$

27. According to Boyle's law

$$V \propto \frac{1}{p} \quad \text{or} \quad p \propto \frac{1}{V}$$

$$p = \frac{K}{V} \qquad \ldots\text{(i)}$$

Differentiating Eq. (i) w.r.t. V at constant T

$$\left(\frac{dp}{dV}\right)_T = -\frac{K}{V^2}$$

28. $\frac{V_1}{V_2} = \left(\frac{T_2}{T_1}\right)^{3/2}$ for reversible adiabatic expansion.

According to van der Waals' equation

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

At low pressure V_m is high so 'b' can be neglected.

$$pV_m + \frac{a}{V_m} = RT, \frac{pV_m}{RT} + \frac{a}{V_m RT} = 1$$

$$Z + \frac{a}{V_m RT} = 1$$

$$Z = 1 - \frac{a}{V_m RT}$$

29. Intermolecular forces and thermal energy decide the state of matter because the former kept the molecules together but later keep them apart.

30. At constant temperature, pV *vs* plot for real gases is not a straight line because molecular interaction and volume of molecules are not negligible.

31. Statement II is the correct explanation of statement I as at critical temperature, density of liquid and gaseous phase becomes equal. Due to which liquid passes into gaseous state imperceptibly and continuously.

32. Liquids tend to reduce no. of molecules or surface tension at there surface, that's why small liquid drops have spherical shape.

33. In the van der Waals' equation, 'a' refers to the attractive forces between the molecules and 'b' is the volume correction.

34. We know that

In the high pressure region $Z = 1 + \frac{pb}{RT}$

$$2 = 1 + \frac{1000b}{RT} \quad \text{...(i)}$$

$$2.2 = 1 + \frac{1200b}{RT} \quad \text{...(ii)}$$

Solving both the equation we get, $\frac{b}{RT} = 10^{-3}$ atm^{-1}

35. $Z = \frac{pV_m}{RT}$ or $V_m = \frac{ZRT}{p}$,

$R = 0.0821$ atm mol^{-1} K^{-1}, $p = 500$ atm,

$T = 200$ K, $Z = 2$

$$\therefore \quad V_m = \frac{2 \times 0.0821 \times 200}{500} = 0.0656 \text{ L}$$

36.

$$200 < T_B < 1000$$

$$200 < \frac{a}{Rb} < 1000$$

$$400 \text{ cal} < \frac{a}{b} < 2000 \text{ cal} \qquad (\because R = 2 \text{ cal mol}^{-1} \text{ T}^{-1})$$

37. From Boyle's law $p_1V_1 = p_2V_2$

$$p_1 = \frac{p_2V_2}{V_1} = \frac{750 \times 250}{15} \quad [V = 235 + 15 = 250 \text{ L}]$$

$$= 12500 \text{ mm Hg} = 16.45 \text{ atm}$$

38. From Charles' law,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_2 = \frac{V_1T_2}{T_1} = \frac{2 \times 250}{300} = 1.67 \text{ L}$$

39. According to Boyle's law, $p \propto \frac{1}{V}$

therefore, graph between p and $\frac{1}{V}$ cannot be a straight line parallel to x-axis.

40. Molecular velocity can be average velocity $= \sqrt{\frac{8RT}{M}}$

root mean square velocity $= \sqrt{\frac{3RT}{M}}$

most probable velocity $= \sqrt{\frac{2RT}{M}}$

In all cases molecular velocity $\propto \sqrt{T}$

41. van der Waals' constant a is due to force of attraction and b due to finite size of molecules.

Thus, greater the value of a and smaller the value of b, larger the liquefaction.

Thus, $a(Cl_2) > a(C_2H_6)$ and $b(Cl_2) < b(C_2H_2)$

42. Rate of diffusion, $r \propto p$

$$r \propto \frac{1}{\sqrt{M}} \quad \therefore \quad r \propto \frac{p}{\sqrt{M}}$$

For gas A, $\quad r_A \propto \frac{p_A}{\sqrt{M_A}} \quad$ ...(i)

For gas B, $\quad r_B \propto \frac{p_B}{\sqrt{M_B}} \quad$ ...(ii)

Eqs. (i)/(ii), we get $\quad \frac{r_A}{r_B} = \frac{p_A}{p_B}\sqrt{\frac{M_B}{M_A}} = \frac{p_A}{p_B}\left(\frac{M_B}{M_A}\right)^{½}$

43. $n = \frac{pV}{RT} = \frac{3170 \times 10^{-3}}{8.314 \times 300} = 1.27 \times 10^{-3}$ mol

Thus, both average kinetic energy and root mean square velocity increase but not significantly when temperature is increased from 10° C to 20°C.

44. Suppose the mass of methane as well as oxygen $= w = 1$g

$$\text{Mole fraction of oxygen} = \frac{\frac{w}{32}}{\frac{w}{32} + \frac{w}{16}} = \frac{\frac{1}{32}}{\frac{3}{32}} = \frac{1}{3}$$

Let the total pressure $= p$

Pressure exerted by oxygen $= \chi_{O_2} \times p_{\text{total}} = p \times \frac{1}{3}$

3 Atomic Structure

JEE Main MILESTONE

- Subatomic Particles
- Thomson Atomic Model
- Rutherford Atomic Model
- Representation of Atom
- Developments Leading to the Bohr's Model of Atom
- Bohr's Model
- Bohr Sommerfeld Model
- Modern Structure of Atom
- Quantum Mechanical Model
- Quantum Numbers
- Rules for Filling of Electrons in Orbitals
- Electronic Configuration of Elements
- Extra Stability of Completely Filled and Half-Filled Orbitals

3.1 Subatomic Particles

A large number of subatomic particles have been discovered hithrtho but only electron, proton and neutron are of great importance among them and hence, are called **fundamental particles.**

Various experiments that lead to the discovery of fundamental particles are as follows

Production of Cathode Rays (Discovery of Electron)

To study the phenomenon of discharge through rarefied gases, a discharge tube with disc shaped aluminium electrode is used and a steady high potential is maintained. At atmospheric pressure, no discharge is observed. If the pressure is reduced to about 10^{-6} atmosphere, the emission of light by air disappears but a fluorescent glow appears. The systematic study of this glow by Thomson, Millikan, Crookes and others proved that its presence is due to a stream of rapidly moving negatively charged particles, called the **cathode rays**.

The discovery of radioactivity, Faraday's law of electrolysis and other observations provided sufficient evidence to prove that atom is not indivisible, but can further be broken down into certain constituents or subatomic particles, such as electron, proton, neutron, meson, neutrino etc. However, it still is the smallest substance that takes part in chemical reactions.

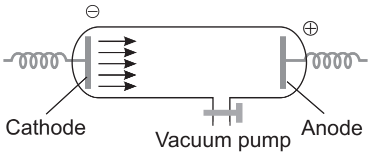


Fig. 3.1 Production of cathode rays

Some of the characteristics exhibited by cathode rays are given below:

1. Cathode rays travel in straight line path away from the cathode and cast shadows of metallic objects placed in their path.
2. Cathode rays can penetrate through thin layers of matter.
3. They produce fluorescence when they strike the glass wall of the discharge tube.
4. Cathode rays cause mechanical motion of a small pin wheel placed in their path. Thus, they possess kinetic energy and must be material particles.

5. Cathode rays are deflected by electric and magnetic field both.
6. Cathode rays produce X-rays when they strike a metallic target.
7. Cathode rays can produce chemical changes and thus, affect photographic plate.
8. The nature of the cathode rays is independent of
   (i) the nature of the cathode and
   (ii) the gas in the discharge tube.

In 1897, **J J Thomson** determined the e/m value (Charge/mass) of the cathode rays particles by studying the deflections of cathode rays in electric and magnetic fields.

He gave the following relation to calculate charge/mass ratio

$$\frac{e}{m} = \frac{E}{rB^2}$$

where, the terms have usual significance.

$$\frac{e}{m} = -1.7588 \times 10^{11}\ \text{C kg}^{-1}$$

In an electric field, the path of a cathode ray particle is parabolic , which is given as

$$y = \frac{eE}{2mv^2} x^2$$

where, y = deflection in the path of cathode ray particle in y-direction

e = charge on cathode ray particle

E = intensity of applied electric field

m = mass of cathode ray particle

v = velocity of cathode ray particle

x = distance between two parallel electric plates within which cathode ray particle is moving.

The path of a cathode ray particle in a magnetic field is circular with radius 'r' and can be given as

$$r = \frac{mv}{eB}$$

where, m = mass of cathode ray particle

v = velocity of cathode ray particle

e = charge on cathode ray particle

B = intensity of applied magnetic field

The radius of the path is proportional to momentum.

By performing a series of experiments, *Thomson proved that whatever gas be taken in the discharge tube and whatever be the material of the electrodes, the value of e/m is always the same. Cathode rays particles are thus common universal constituents of all atoms.*

Charge on Cathode Rays Particles

The first precise measurement of the charge on the electron was made by **Robert A. Millikan** in 1909 by oil drop experiment by measuring the terminal velocity of a charged spherical oil-drop which is made stationary between two electrodes on which a very high potential is applied.

$$\text{Charge on an electron '}q\text{'} = \frac{6\pi\eta r}{E}(v_1 + v_2)$$

where, η = coefficient of viscosity of the gas medium

v_1, v_2 = terminal velocities

E = field strength

r = radius of the oil drop $= \sqrt{\dfrac{9\eta v_1}{2(f-\sigma)g}}$

(f = density of oil; σ = density of gas: g = gravitational force)

By oil drop experiment, the charge (e) on cathode rays particles was determined to be -1.602×10^{-19}C or -4.803×10^{10} esu. *Since an electron has the smallest charge known, it was, thus, termed as unit negative charge.*

Mass of Cathode Rays Particles

The mass of cathode rays particles can thus, be derived by

$$m = \frac{e}{e/m} : \frac{-1.602 \times 10^{-19}}{-1.76 \times 10^{11}} = 9.108 \times 10^{-31}\text{kg}$$

This is termed as the rest mass of the cathode rays particle *i.e.*, mass of the cathode rays particle when moving with low speed. The mass of a moving cathode rays particle may be calculated by applying the following formula

Mass of moving cathode rays particle

$$= \frac{\text{rest mass of cathode rays particle}}{\sqrt{1 - \left(\dfrac{v}{c}\right)^2}}$$

where, v is the velocity of the cathode rays particle and c is the velocity of light. When v becomes equal to c, mass of the moving cathode rays particle becomes infinity and when the velocity of the cathode rays particle becomes greater than c, mass of the cathode rays particle becomes imaginary.

Mass of the Electron Relative to that of Hydrogen Atom

Mass of hydrogen atom =1.008 u

$$= 1.008 \times 1.66 \times 10^{-24}\ \ (\text{since } 1\text{u} = 1.66 \times 10^{-24}\ \text{g})$$

$$= 1.673 \times 10^{-24}\text{g}$$

$$\frac{\text{Mass of hydrogen atom}}{\text{Mass of the electron}} = \frac{1.673 \times 10^{-24}}{9.1096 \times 10^{-28}} = 1837$$

$$\text{Thus, mass of an electron} = \frac{1}{1837} x \text{ mass of hydrogen atom}$$

$$= \frac{1.008}{1837} = 0.000549\ \text{u}$$

Lorentz considered them as subatomic particle *i.e.*, a fundamental constituent of all matter having a mass of 9.108×10^{-31} kg and charge equal to -1.602×10^{-19} C.

These particles (cathode rays particles) *were named as electrons by Stoney.*

Electrons can also be produced by the action of ultraviolet light of X-rays on metal and from heated filaments. $\beta-$particles emitted by radioactive materials are also electrons.

Remember that all electrons carry the same charge. If they did not, they would be deflected by different amounts on passing through electric or magnetic fields.

Positive Rays (Discovery of Proton)

In 1886, **Eugen Goldstein** used a discharge tube with a hole in the cathode. He observed that while cathode rays were streaming away from the cathode, there were coloured rays produced simultaneously which passed through the perforated cathode and caused a glow on the wall opposite to the anode. Thomson observed that these rays consisted of positively charged particles and named them as positive rays. These rays are also known as **canal rays** or **anode rays.**

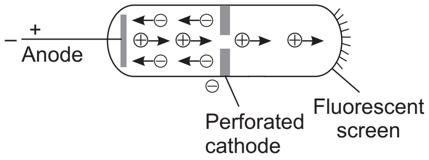


Fig. 3.2 Production of positive rays

Some of the characteristics exhibited by positive rays are as given below

1. These rays travel in straight lines and cast a shadow of the object placed in their path.
2. They possess mass many times the mass of an electron.
3. Like cathode rays, these rays also rotate the wheel placed in their path. Thus, these also possess kinetic energy.
4. The rays produce flashes of light on zinc sulphide screen.
5. The rays are deflected by electric and magnetic fields in a direction opposite to that of cathode rays.

The specific charge (e/m) of positive rays particles was found to vary with nature of gas and was maximum if H_2 is used.

Positive rays particles were thus, called positively charged gaseous atoms left after the removal of electron. Thus, a subatomic particle, *i.e.,* a fundamental constituent of all matter having a mass 1.673×10^{-27} kg and charge $+1.602 \times 10^{-19}$ C was called a **proton.**

Sample **Problem 1** *The ratio of specific charge of a proton and an* α*-particle is*

(*a*) 2 : 1 (*b*) 1 : 1
(*c*) 1 : 4 (*d*) 1 : 2

Interpret (*a*) Before solving this problem, remember that α-particles are actually helium nuclei (He^{2+} ion). Thus, it carries two unit positive charge and 4 u (6.67×10^{-27} kg) mass. Thus,

$$\frac{(e/m)_p}{(e/m)_a} = \frac{+1/1}{2/4} = 2:1$$

Discovery of Neutrons

Chadwick (1932) bombarded beryllium (Be) or boron (B) sheet with high speed alpha (α) particles and noticed the emission of neutral particles, *i.e.,* neutrons of mass nearly equal to protons and with no charge.

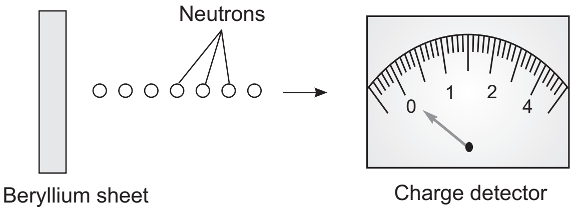


Fig. 3.3 Ejection of neutron (Chadwick experiment)

Neutron is, therefore, having a mass 1.675×10^{-27} kg and no net charge, usually represented as ${}_0n^1$.

$$_4\text{Be}^9 + {}_2\text{He}^4 \longrightarrow {}_6\text{C}^{12} + \underset{\text{Neutron}}{{}_0n^1}$$

Table 3.1 **Properties of Fundamental Particles**

Particles	Mass in			Charge in		Charge in units	Symbol	Discoverer	Location
	CGS	SI (kg)	amu (u)	esu	SI (Coulomb)				
Electron	9.1×10^{-28}	9.1×10^{-31}	0.000549	4.8×10^{-10}	1.602×10^{-19}	−1	${}_{-1}e^0$	JJ Thomson	Outside the nucleus
Proton	1.6×10^{-24}	1.672×10^{-27}	1.00727	—	1.6×10^{-19}	+1	${}_{+1}p^1$ or ${}_{+1}H^1$	Rutherford	In the nucleus
Neutron	1.6×10^{-24}	1.674×10^{-27}	1.00867	0	0	0	${}_0n^1$	Chadwick	In the nucleus

Other Sub-Atomic Particles

Particles other than the fundamental particles may also be present in atom but their existence is not certain.

Some of them are given below

(a) **Positron** $({}_{+1}e^0)$ It was discovered by CD Anderson in 1932. its bears a unit positive charge, and mass equal to mass of an electron. It merges with an electron and emits electromagnetic radiations.

(b) **Meson** (π) In 1935, Yukawa discovered this particle. Different types of meson particles *i.e.*, positive, negative or neutral meson can be found in an atom.

(c) **Neutrino** $({}_0e^0)$ Pauling discovered this particle in 1927. It does not bear any charge, *i.e.,* it is an electroneutral particle.

(d) **Antiproton** This particle was discovered by Segre in 1956. It bears a unit negative charge, and its mass is equal to that of a proton.

Major Problems after the Discovery of Fundamental Particles

When the fundamental particles were discovered, scientists faced other major problems, which were

1. How are these particles arranged in an atom?
2. Why does one element differ from another?
3. How do electromagnetic radiation originate and what is their nature?

To find the answer of these questions, various models were proposed. These models were called atomic models.

3.2 Thomson Atomic Model

JJ Thomson (who discovered electron) proposed a model in 1898, according to which an atom consists of a uniform sphere (radius approximately 10^{-10} m) of positive charge with electrons embedded in such a way so as to give most stable electrostatic arrangement, *i.e.,* he visualised atom as a pudding or cake of positive charge with electrons embedded into it. This model is often called **raisin pudding model** (raisin = electrons) or **plum pudding** or **water melon model.**

This model of atom could account for the electrical neutrality of atom but it could not explain the results of gold foil scattering experiments of Rutherford.

3.3 Rutherford Atomic Model

Rutherford along with Marsden gave the model which was based upon his famous **alpha particle scattering experiment.**

Alpha Particle Scattering Experiment

In this experiment, Rutherford bombarded the gold foil (thickness ≈ 100 nm) with high energy positively charged helium ions (charge +2, mass 4u). The gold foil had a circular fluorescent ZnS screen around it. Whenever an α-particle struck the screen, a tiny flash of light was produced at that point.

Rutherford knew that α-particles had enough energy to pass directly through such atom (having evenly distributed mass spread over the entire atom) and expected the particles to slow down and change direction only by a small angle as they passed through the foil.

The results of such an experiment were, however, quite unexpected as he observed that

1. Most of the α-particles passed through undeflected.

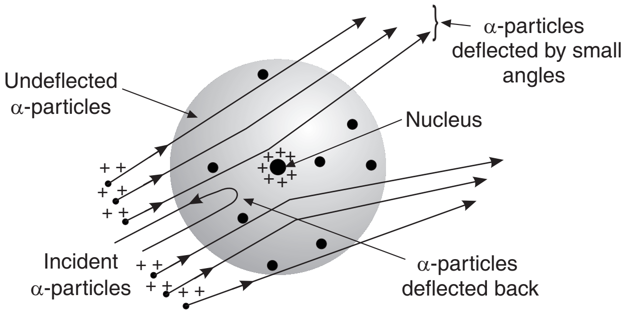


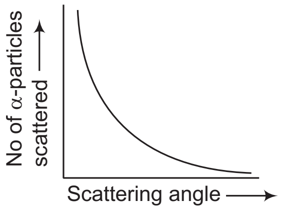
Fig. 3.4 Scattering of α-particles by a dense, positively charged nucleus

2. A small fraction of α-particles was deflected by small angles.
3. A very few α-particles (1 in 20000 approximate) bounced back, *i.e.,* were deflected by nearly 180°.

On the basis of observations, Rutherford concluded that

1. Atom consists of a heavy and positively charged part at its centre, called the **nucleus** (diameter = 10^{-14} m).
2. The entire mass of an atom resides in its nucleus and is equal to the sum of masses of protons and neutrons, since the mass of electron is negligible.
3. The volume occupied by nucleus is very less as compared to the total volume of atom.
4. The atom consists of lot of empty space around nucleus.
5. Electrons revolve around the nucleus in closed orbits (like planets around the sun) and almost all the space around nucleus is occupied by revolving electrons (in the diameter of about 10^{-10} m).

The graph between angle of scattering and the number of α-particles scattering in the corresponding direction is as shown in the figure.



Informations of Rutherford's scattering equation can be memorised by the following relations

(a) Kinetic energy of α-particles

$$N = K_1 / [(1/2)mv^2]^2$$

(b) Scattering angle 'θ':

$$N = K_2 / [\sin^4(\theta/2)]$$

(c) Nuclear charge

$$N = K_3(Ze)^2$$

Here, N = Number of α-particles striking the screen and K_1, K_2 and K_3 are the constants.

Dissimilarities between Nuclear Atomic Model and Solar System

(i) The sun and the planets are very big bodies and uncharged while the nucleus and electrons are very small objects and charged.

(ii) The revolution of the planets in the solar system is governed by gravitational forces, while the revolution of electrons around the nucleus is governed by electrostatic forces.

(iii) In the solar system, there is only one planet which revolves in any particular orbit, but in the nuclear atomic model more than one electron may rotate in any particular orbit.

Drawbacks of Rutherford Model

1. According to classical theory of electromagnetism, if a charged particle revolves around oppositely charged particle, the former one will radiate energy resulting to decrease in its speed. The circular orbit becomes spiral gradually due to such release of energy and electron finally falls on nucleus. But this does not happen.

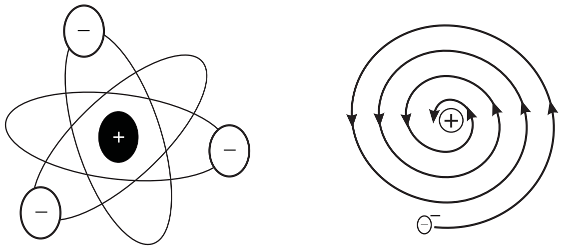


Fig. 3.5 (a) Rutherford's model of atom; electrons orbiting around nucleus

(b) Orbiting electron would radiate energy and spiral into the nucleus

2. If the electron lose energy continuously, the observed spectrum should be continuous but the actual observed spectrum consists of well defined lines of definite frequencies. Hence, the loss of energy by the electrons is non-continuous in an atom.
3. The most important drawback is that this model tells nothing about the electronic structure of atom. In other words, it does not tell about the distribution of electrons around the nucleus.

Sample **Problem 2** *If Rutherford performed his experiment using β-rays, what would have been his observations?*

(a) *Most part of β-particles would have passed undeflected.*

(b) *A sharply defined pencil of β-rays, produced by passing the rays through pinhole, would had become more focussed (contracted) after passing through metal foil.*

(c) *A very few β-particles would had been completely absorbed.*

(d) *All of the above*

Interpret (*d*) In case of β-rays all the given observations are true because β-rays are infact negatively charged and hence, attracted towards nucleus.

Sample **Problem 3** *In Rutherford's experiment, generally the thin foil of heavy atoms, like gold, platinum, etc., have been used to be bombarded by the α-particles. If the thin foil of light atoms like aluminium, etc., is used, what difference would be observed from the above results?* **[NCERT]**

(a) *All the α-particles pass through without the much effect*

(b) *The number of α-particles deflected back becomes half*

(c) *The number of α-particles deflected increases*

(d) *The results are same in both the case*

Interpret (a) Heavy atoms such as gold, platinum have heavy nucleus. Heavy nucleus contains large amount of positive charge. When a beam of α-particles is shot at a thin gold foil, most of them pass through without much effect. Some however, are deflected back or by small angles due to enormous repulsive force of heavy nucleus. If light aluminium foil is used, the number of α-particles deflected back or those deflected by small angles will be negligible.

3.4 Representation of Atom

An atom is generally represented by the following symbol

$${}_{Z}X^{A}$$

In this symbol, Z represents the atomic number (which is generally equal to the number of protons). A represents mass number. It is the sum of number of protons and number of neutrons in an atom.

Mass number = number of protons + number of neutrons

In case of neutral atom, number of protons and number of electrons are equal.

Sample Problem 4 *An element with mass number 81contains 31.7% more neutrons as compared to protons. Assign the atomic symbol* **[NCERT]**

(a) $^{81}_{35}\text{Br}$ (b) $^{81}_{34}\text{Se}$

(c) $^{82}_{35}\text{Br}$ (d) $^{81}_{36}\text{Kr}$

Interpret (*a*) We know that mass number of the element. $A = p + n = 81$ ...(i)

Let the number of protons, $p = x$

Then, number of neutrons, $n = x + \frac{31.7}{100}x = 1.317x$

(as number of neutrons are 31.7% more than the protons).

Hence, from Eq. (i) $x + 1\ .317x = 81$

$$2.317x = 81$$

or $$x = \frac{81}{2.317} = 34.958 \approx 35$$

Therefore, number of protons = 35 and the symbol is $^{81}_{35}\text{Br}$

(Remember number of protons = Atomic number)

Types of Atomic Species

Atomic species are of following types

(a) Isotopes

These are the atoms that have same atomic number (Z) but different mass number (A). *e.g.*, $_1H^1$, $_1H^2$, $_1H^3$ are three isotopes of hydrogen.

(b) Isobars

These are the atoms of different elements that have same mass number (A) but different atomic number, *e.g.*,, $_{18}Ar^{40}$, $_{19}K^{40}$.

(c) Isoelectronic

These species have same number of electrons, *e.g.*, Na^+ ,Mg^{2+} both have 10 electrons.

(d) Isotones

These are the species in which atomic number as well as mass number are different but number of neutrons are same, *e.g.*, $_1H^3$ and $_2He^4$ both have 2 neutrons.

(e) Isodiaphers

These species have same isotopic number, which is obtained by subtracting double of atomic number from atomic mass (or mass number), *i.e.*, Isotopic number = mass number − 2 × atomic number. $_{19}K^{39}$ and $_9F^{19}$ are isodiaphers.

Sample Problem 5

Assertion (A) *All isotopes of a given element show the same type of chemical behaviour.*

Reason (R) *The chemical properties of an atom are controlled by the number of electrons in the atom.* **[NCERT Exemplar]**

(a) *Both A and R are true and R is the correct explanation of A.*

(b) *Both A and R are true but R is not the correct explanation of A.*

(c) *A is true but R is false.*

(d) *Both A and R are false.*

Interpret (a) Isotopes have the same atomic number, *i.e.*, same number of electrons which are responsible for their chemical behaviour. Hence, these exhibit similar chemical properties.

3.5 Developments Leading to the Bohr's Model of Atom

Nature of electromagnetic radiations and spectrum play an important role in the development of Bohr's model.

Wave Nature of Electromagnetic Radiations

Light, X-rays and γ-rays are examples of radiant energy. Indeed, radiation is a mode of transference of energy of different forms.

Clark Maxwell in 1856 showed that radiant energy has wave properties and called them **electromagnetic waves** or **electromagnetic radiations**. All these radiations travel with the speed of light and do not require any medium for their propagation or transmission.

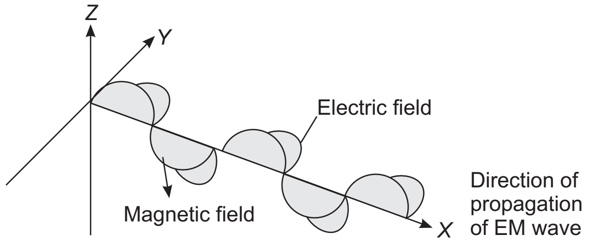
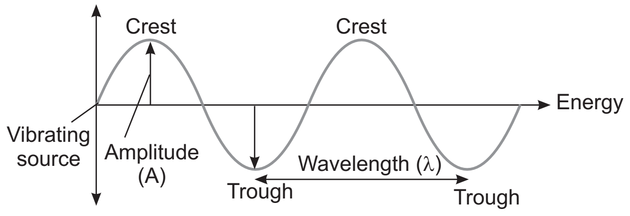


Fig. 3.6 Electric and magnetic fields associated with an electromagnetic wave

A wave is a periodic disturbance in space or in a medium that involves elastic displacement of material particles or a periodic change in some physical quantities such as temperature, pressure, electric potential, electromagnetic field. Thus, wave motion represents propagation of a periodic disturbance carrying energy.



Light wave

Characteristics of Wave

(a) Wavelength

It is defined as the distance between two successive crests or troughs of a wave *i.e.,* distance between successive points of equal phase. It is denoted by the Greek letter 'λ'. It is expressed in centimetres, metres or in angstrom units.

$$\begin{aligned} 1\,\text{Å} &= 10^{-8}\ \text{cm} \\ &= 10^{-10}\ \text{m} \\ 1\ \text{nm} &= 10^{-9}\ \text{m} \end{aligned}$$

(b) Frequency

The frequency is the number of waves which pass through a given point in one second or it is the number of cycles or oscillations or vibrations of a wave motion in unit time. It is denoted by the letter 'ν' (nu) and is expressed in hertz (Hz) or cycles per second (cps).

$$\boxed{\nu = \frac{\text{velocity}}{\text{wavelength}}}$$

(c) Velocity

It is defined as the distance covered in one second by the waves. It is denoted by the letter 'c'. All the electromagnetic waves travel with the same velocity, *i.e.,* 3×10^{10} cm/s.

(d) Wave Number

Another quantity used to characterise radiation is the wave number. This is inverse of the wavelength and is given by symbol '$\bar{\nu}$' (nu bar).

$$\boxed{\bar{\nu} = \frac{1}{\lambda}}$$

The wave number is the number of wavelength per unit of length covered. Its unit is cm^{-1} or m^{-1}.

(e) Amplitude

It is defined as the height of the crest or depth of the trough of a wave. It is denoted by the letter 'a'. It determines the intensity of the radiation.

(f) Time Period

Time taken by the wave for one complete cycle or vibration is called time period. It is denoted by T. It is expressed in second per cycle.

$$T = \frac{1}{\nu}$$

Electromagnetic radiations are of various types depending upon their wavelength (λ) or frequency (ν). These radiations constitute the electromagnetic spectrum. The various regions of electromagnetic radiations are identified by different names.

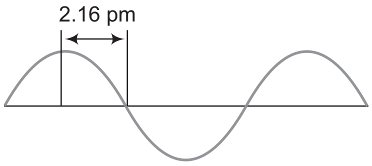
These names alongwith important characteristics of that region are summarised in the following table

Table 3.2 **Characteristics of Various Electromagnetic Radiations**

S. No.	Name	Wavelength (Å)	Frequency (Hz)	Source	Uses
1.	Radiowave	$3 \times 10^{14} - 3 \times 10^{7}$	$1 \times 10^{5} - 1 \times 10^{9}$	Alternating current of high frequency	Signal transmission
2.	Microwave	$3 \times 10^{7} - 6 \times 10^{6}$	$1 \times 10^{9} - 5 \times 10^{11}$	Klystron tube	Cooking radar
3.	Infrared (IR) waves	$6 \times 10^{6} - 7600$	$5 \times 10^{11} - 3.95 \times 10^{14}$	Incandescent objects	Heating
4.	Visible	7600 – 3800	$3.95 \times 10^{14} - 7.9 \times 10^{14}$	Electric bulb, sun rays	Illumination
5.	Ultraviolet wave (UV)	3800 – 150	$7.9 \times 10^{14} - 2 \times 10^{16}$	Sun rays, mercury vapour	Germisidal lamps
6.	X-rays	150 – 0.1	$2 \times 10^{16} - 3 \times 10^{19}$	Cathode rays striking metal plate	Medical pictures, material testing
7.	γ-rays	0.1 – 0.01	$3 \times 10^{19} - 3 \times 10^{20}$	Radioactive decay	Cancer treatment
8.	Cosmic rays	0.01 – zero	3×10^{20} – infinity	Outer space	

Sample **Problem 6** *A hypothetical electromagnetic wave is shown in the figure. Find out the wavelength of the radiation.*

[**NCERT** Exemplar]



(*a*) 2.16 (*b*) 4.32
(*c*) 6.48 (*d*) 8.64

Interpret (*d*) Wavelength is the distance between two successive peaks or two successive troughs of a wave.

Therefore, $\lambda = 4 \times 2.16 \text{ pm} = 8.64 \text{ pm}$

Particle Nature of Electromagnatic Radition

The phenomenon like diffraction, interference can, however, be well explained by wave nature of EMR but it fails to explain the other phenomenon like black body radiation, photoelectric effect etc.

Black Body Radiation and Planck's Quantum Theory

The ideal body, which emits and absorbs all possible frequencies is called a **black body** and the radiation emitted by this body are called **black body radiation.**

In 1900, *Max Planck provided an explanation to this behaviour, according to which*

1. **Atoms** and **molecules** could emit or absorb energy in discrete quantities only, which are called **quantum.**
2. The energy of a **quantum** is proportional to its frequency as $E = h\nu$
   where, h is the proportionality constant, called the Planck's constant with the value 6.626×10^{-34} Js.
3. Energy is always emitted in integral multiples of $h\nu$ as $2h\nu$, $3h\nu$ etc. In other words, energy is quantised.
   Planck was unable to explain that why energies are quantized in this manner. However, **Einstein** explained the quantized nature of light while explaining the phenomenon of photoelectric effect.

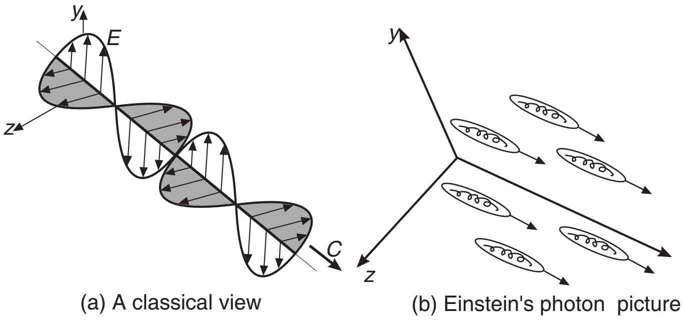
Caution Point *An electron coming to a lower orbit always emits photons of higher energy (shorter wavelength) than the photons emitted when electron comes to higher orbit irrespective of the original orbit number of electron.*

Photoelectric Effect

When a light of certain frequency strikes the surface of a metal, electrons are ejected or given out from the metal surface. This phenomenon of ejection of the electrons from the metal surface under the influence of incident radiation is called *photoelectric effect*. The electrons ejected from a substance in this manner are called *photoelectrons*.

The photoelectric effect is only shown by a few metals under the influence of visible light. However, most of the metals exhibit this effect under the influence of more energetic ultraviolet light.

According to wave theory of light, both the number of electrons ejected and their energies should depend upon the intensity of incident light, however in practice, it is found that only the number of ejected electrons depends upon incident light intensity while their energies do not. Einstein suggested that light consists of streams of particles, called *photons* which move with the speed of light.



(a) A classical view (b) Einstein's photon picture

Fig. 3.7 Picture of a travelling light wave

Using Planck's quantum theory of radiation as a starting point, he deduced that each photon possess energy, E which is equal to

$$\boxed{E = h\nu = \frac{hc}{\lambda}} \qquad \left(\because \ \nu = \frac{c}{\lambda}\right)$$

$$= hc\bar{\nu}$$

where, ν = frequency of light.

Thus, shooting a beam of light on a metal surface means shooting a beam of photons. An electron is ejected when a photon strikes that electron and transfers all of its energy to electron.

There is a characteristic minimum frequency for each metal, called **threshold frequency** (ν_0) below which the 'photoelectric effect' does not occur. We can calculate, minimum amount of energy required to remove an electron from the metal surface, with the help of this frequency as

$$E = h\nu_0$$

This is also called **work function** (W) of metal.

Since, the striking photons have energy equal to $h\nu$ and the minimum energy required to eject an electron is $h\nu_0$, then $h\nu - h\nu_0$ will be transformed as KE of photoelectron, *i.e.,* $\frac{1}{2} m_e v^2$, and as the total energy has to be conserved,

We can write Einstein equation as

$$\frac{1}{2} m_e v^2 = h\nu - h\nu_0$$

$$\boxed{\frac{1}{2} m_e v^2 = h(\nu - \nu_0)}$$

Caution Point *The maximum kinetic energy* (KE_{max}) *of photoelectrons is directly proportional to the frequency of incident light and is independent of its intensity.*

Sample Problem 7 *Neon gas is generally used in sign boards. If it emits strongly at 616 nm, calculate*

(*i*) *the frequency of emission and*

(*ii*) *number of quanta present if produces 2 J of energy respectively* **[NCERT]**

(a) $4.9 \times 10^{14} s^{-1}, 4.2 \times 10^{18}$

(*b*) $8.2 \times 10^{14} s^{-1}, 5.3 \times 10^{18}$

(*c*) $2.6 \times 10^{14} s^{-1}, 42 \times 10^{18}$

(*d*) $4.9 \times 10^{14}\ s^{-1}\ 6.2 \times 10^{18}$

Interpret (*d*) (i) Frequency, $\nu = \frac{c}{\lambda}$

$$\lambda = 616 \text{ nm} = 616 \times 10^{-9} \text{m}$$

$$\nu = \frac{3.0 \times 10^8 \text{ ms}^{-1}}{616 \times 10^{-9} \text{m}} = 4.870 \times 10^{14} \text{s}^{-1}$$

(ii) Energy of quantum (or photon),

$$E = h\nu = 6.626 \times 10^{-34} \text{ Js} \times 4.870 \times 10^{14} \text{s}^{-1}$$

$$= 32.268 \times 10^{-20} \text{ J} = 32.27 \times 10^{-20} \text{J}$$

$$\text{Number of quanta present} = \frac{\text{Total energy produced}}{\text{Energy of 1 quanta}}$$

$$= \frac{2\text{J}}{32.27 \times 10^{-20} \text{J}} = 6.197 \times 10^{18} \approx 6.2 \times 10^{18} \text{ quanta}$$

Sample Problem 8 *Threshold frequency* ν_0 *is the minimum frequency which a photon must possess to eject an electron from a metal. It is different for different metals. When a photon of frequency* $1.0 \times 10^{15} \text{s}^{-1}$ *was allowed to hit a metal surface, an electron having* 1.988×10^{-19} *J of kinetic energy was emitted. If a photon with a wavelength equal to 600 nm hits the metal surface,* **[NCERT Exemplar]**

(a) *the electrons will be ejected*

(*b*) *no electron will be emitted*

(*c*) *four electrons will be emitted*

(*d*) *cannot say anything*

Interpret (*b*) We know that $h\nu = h\nu_0 + \text{KE}$ or $h\nu - \text{KE} = h\nu_0 = (6.626 \times 10^{-34} \text{Js} \times 1 \times 10^{15} \text{s}^{-1}) - 1.988 \times 10^{-19} \text{J}$

$$h\nu_0 = 6.626 \times 10^{-19} - 1.988 \times 10^{-19} \text{J}$$

$$h\nu_0 = 4.638 \times 10^{-19} \text{ J}$$

$$\nu_0 = \frac{4.638 \times 10^{-19} \text{J}}{6.626 \times 10^{-34} \text{Js}}$$

$$= 0.669 \times 10^{15} \text{ s}^{-1}$$

when, $\lambda = 600 \text{nm} = 600 \times 10^{-9} \text{m}$

$$\nu = \frac{c}{\lambda} = \frac{3.0 \times 10^8 \text{ms}^{-1}}{6.0 \times 10^{-7} \text{m}}$$

$$= 0.5 \times 10^{15} \text{s}^{-1}$$

Thus, $\nu < \nu_0$.

Hence, no electron will be emitted.

Spectrum

A spectrum can be defined as "pictorial representation of arrangement of radiations in increasing order of wavelength or decreasing order of frequency". The spectrum may be emission or absorption spectrum on the basis of energy absorbed or emitted.

Atom, molecule and **ions** emit radiations after being excited, *i.e.,* after absorbing energy. The spectrum of such emitted radiations is called **emission spectra.**

An **absorption spectra** is like the photographic negative of an emission spectra. Here a continum of radiations is passed through a sample which absorbs the radiations of certain wavelengths. The missing wavelengths (which correspond to radiations absorbed), leave dark spaces in bright continuous spectrum. Such a spectrum is called **absorption spectrum.**

Both type of spectra, further may be continuous (*i.e.,* one radiation merges with other at its boundary, or., when there is no sharp boundary between the radiations) or discontinuous (*i.e.,* have sharp boundaries).

The emission spectrum of atoms in gaseous phase do not show a continuous spread of wavelengths, here they emit radiation only at specific wavelengths. Such an spectra which contains bright lines with sharp boundaries is called **line spectra** or **discontinuous spectra.**

Hot Spot 1

ATOMIC Spectrum of Hydrogen

It is an important topic for JEE Main examination. The questions are generally numerical type and their level may vary from average to difficult. However, a regular practice help you to solve out problems based on this topic.

The atomic spectrum of hydrogen was proved quite helpful in the development of atomic structure. It can be obtained by passing the light, being emitted from the discharge tube containing hydrogen at low temperature, through spectrograph. Actually the electric discharge dissociates H_2 molecules and energetically excited hydrogen atoms are produced. These hydrogen atoms emit electromagnetic radiations of discrete frequencies.

The spectrum obtained consists of large number of sharp lines each of which corresponds to a particular frequency. These lines are present in UV, visible and infra-red regions of electromagnetic spectrum.

The lines in emission spectrum of hydrogen are classified into six series as follows

1. Lyman series]—UV region
2. **Balmer series**]—Visible region
3. **Paschen series**
4. **Brackett series** } — IR region
5. Pfund series
6. Humphery series - Far IR region

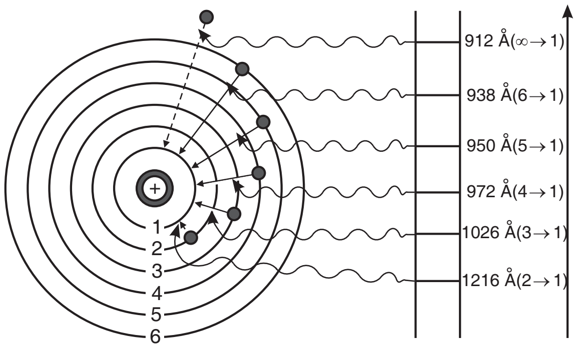


Fig. 3.8 Jump of hydrogen electron (shown by black circle) from higher energy level to 1st energy level to produce spectral lines of Lyman series. The electronic jumps have been shown in brackets. The electronic jump from $n_2 = \infty$ to $n_1 = 1(\infty \rightarrow 1$ jump) has been shown by a dotted arrow.

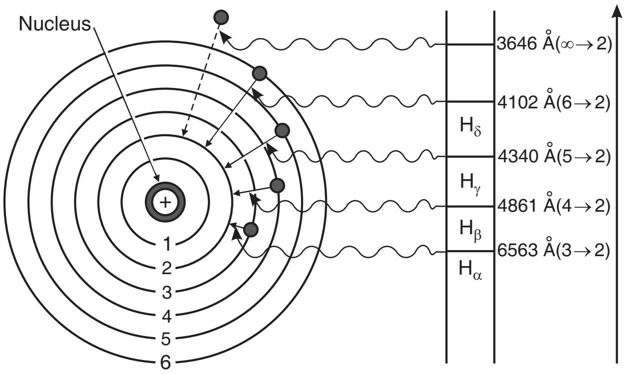


Fig. 3.9 Jump of hydrogen electron (shown by black circle) from higher energy levels to 2nd energy level to produce spectral lines of Balmer series. The electronic jumps have been shown in brackets. The electronic jump from $n_2 = \infty$ to $n_1 = 2(\infty \rightarrow 2$ jump) has been shown by a dotted arrow.

Balmer, in 1885 showed that if spectral lines are expressed in terms of wave number $\bar{\nu}$, then the visible lines of hydrogen spectrum obey the following formula

$$\text{Wave number, } \bar{\nu} = 109{,}677\left(\frac{1}{2^2} - \frac{1}{n^2}\right)\text{cm}^{-1}$$

here, n = an integer equal to or greater than 3.

Swedish spectroscopist **Rydberg** gave above formula in more generalised form which is applicable to all the series of hydrogen spectrum and can be written as

$$\bar{\nu}_H(\text{cm}^{-1}) = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \text{here, } R_H = 1{,}09{,}677 \text{ cm}^{-1}$$

The n_1 and n_2 are integers where $n_2 > n_1$.

For a particular series n_1 is constant.

The values of n_1 and n_2 for different series of hydrogen spectrum will be

(i) Lyman series, $n_1 = 1, \; n_2 = 2, 3, 4, \ldots$
(ii) Balmer series, $n_1 = 2, \; n_2 = 3, 4, 5, \ldots$
(iii) Paschen series, $n_1 = 3, \; n_2 = 4, 5, 6, \ldots$
(iv) Brackett series, $n_1 = 4, \; n_2 = 5, 6, 7, \ldots$
(v) Pfund series, $n_1 = 5, \; n_2 = 6, 7, 8, \ldots$
(vi) Humphery series, $n_1 = 6, \; n_2 = 7, 8, 9 \ldots$

For elements *except hydrogen*, the formula is written as

$$\text{wave number,} \qquad \bar{\nu} = R_H \cdot Z^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

where, $R_H = 109677 \text{ cm}^{-1}$, Z = atomic number of element

The Balmer series of lines is the only series which appears in the visible region of EM spectrum.

Always keep in mind, while solving problems based on this topic.

Inter-relate the quantity you have to calculate with the formula you know or divide the question in two steps. For example see the sample problem given below.

Sample **Problem 9** *Find the wavelengths of the first line of* He$^+$ *ion spectral series whose interval between extreme lines is* $\dfrac{1}{\lambda_1} - \dfrac{1}{\lambda_2} = 2.7451 \times 10^4 \text{ cm}^{-1}$

[$R_H = 109677.76 \text{ cm}^{-1}$]

(*a*) 8968 Å
(*b*) 4689 Å
(*c*) 9378 Å
(*d*) 2345 Å

Interpret (*b*) Extreme lines means first and last.

$$\frac{1}{\lambda_1}-\frac{1}{\lambda_2}=R_HZ^2\left[\frac{1}{n_1^2}-\frac{1}{\infty^2}\right]-R_HZ^2\left[\frac{1}{n_1^2}-\frac{1}{(n_1+1)^2}\right]=\frac{RZ^2}{(n_1+1)^2}$$

$$2.7451\times10^4=\frac{109677.76\times2^2}{(n_1+1)^2}$$

$$(n_1+1)=4$$

$$n_1=3$$

Wavelength of first line

$$\frac{1}{\lambda}=109677.76\times2^2\times\left[\frac{1}{3^2}-\frac{1}{4^2}\right]$$

$$\lambda=4689\times10^{-8}\text{cm}=\ 4689\ \text{Å}$$

Sample **Problem10** *The wave number of the first line in the Lyman series in hydrogen spectrum is*

(*a*) 72755.5 *cm*$^{-1}$ (*b*) 109678 *cm*$^{-1}$

(*c*) 82258.5 *cm*$^{-1}$ (*d*) 65473.6 *cm*$^{-1}$

Interpret (*c*) Applying Rydberg formula,

$$\frac{1}{\lambda}=R_H\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]\text{cm}^{-1}$$

For the first line in Lyman series, $n_1=1$ and $n_2=2$

So, $$\frac{1}{\lambda}=109678\left[\frac{1}{1^2}-\frac{1}{2^2}\right]$$

$$=\frac{109678\times3}{4}=82258.5\ \text{cm}^{-1}$$

$\lambda\propto\frac{1}{n}$ and $E\propto\frac{1}{\lambda}$

Thus, for shortest wavelength or maximum energy or maximum frequency, *n* has to be maximum and for maximum wavelength or minimum energy or minimum frequency, *n* has to be minimum. This can be best understood by sample problem14.

Sample **Problem 11** *The series limits of wavelengths in the Paschen series of* He$^+$ *ion is*

(*a*) 250 – 468.7 *nm* (*b*) 468 . 7 – 350 *nm*

(*c*) 760 – 380 *nm* (*d*) 380 – 150 *nm*

Interpret (*a*) For He$^+$ion, $Z=2$ and the modified Rydberg's formula applicable to Paschen's series is

$$\frac{1}{\lambda}=R_HZ^2\left[\frac{1}{9}-\frac{1}{n^2}\right]\text{where, }n=4,5,6,\ldots\infty$$

For, shortest wavelength, *n* = has to be maximum *i.e.*,

$$\therefore\quad\frac{1}{\lambda_{\min}}=\frac{4}{9}R_H$$

or $$\lambda_{\min}=\frac{9}{4R_H}=205\times10^{-9}\text{m}=205\text{nm}$$

For maximum λ, *n* has to be minimum, 4 in the present case.

$$\frac{1}{\lambda_{\max}}=4R_H\left[\frac{1}{9}-\frac{1}{16}\right]=\frac{7R_H}{36}$$

$$\frac{1}{\lambda_{\max}}=\frac{36}{7R_H}=468.7\times10^{-9}\text{m}\ =468.7\text{nm}$$

⇒ Hence, the required series limit is $\{\lambda:250-468.7\text{nm}\}$

Sample **Problem 12** *Calculate the energy and frequency of the radiation emitted when an electron jumps from n = 3 to n = 2 in a hydrogen atom.*

[NCERT Exemplar]

(*a*) 3.028×10^{-9}, 4.57×10^{12}

(*b*) 3.028×10^{-19}, 2.89×10^{14}

(*c*) 3.028×10^{-19}, 4.57×10^{14}

(*d*) 2.128×10^{-19}, 4.57×10^{12}

Interpret (*c*) Here we divide the question into two parts (i) we calculate wavelength or wave number (ii) with the help of wavelength or wave number we calculate energy and frequency.

Wave number , $\bar{\nu}=109677\text{cm}^{-1}\left(\frac{1}{2^2}-\frac{1}{3^2}\right)$

$$\bar{\nu}=109677\times\frac{5}{36}=15232.9\ \text{cm}^{-1}$$

$$\bar{\nu}\ =\frac{1}{\lambda}\text{ or }\lambda=\frac{1}{\bar{\nu}}=\frac{1}{15232.9}=6.564\times10^{-5}\ \text{cm}$$

Wavelength, $\lambda=6.564\times10^{-7}\text{m}$

Energy, $E=\frac{hc}{\lambda}$

$$=\frac{6.626\times10^{-34}\text{Js}\ \times3.0\times10^8\text{ms}^{-1}}{6.564\times10^{-7}\text{m}}=3.028\times10^{-19}\ \text{J}$$

Frequency, $$\nu=\frac{c}{\lambda}=\frac{3.0\times10^8\text{ms}^{-1}}{6.564\times10^{-7}\text{m}}=0.457\times10^{15}\ \text{s}^{-1}$$

$$\nu=4.57\times10^{14}\ s^{-1}$$

Alternate We first inter-relate the two formulae and then put the values: *e.g.,*

$$\bar{\nu}=\frac{1}{\lambda}=R_H\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$

$$=\frac{c}{\lambda}=R_Hc\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)=\nu\text{ (frequency)}$$

Now by putting the value, we directly calculate the frequency. Similarly,

$$\nu=\frac{c}{\lambda}=R_Hc\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)=\frac{hc}{\lambda}=R_Hhc\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$

$$\therefore\qquad E=R_Hhc\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$

By putting the values in the above formula, you can calculate *E* directly.

You have to remember the value of *n*, for different series. (There is no need to remember the value of n_2 because $n_2>n_1$). For example see sample problem 13.

Caution Point *When an electron returns from n_2 to n_1 state, the number of lines in the spectrum will be equal to*

$$\frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$$

3.6 Bohr's Model

The weaknesses of Rutherford's model was removed by **Neils Bohr,** who proposed an improved form of Rutherford's model, *according to which*

1. Electrons revolve around the nucleus in specific circular orbits having angular momentum integral multiple of $\frac{h}{2\pi}$ *i.e.,* $mvr = \frac{nh}{2\pi}$ (situated at definite distance from the nucleus) with a definite velocity.

   Number of revolution per second by an electron in a shell

   $$= \frac{\text{velocity}}{\text{circumference}} = \frac{v}{2\pi r}$$

2. As long as electron remains in a particular orbit, it neither emits (loose), nor gains (absorb) energy. This simply means that in a particular orbit, the energy of a particular electron remains stationary or constant. The orbits of such a constant energy are called stationary orbits or stationary energy levels or simply energy levels.
3. Each stationary orbit is associated with a definite amount of energy. The greater is distance of the orbit from the nucleus , more shall be the energy associated with it. These orbits are also called *energy levels* and are numbered as 1, 2, 3, 4, ... or *K, L, M, N,* ... from nucleus outwards.

   i.e., $$E_1 < E_2 < E_3 < E_4 \ldots$$
   $$(E_2 - E_1) > (E_3 - E_2) > (E_4 - E_3) \ldots\ldots$$

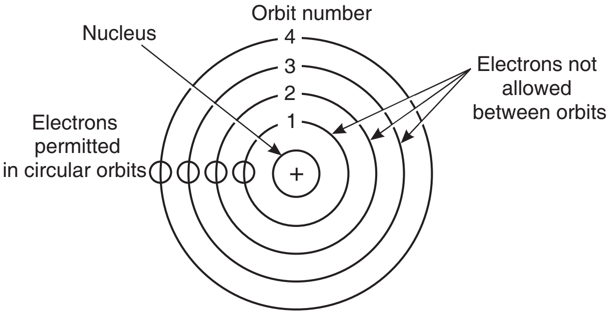


Fig 3.10 Circular electron orbits or stationary levels in an atom

4. An electron can move from one energy level to another through quantum or photon jumps only. When it resides in an orbit with lowest energy, it is said to be in **ground state.** It can jump from its lower energy level to higher energy level after absorbing energy. Here, at higher energy level, it is said to be in **excited state.**

   So, an electron can move only from its ground state to its excited state (after absorbing energy) or from its excited state to ground state (after releasing energy).
5. During transition between two stationary states of different energy, the frequency of radiation absorbed or emitted,

   $$\nu = \frac{E_2 - E_1}{h}$$

   This expression is called **Bohr's frequency rule.**

Bohr Calculations

(a) Radii of Various Orbits

Consider an electron of mass '*m*' and charge '*e*' revolving around the nucleus of charge *Ze* (*Z* = atomic number). Let '*v*' be the tangential velocity of the revolving electron and '*r*' the radius of the orbit. The electrostatic force of attraction between the nucleus and electron (applying Coulomb's law)

$$F = \frac{KZe \times e}{r^2} = \frac{KZe^2}{r^2}$$

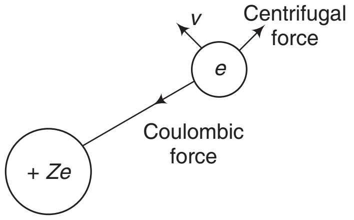


Fig 3.11 Revolution of electron around the nucleus

where, $K = \frac{1}{4\pi\varepsilon_0}$ (where ε_0 is permitivity of free space)

$$K = 9 \times 10^9 \text{ Nm}^2\text{C}^{-2}$$

In CGS units, value of K =1 dyne cm^2 (esu)$^{-2}$

The centrifugal force acting on the electron is $\frac{mv^2}{r}$

Since the electrostatic force balance the centrifugal force, for the stable electron orbit.

$$\frac{mv^2}{r} = \frac{KZe^2}{r^2} \qquad \ldots \text{(i)}$$

or

$$v^2 = \frac{KZe^2}{mr} \qquad \ldots \text{(ii)}$$

According to Bohr's postulate of angular momentum quantization, we have

$$mvr = \frac{nh}{2\pi}$$

$$\therefore \qquad v = \frac{nh}{2\pi mr}$$

$$v^2 = \frac{n^2h^2}{4\pi^2m^2r^2} \qquad \text{...(iii)}$$

Equating (ii) and (iii)

$$\frac{KZe^2}{mr} = \frac{n^2h^2}{4\pi^2m^2r^2}$$

Solving for r we get $\qquad r = \dfrac{n^2h^2}{4\pi^2mkZe^2}$

where $\qquad n = 1,2,3, \dots \infty$

Hence, only certain orbits whose radii are given by the above equation are available for the electron. The greater the value of n, *i.e.,* farther the level from the nucleus, the greater is the radius. The radius of the smallest orbit ($n = 1$) for hydrogen atom ($Z = 1$) is r_0.

$$r_0 = \frac{n^2h^2}{4\pi^2me^2K}$$

$$= \frac{1^2 \times (6.626 \times 10^{-34})^2}{4 \times (3.14)^2 \times 9.1 \times 10^{-31} \times (1.6 \times 10^{-19})^2 \times 9 \times 10^9}$$

$$= 5.29 \times 10^{-11}\text{m} \qquad r_0 = 0.529\text{Å}$$

Radius of nth orbit for an atom with atomic number Z is simply written as

$$\boxed{r_n = r_0 \frac{n^2}{Z} = 0.529 \times \frac{n^2}{Z}\text{ Å}}$$

Sample Problem 13 *The radius of hydrogen atom in the ground state is 0.53 Å. The radius of $_3Li^{2+}$ in the similar state is*

(a) 1.06 Å
(b) 0.53 Å
(c) 0.265 Å
(d) 0.17 Å

Interpret (d) $r_{Li} = \dfrac{r_H \times n^2}{Z}$

($n = 1$, because state is same as hydrogen, *i.e.*, ground state for Li, $Z = 3$)

$$r_{Li} = \frac{0.53 \times (1)^2}{3} = 0.17\text{ Å}$$

(b) Energy Level of Hydrogen Atom

The total energy, E of the electron is the sum of kinetic energy and potential energy. Kinetic energy of the electron $= 1/2\, mv^2$

$$\text{Potential energy} = \frac{-KZe^2}{r}$$

$$\text{Total energy} = \frac{1}{2}mv^2 - \frac{KZe^2}{r} \qquad \text{...(iv)}$$

From Eq. (i) we know that

$$\frac{mv^2}{r} = \frac{KZe^2}{r^2}$$

$$\therefore \qquad \frac{1}{2}mv^2 = \frac{KZe^2}{2r}$$

Substituting this in Eq. (iv)

$$\text{Total energy} \quad (E) = \frac{KZe^2}{2r} - \frac{KZe^2}{r} = -\frac{KZe^2}{2r}$$

$$\text{KE} = -\frac{1}{2}\text{PE}, \text{KE} = -\text{TE}$$

Substituting for r, gives us $E = -\dfrac{2\pi^2mZ^2e^4K^2}{n^2h^2}$

where $n = 1,2,3,\dots$

This expression shows that only certain energies are allowed to the electron. Since this energy expression consists so many fundamental constant, we are giving you the following simplified expressions.

$$\boxed{\begin{aligned} E &= -21.8 \times 10^{-12} \times \frac{Z^2}{n^2}\text{ erg/atom} \\ &= -21.8 \times 10^{-19} \times \frac{Z^2}{n^2}\text{ J/atom} \end{aligned}}$$

$$E_n = -13.6 \times 10^{-19} \times \frac{Z^2}{n^2}\text{ eV/atom}$$

$$[\because 1\text{eV} = 3.83 \times 10^{-23}\text{ kcal} = 1.602 \times 10^{-12}\text{erg} = 1.602 \times 10^{-19}\text{J}]$$

$$E = -313.6 \times \frac{Z^2}{n^2}\text{ kcal/ mol} \quad (\therefore 1\text{ cal} = 4.18\text{ J})$$

The energies are negative since the energy of the electron in the atom is less than the energy of a free electron (*i.e.*, the electron is at infinite distance from the nucleus), which is taken as zero. The lowest energy level of the atom corresponds to $n = 1$ and as the quantum number increase, E becomes less negative.

When $n = \infty, E = 0$ which corresponds to an ionized atom *i.e.*, the electron and nucleus are infinitely separated.

$$\text{H} \longrightarrow \text{H}^+ + e^- \qquad \text{(ionization)}$$

Sample Problem 14 *The ratio of the difference between 1st and 2nd Bohr's orbits energy to that between 2nd and 3rd orbit energy is*

(a) $\frac{1}{2}$
(b) $\frac{1}{3}$
(c) $\frac{27}{5}$
(d) $\frac{5}{27}$

Interpret (c) $\Delta E_{1,2} = E_2 - E_1$

$$= \frac{E_H}{(n_2)^2} - \frac{E_H}{(n_1)^2}$$

$$= E_H\left(\frac{1}{(2)^2} - \frac{1}{(1)^2}\right) = -\frac{E_H \times 3}{4}$$

$$\Delta E_{2,3} = E_3 - E_2 = -E_H \times \frac{5}{36}$$

$$\frac{\Delta E_{1,2}}{\Delta E_{2,3}} = E_H \times \frac{3}{4} \times \frac{36}{E_H \times 5} = \frac{27}{5}$$

Sample **Problem 15** *How far from the nucleus is the electron in a hydrogen atom if it has energy of -0.850 eV?*

(a) 2.39 Å (b) 5.69 Å

(c) 8.46 Å (d) 9.38 Å

Interpret (c) $E_n = -\frac{Z^2}{n^2}\times 21.8\times 10^{-19}$

$$\therefore \qquad -\frac{Z^2}{n^2}\times 21.8\times 10^{-19} = -\,0.85\times 1.6\times 10^{-19}$$

$$\text{Or} \qquad n = 4 \qquad (\because Z = 1)$$

$$r = \frac{n^2}{Z}\times 0.529 = \frac{16}{1}\times 0.529 = 8.46\text{Å}$$

(c) Bohr Velocity or Velocity of Electron

We know that, $mvr = \frac{nh}{2\pi}$; $v = \frac{nh}{2\pi mr}$

By substituting for r we are getting

$$v = \frac{2\pi KZe^2}{nh}$$

where excepting n and Z all are constant $v = 2.18\times 10^8\,\frac{Z}{n}$ cm/s.

Thus, the velocity of an electron in nth orbit of H-atom,

$$V_n = \frac{2\pi e^2}{nh} = \frac{2.1847\times 10^8}{n}\ \text{cm s}^{-1}$$

For H-like atom

$$V_{n\,(\text{H-like atom})} = V_{n\,(\text{H-atom})}\times Z$$

$$\text{Also,} \qquad \boxed{V_n = \frac{2.1\times 10^8\times Z}{n}\ \text{cm s}^{-1}}$$

Sample **Problem 16** *Determine the number of revolutions made by electron in one second in the 2^{nd} Bohr orbit of hydrogen atom.*

(a) 6. 29 $\times 10^{12}$ (b) 5.29 $\times 10^{13}$

(c) 2.39 $\times 10^{15}$ (d) 8.23 $\times 10^{14}$

Interpret (d) If V is the speed of moving electron in the said Bohr orbit then the number of revolutions made by electron in one second would be

$$rps = \frac{v}{2\pi r}$$

$$\text{Also} \qquad v = \frac{nh}{2\pi mr}$$

$$\Rightarrow \qquad rps = \frac{nh}{4\pi^2 mr^2}$$

$$= \frac{nh}{4\pi^2 m\left(\frac{a_0 n^2}{Z}\right)^2}$$

$$= \frac{h\cdot Z^2}{4\pi^2 m a_0^2 n^3}$$

$$= \frac{6.626\times 10^{-34}\times (1)^2}{4\times (3.14)^2\times 9.1\times 10^{-31}\times (0.53\times 10^{-10})^2\times (2)^3}$$

$$= 8.23\times 10^{14}\ \text{Revolution/s}$$

Caution Point *The Bohr's model is applicable only to hydrogen atom and like species i.e., to the one-electron system e.g.,* He^+, Li^{2+}, Be^{3+}, B^{4+} *etc.*

Limitations of Bohr's Model

Bohr left the following facts unexplained

1. Fine structure of atom,
2. Spectrum of multi-electron system,
3. **Zeeman effect** (effect of magnetic field on an excited atom) and **Stark effect** (effect of electric field on an excited atom). Split (resolution) of spectral lines occur in both the effects,
4. Three dimensional existence of atom,
5. Dual nature of electron.

3.7 Bohr Sommerfeld Model

Sommerfeld (1915) suggested the existence of elliptical orbits alongwith circular orbits (with situation of nuclei at one of the foci of ellipse) to explain the fine structure in hydrogen spectrum.

Due to the presence of such orbits the tangential velocity of an electron at any instance can be resolved into two components, *i.e.,* the **radial velocity** (one along the radius vector) and the **transverse** or **angular velocity** (one perpendicular to the radius vector). These two velocities give rise to **radial** and **angular** or **azimuthal momentum** as

$$\text{Radial momentum} = n_r\times\frac{h}{2\pi}$$

$$\text{Azimuthal momentum} = n_\phi\times\frac{h}{2\pi}$$

here, n_r = radial quantum number

n_ϕ = azimuthal quantum number

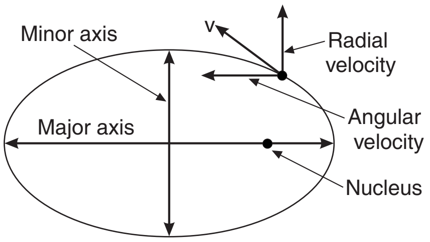


Fig. 3.12 An ellipse with electron showing radial and angular velocities

These n_r and n_ϕ are related to principal quantum number of Bohr (n) as

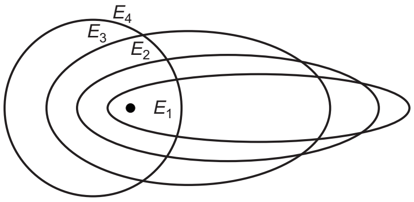
$$n = n_r + n_\phi$$

$$\frac{n}{n_\phi} = \frac{n_r + n_\phi}{n_\phi} = \frac{\text{length of major axis}}{\text{length of minor axis}}$$

Always remember that

1. **The value of n_ϕ can never be zero,** because if $n_\phi = 0$, that means the minor axis of ellipse will also be zero, *i.e.*, the electron is moving in a straight line which is impossible.
2. **n_ϕ cannot be greater than n** because in such cases the path will not be elliptical as minor axis of ellipse exceeds its major axis.
3. **n_ϕ equal to n is possible** but in that case the orbit will be circular (circular orbit is the special case of ellipse, where major axis equals the minor axis).
4. **n_ϕ smaller than n is possible** and in all such cases the orbit will remain elliptical.

If $n = 4$, four values of n_ϕ are possible as 1, 2, 3, 4 (shown as E_1, E_2, E_3 and E_4 in the following figure)



$n = 4$
$n_\phi = E_1, E_2, E_3, E_4$

Sommerfeld also modified the expression of energy of moving electron in elliptical orbit for hydrogen as

$$E_n = -\frac{2\pi^2 me^4}{(n_\phi + n_r)^2 h^2}$$

Drawbacks of Sommerfeld Model

The weak points of Bohr-Sommerfeld model are

(i) Experimental and theoretical observations based on wave mechanics show different values of n_ϕ (azimuthal quantum number) as 0, 1, 2, 3, … till $(n - 1)$, in the place of 1, 2, 3, ... till n as given by *Sommerfeld.*

(ii) This new quantum number beginning with zero and ending at $(n - 1)$ has been represented by l (to avoid the confusion with n_ϕ). This l is related to n as

$$l = \text{zero to } (n - 1)$$

(iii) This theory cannot give the exact idea of number of lines observed in fine spectrum, alongwith the information about the relative intensities of these lines.

(iv) The exact definition of position and momentum of electron can be given by this theory which is contrary to Heisenberg's uncertainty principle.

Check Point 1

1. What did Rutherford's alpha particle scattering experiment prove?
2. Which experiment neglected Thomson's model of the atom as an intimate mixture of negative and positive particles?
3. Why does the charge to mass ratio of positive rays depend on the residual gas in the discharge tube? Why is the charge to mass ratio of all cathode rays same?
4. Write wave number for the longest and the shortest wavelength of visible light.
5. Light of wavelength, λ strikes on a metal surface with intensity X, and the metal emits Y electrons per second of average, Z. What will happen to Y and Z, if X is doubled?

3.8 Modern Structure of Atom

Dual Nature of Matter: de-Broglie Equation

The French physicist **Lewis de-Broglie,** in 1924, proposed that matter like radiation also possesses dual nature, *i.e.,* has wave nature as well as particle nature. In other words, he said that electrons have momentum as well as wavelength just like photons. He examined the consequences of combining two of the more powerful equations in all of physics, the energy equation of Planck's and Einstein. A highly simplified version of what he did has been illustrated here

For an electron moving in an orbit, the energy expression, according to Planck's theory is

$$E = h\nu = \frac{hc}{\lambda} \qquad \text{...(i)}$$

Also, for energy of electron of mass m moving with speed c, the Einstein equation gives

$$E = mc^2 \qquad \text{...(ii)}$$

For the same electron, the two energy values must be identical. Therefore, by equating the right sides of the above two Eqs. (i) and (ii) we get

$$mc = \frac{h}{\lambda}$$

$$\boxed{\lambda = \frac{h}{mc} = \frac{h}{P}} \quad \text{where, } P = mc \text{ (momentum)} \qquad \text{... (iii)}$$

The above relation between wavelength (λ) and momentum (p) correlates the wave–matter duality of electron and known as **de-Broglie equation**. Putting real numbers into the de-Broglie equation shows that for any object in the normal world that the de-Broglie wavelength is too small to detect. However, when we enter the realm of atoms and the electrons, the dimensions of the waves become significant. Infact, the electron's wave is about the size of the atom.

In case kinetic energy, E of the particle is given, the de-Broglie wavelength can be calculated by the

$$\lambda = \frac{h}{\sqrt{2mE}} \qquad [\because P = \sqrt{2mE}]$$

Davisson and **Germer** made the following modification in de-Broglie equation

Let a charged particle say an electron be accelerated with a potential of V then kinetic energy may be given as

$$\frac{1}{2}mv^2 = eV$$

$$m^2v^2 = 2eVm$$

$$mv = \sqrt{2eVm} = P$$

$$\boxed{\lambda = \frac{h}{\sqrt{2eVm}}}$$

$\lambda = \frac{h}{\sqrt{2qVm}}$ for charged particles of charge q. de-Broglie waves are not radiated into space, *i.e.,* they are always associated with electron. Thus, for various sub-atomic particles the value of λ can be give by the following expressions

(i) **For electron**

$$\lambda = \frac{12.27}{\sqrt{V}} \text{Å}$$

(ii) **For proton**

$$\lambda = \frac{0.268}{\sqrt{V}} \text{Å}$$

(iii) **For α –particles** $\lambda = \frac{0.101}{\sqrt{V}} \text{Å}$

where, V = accelerating potential of these particles,

(iv) **For neutrons** $\lambda = \frac{h}{\sqrt{2Em}}$

$$= \frac{6.62 \times 10^{-34}}{\sqrt{2 \times 1.67 \times 10^{-27} \times E}}$$

$$= \frac{0.286}{\sqrt{E(eV)}} \text{Å}$$

(v) **For gas molecules**

$$\lambda = \frac{h}{m \times v_{\text{rms}}} \text{Å} = \frac{h}{\sqrt{3mkT}}$$

where, k = Boltzmann constant,

Bohr Theory *vs* de-Broglie Equation

As de-Broglie realized, the simplest way to introduce quantum ideas into an atomic model was to ascribe wave properties to the electron. A standing wave must have integral wavelengths with no possibility of fractional wavelengths with this superposition; the number of de-Broglie wavelengths in a given Bohr's orbit is always equal to the orbit number as

$$mvr = \frac{nh}{2\pi} \Rightarrow \boxed{2\pi r = \frac{nh}{mv} = n\lambda}$$

Sample **Problem 17** *The velocity associated with a proton moving in a potential difference of* 1000 *V is* $4.37 \times 10^5\ ms^{-1}$. *If the hockey ball of mass* 0.1 *kg is moving with this velocity, calculate the wavelength associated with this velocity.* **[NCERT]**

(a) 1.2×10^{-37} m (b) 1.9×10^{-39}
(c) 1.5×10^{-38} m (d) 2.6×10^{-38} m

Interpret (c) Wavelength associated with the velocity of hockey ball

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}\ \text{kg m}^2\text{s}^{-1}}{0.1\ \text{kg} \times 4.37 \times 10^5\ \text{m s}^{-1}}$$

$$= 15.16 \times 10^{-39}\ \text{m} = 1.516 \times 10^{-38}\ \text{m}$$

Sample **Problem 18** *Determine the de-Broglie wavelength (Å) associated with* He *atom at* 500*K*.

(a) 0.565 (b) 0.435
(c) 0.223 (d) 0.195

Interpret (a) For a gaseous atom, a measure of its average speed is the root mean square speed (rms) as

$$V_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

$$= \sqrt{\frac{3 \times 8.314 \times 500}{4 \times 10^{-3}}} = 1766\ \text{ms}^{-1}$$

$$\text{Mass of a He atom} = \frac{4 \times 10^{-3}}{6.023 \times 10^{23}} = 6.64 \times 10^{-27}\ \text{kg}$$

$$\therefore \text{ de-Broglie wavelength } (\lambda) = \frac{h}{mv} = \frac{6.626 \times 10^{-34}}{6.64 \times 10^{-27} \times 1766}$$

$$= 5.65 \times 10^{-11}\ \text{m} = 0.565 \text{Å}$$

Heisenberg's Uncertainty Principle

Werner Heisenberg of Germany, gave the principle of uncertainty in which he stated that *the exact position and exact velocity* (or momentum) *of a sub- atomic particle can not be measured simultaneously.* This principle was exactly opposite to Bohr's theory with regard to the fixed position of electron and definite energy of orbits. The principle can be expressed mathematically as

$$\boxed{\Delta P \cdot \Delta x \geq \frac{h}{4\pi}}$$

here, ΔP = uncertainty in momentum,
Δx = uncertainty in position,
h = Planck's constant

Now since, $P = mv$; hence, $\Delta P = m\Delta v$

By putting the value of ΔP in the above expression, we get

$$m \cdot \Delta v \times \Delta x \geq \frac{h}{4\pi}$$

or $$\boxed{\Delta v \times \Delta x \geq \frac{h}{4\pi \times m}}$$

The above expression means that the position and velocity of an object cannot be simultaneously known with certainty.

Uncertainty in velocity or position varies inversely with mass, thus is negligible for macroscopic objects.

Suppose, we locate the position of an electron with uncertainty, $\Delta x = 10^{-2}$ m. Substituting the value in Heisenberg's formula

$$\Delta P_x = \frac{h}{4\pi\Delta x} = \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 10^{-12}}$$
$$= 5.27 \times 10^{-23} \text{ kg ms}^{-1}$$

The above uncertainty in momentum would be quite negligible in a macroscopic system but it is far from negligible for systems containing electrons and like microparticles, since we are then dealing with masses of the order of 10^{-30} kg. So far our concept of microscopic and macroscopic system is based on the size of the particle, thus microscopic particle cannot have a definite position and a definite momentum simultaneously.

Therefore, we cannot draw a trajectory of a microparticles in contrast to a macroparticle and hence, in light of the Heisenberg's principle, the Bohr's concept of the orbit of an electron becomes untenable.

For precise measurement of position one need to use radiations of very short wavelengths *e.g.*, gamma-rays and alternatively for preciseness in measurement of momentum, radiations of longer wavelength would be needed.

For other canonical conjugates of motion, the equation for Heisenberg uncertainty principle may be given as

$$\text{Momentum} = \text{mass} \times \text{velocity}$$
$$= \text{mass} \times \frac{\text{velocity}}{\text{time}} \times \text{time}$$
$$= \text{force} \times \text{time}$$
$$\text{Momentum} \times \text{Distance} = \text{force} \times \text{distance} \times \text{time}$$
$$= \text{energy} \times \text{time}$$
$$\Delta P \Delta x = \Delta E \Delta t$$
$$\Delta E\, \Delta t \geq \frac{h}{4\pi} \quad \text{(for energy and time)}$$

Similarly, $$\Delta\phi\, \Delta\theta \geq \frac{h}{4\pi} \quad \text{(for angular motion)}$$

On the basis of this principle, therefore, Bohr picture of an electron in an atom, which gives a fixed position in a fixed orbit and definite velocity to an electron, is no longer tenable. The best we can think of in terms of probability of locating an electron with a probable velocity in a given region of space at a given time. The space or a three–dimensional region around the nucleus where there is maximum probability of finding an electron of a specific energy is called an **atomic orbital**.

Caution Point *Heisenberg's uncertainty principle is applicable only when the location and momentum are along the same axis, i.e., if Δx is uncertainty in position along the z-axis then ΔP must also be uncertainty in momentum along the z-axis.*

Sample Problem 19 *If uncertainty in the measurement of position and momentum are equal then uncertainty in the measurement of velocity is equal to*

(a) $\frac{1}{2m}\sqrt{\frac{2h}{\pi}}$
(b) $\frac{1}{2m}\sqrt{\frac{h}{\pi}}$
(c) $\frac{1}{4m}\sqrt{\frac{h}{\pi}}$
(d) $\frac{1}{2m}\sqrt{\frac{h}{2\pi}}$

Interpret (*b*) By Heisenberg's uncertainty principle for minimum uncertainty,

$$\Delta x \cdot \Delta P = \frac{h}{4\pi}$$

Given, $$\Delta x = \Delta P$$

So, $$(\Delta P)^2 = (\Delta x)^2 = \frac{h}{4\pi}$$

$\therefore$ $$\Delta P = \sqrt{\frac{h}{4\pi}}$$

or $$m\Delta v = \frac{1}{2}\sqrt{\frac{h}{\pi}}$$
$$\Delta v = \frac{1}{2m}\sqrt{\frac{h}{\pi}}$$

3.9 Quantum Mechanical Model

In Bohr model, an electron is regarded as a charged particle moving in well defined circular orbits about the nucleus. An orbit can completely be defined only if both the position and the velocity of the electron are known exactly at the same time. This is not possible according to the Heisenberg's uncertainty principle. Further more, the wave character of the electron is not considered in Bohr model.

Therefore, concept of movement of an electron in an orbit was replaced by the concept of probability of finding electron in an orbital due to de-Broglie concept of dual nature of electron and Heisenberg's uncertainty principle. The changed model is called quantum mechanical model of the atom.

On the basis of dual nature of matter and Heisenberg uncertainty principle, **Erwin Schrodinger,** an Austrian physicist, in 1926 developed a new branch of science, called the **quantum mechanics** or **wave mechanics** and gave a model for atom, called **'wave mechanical model'** of atom. In his model he visualised electron as a three dimensional 'wave in the electronic field' of a positively charged nucleus inside the atom.

The quantum mechanical study of any system consists of

(i) Writing Schrodinger equation for the system.

(ii) Solving Schrodinger equation for the meaningful solutions of the wave functions and corresponding energies. The meaningful solutions of wave function must follow the conditions, *i.e.,* they have to be single valued, continuous and finite.

(iii) Calculation of all the observable properties of the system from wave function.

Schrodinger Equation

Schrodinger derived an equation for an electron which describes the wave motion of an electron wave along any of three axis, *i.e., x, y* and *z*. This equation is

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi=0$$

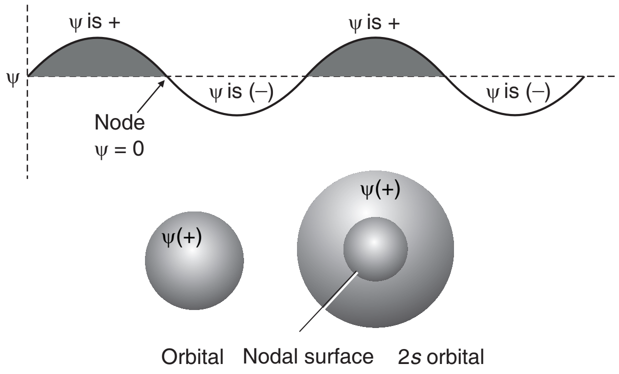
here, ψ = wave function,

h = Planck's constant

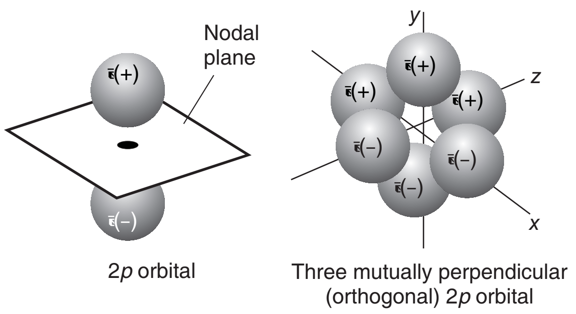
E = total energy of electron, *i.e.,* KE + PE for electron

V = potential energy of electron.

The wave function, ψ (psi) may be regarded as the amplitude function expressed in terms of coordinates *x, y* and *z*. The wave function values may be positive or negative depending upon the values of coordinates. Its comparison with a wave is given below



(a) In *s* orbital



(b) In *p* orbital

Fig. 3.13 The visualisation of wave function in orbitals as compared with a wave

The Schrodinger wave equation can also be written as

$$\nabla^2\psi+\frac{8\pi^2 m}{h^2}(E-V)\psi=0$$

here, $$\nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$$

i.e., the differential (Laplacian) operator. The acceptable solutions of Schrodinger wave equation are called **eigen function.**

Infact, Schrodinger gave a generalised equation, for a system, such as, an atom or a molecule, whose energy does not change with time (time independent) which is written as

$$\hat{H}\psi=E\psi$$

here, $\hat{H}$ is the total energy operator for electron, called **hamiltonian.** (In quantum mechanics, there is an operator corresponding to every observable property. It is like a mathematical command which act on a mathematical function.)

The hamiltonian is the sum of kinetic energy operator $\hat{T}$ and potential energy operator $\hat{V}$, *i.e.,*

$$\hat{H}=\hat{T}+\hat{V}$$

Thus, above equation can be written as

$$(\hat{T} + \hat{V})\psi = E\psi$$

here, E = total energy of the system.

Schrödinger equation for electron wave is the differential equation of second order, hence has several solutions (eigen function) for ψ, many of which are imaginary and not valid.

Only those values of ψ are valid which satisfy following conditions

(i) The wave function must be finite and continuous.

(ii) The solution must be single valued, *i.e.,* at a given point there can never be more than one value for amplitude ψ.

(iii) $\frac{\partial\psi}{\partial x}, \frac{\partial\psi}{\partial y}$ and $\frac{\partial\psi}{\partial z}$ must be continuous functions of x, y and z respectively.

(iv) The probability of finding the electron over all spaces from plus infinity to minus infinity must be equal to one.

The Schrodinger wave equation when fully solved with the help of advanced mathematics gives the same expression as given by Bohr for the energy of an electron. Infact, this equation in polar coordinates is solved for hydrogen atom and its solution gave possible energy states and their corresponding wave functions. For several wave functions, *e.g.,* $\psi_1, \psi_2, \psi_3, \ldots$ several corresponding energies are given as $E_1, E_2, E_3, \ldots$ **Each of these wave functions is called an 'orbital' by analogy** (functional similarity) **with Bohr's orbit.** ***e.g.,*** in the hydrogen atom, the single electron occupies the lowest of the energy levels E_1 and the corresponding wave function ψ_1 describes the orbital, *i.e.,* the volume in space where there is a high probability of finding an electron.

Thus, orbitals can be visualised as diffused negatively charged clouds of different shapes, sizes and orientations around the nucleus.

Concept of Atomic Orbitals as One Electron Wave Functions

A hydrogen atom is the simplest chemical system consisting of one proton and one electron. Assuming that the electron moves at a distance r around the stationary nucleus, the nucleus can be taken as the origin of a coordinate system.

The Schrodinger equation for the hydrogen atom can be written in terms of the Cartesian coordinates (x, y, z) or in terms of the spherical polar coordinates (r, θ, φ) of the electron with respect to the nucleus. Since an atom has spherical symmetry, it is more convenient to write Schrodinger equation in terms of polar coordinates. The relationships between the two coordinate systems are shown below in the Fig. 3.14.

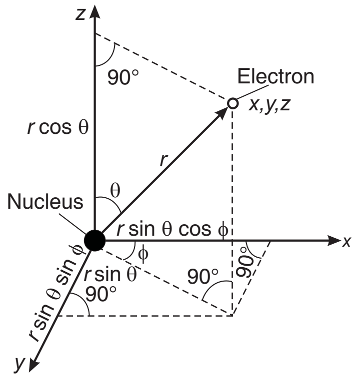


Fig. 3.14 Relationship between cartesian (x, y, z) and polar coordinates (r, θ, φ)

The coordinates x, y, and z of the electron with respect to nucleus in terms of polar coordinates are given by

$$x = r\sin\theta\cos\varphi$$
$$y = r\sin\theta\sin\varphi$$
$$z = r\cos\theta$$
$$x^2 + y^2 + z^2 = r^2$$

When the Schrodinger equation in polar coordinates is solved for the hydrogen atom, it gives the possible energy states and the corresponding wave function $[\psi(r, \theta, \varphi)]$ (called atomic orbitals or hydrogenic orbitals, which are in fact the mathematical function of the coordinates of the electron associated with each energy state). An atomic orbital is a mathematical function of the three coordinates (r, θ and ϕ) and can be factorised into three separate parts, each of which is a function of only one coordinate.

$$\psi(r, \theta, \phi) = R(r)\ominus(\theta)\ \phi(\phi)$$

Here, $R(r)$ = radial function and gives the dependence of orbital upon distance r of electron from the nucleus

$\ominus(\theta)$ and $\phi(\phi)$ = angular functions giving the angular dependence of orbital on θ and ϕ respectively.

The radial function depends upon quantum numbers n and l whereas angular functions depend upon quantum numbers l and m, *i.e.,* these are independent of n. The total wave function may, therefore, be written as :

$$\psi(r, \theta, \phi) = \underset{\text{(radial part)}}{r_{n.l}}\ \underset{\text{(angular part)}}{\theta_{l.m}\ \phi_n}$$

The probability of finding an electron in a given volume of element can be represented by two types of probability distribution curves which are

(i) Radial probability distribution curve,

(ii) Angular probability distribution curve.

The radial probability distribution curves tell, *how the probability of finding an electron varies with its radial distance from the nucleus without any reference to its direction from the nucleus*. Since, the atoms have spherical symmetry, it is more useful to discuss the probability of finding the electron in a spherical shell between the spheres of radius $(r + dr)$ and r as shown in the figure below.

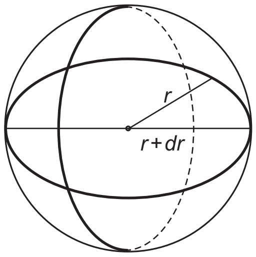


Fig. 3.15 Spherical shell of thickness *dr*

The volume of the shell is equal to

$$\frac{4}{3}\pi(r + dr)^3 - \frac{4}{3}\pi r^3 = 4\pi r^2 dr$$

and the radial probability function $(R) = 4\pi r^2 dr\psi^2$

This can be defined as *"the probability of finding the electron at a distance r from the nucleus regardless of direction."*

Significance of ψ

The wave function may be regarded as the amplitude function expressed in terms of coordinates *x, y,* and *z*. The wave function may have positive or negative values depending upon the values of coordinates.

The main aim of Schrodinger equation is to give a solution for the probability approach. When the equation is solved, it is observed that for some regions of space, the value of ψ is positive and for other regions, the value of ψ is negative. But the probability must be always positive and cannot be negative. It is, thus proper to use ψ^2 in favour of ψ.

Significance of ψ^2

ψ^2 is a probability factor. It describes the probability of finding an electron within a small space. The space in which there is maximum probability of finding an electron is termed as orbital.

The solution of the wave equation is beyond the scope of this book. The important point of the solution of this equation is that it provides a set of numbers, called **quantum numbers,** which describe energies of the electrons in atoms, information about the shapes and orientations of the most probable distribution of electrons around the nucleus.

Variation of ψ and ψ^2 with *'r'*

Wave function ψ can be plotted against distance '*r*' from the nucleus as

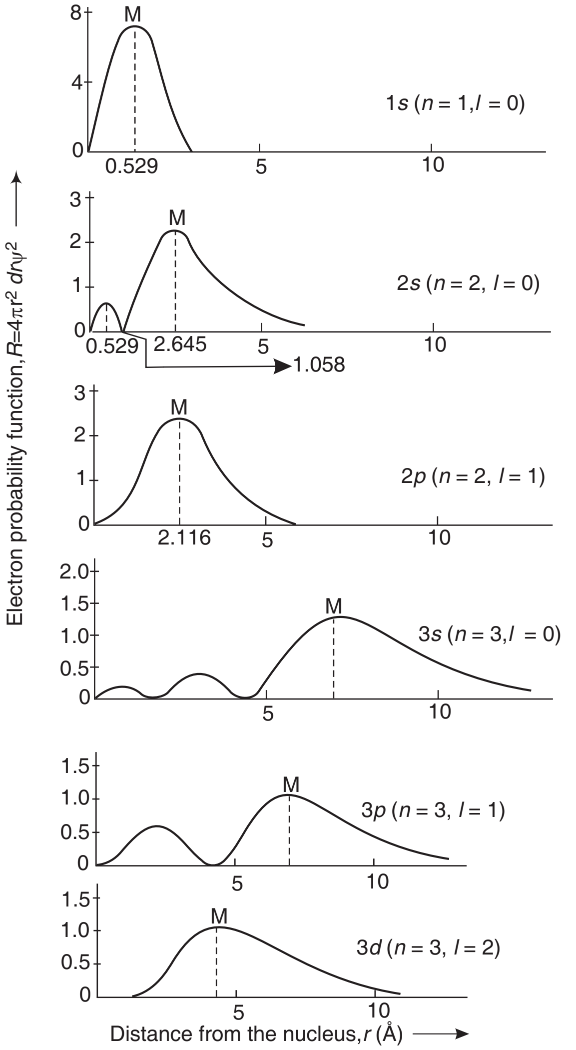


Fig. 3.16 Radial probability distribution curves for 1*s*, 2*s*, 2*p*, 3*s*, 3*p* and 3*d* orbitals. The point M in each curve represents the maximum electron density

These curves (radial distribution) tells us about following

(i) In each case, the probability of finding the electrons at the origin (nucleus) is zero, *i.e.*, **electron will never be found at the nucleus.**

(ii) The distance for maximum probability in an orbital increases with the value of *n* (principal quantum number). *e.g.*, This distance for 1*s*, 2*s* and 3*s* is in the order 1*s* < 2*s* < 3*s*.

(iii) The total number of peaks appearing in the curves for *s, p* and *d* orbitals is equal to n, $(n-1)$ and $(n-2)$ respectively, where, n = principal quantum number.

(iv) From the curve of 1*s* electron, the value of R is zero at nucleus where r is also zero. It then increases as r increases passes through a maximum (peak) at $r = 0.529$ Å, which is equal to the radius of Bohr's first orbit and then falls to zero as r tends to infinity. Thus, for 1*s* electron $R = 0$ at $r = 0$ and R = maximum at $r = 0.529$ Å.

(v) For 2*s* electron, the value of R is zero at $r = 0$. The value of R increases as r increases, passes through a maximum at $r = 0.529$ Å and falls to zero again at $r = 1.058$ Å. R reaches second highest at $r = 5 \times 0.529$ Å and then finally approaches zero as r tends to infinity. *The distance i.e.,* 1.058 Å *at which the probability of finding electron is zero is called node or nodal plane or nodal surface*. Thus, with in the orbital (where probability of finding an electron is maximum), there is a space, called node surrounding nucleus where probability of finding electron is zero.

For an *s* orbital, number of nodes = $(n-1)$, *i.e.*, 1*s* orbital contains no node, 2*s* orbital contains one node, 3*s* orbital contains 2 nodes and so on.

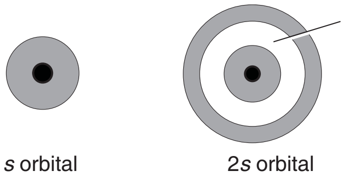


Fig. 3.17 Spherical *s* orbital, symmetrically disposed about the nucleus

Similarly, for a *p* orbital, number of nodes = $(n-2)$. In both the above cases n = principal quantum number.

(vi) For a hydrogen atom wave function, of principal quantum number n, there are
  (1) $(n-l-1)$ radial nodes (or spherical nodes)
  (2) l angular nodes (or non-spherical nodes)
  (3) $(n-1)$ total nodes.

Sample **Problem 20** *Calculate the total number of angular nodes and radial nodes present in 3p-orbital.*

[NCERT Exemplar]

(a) 1, 1	(b) 2, 1
(c) 2, 2	(d) 1, 2

Interpret (a) For 3*p*-orbital, principal quantum number, $n = 3$ and azimuthal quantum number, $l = 1$

Number of angular nodes = $l = 1$

Number of radial nodes = $n - l - 1 = 3 - 1 - 1 = 1$

Structure of Atom on the Basis of Wave Mechanical Model

According to wave mechanical model, the structure of atom can be summarised as

1. The electron in an atom are arranged in shells or different energy levels which are indicated by numbers, 1, 2, 3, ... or letters *K, L, M,* ...
2. With in each shell, there are subshells or sub levels which are designated as *s, p, d* and *f.*
3. Electrons of different energy levels are present in discrete volumes of different shapes, sizes and orientations in the sub-levels around the nucleus.
4. **Each of such discrete volume is called an orbital** which has the maximum probability of finding a particular electron of a particular energy level.
5. Each orbital may hold up two electrons of exactly equal energy provided they have opposite spins.
6. There are in all four quantum numbers to define an electron in an atom. Out of these four, three, *i.e., n, m* and *l* are needed to define the **orbital** and the 4th one defines the spin of electron in it.

Check Point 2

1. Why does Heisenberg's uncertainty principle has no significance in case of macroscopic objects?
2. In what ways do the spatial distributions of the orbitals in given pair differ from each other (2*s* and 2*p*)?
3. Draw a representation of a 3*p* orbital, including in your sketch the information that it has the planar node characteristic of *p* orbitals but in addition has a spherical node.

3.10 Quantum Numbers

The term quantum number is used to identify the various energy levels that are available to an electron. The word quantum is used to signify that all the energy levels which are available to an electron are governed by the laws of quantum mechanics. Four quantum numbers are necessary to characterise completely particular electrons in a particular orbit. These are discussed below

Principal Quantum Number (n)

It defines the principal shell in which the electron is revolving around the nucleus. It designates the average distance of the electron from the nucleus. Hence, this quantum number represents the size of the electron orbits.

In a polyelectron atom or ion, the electron that has a higher principal quantum number is at a higher energy level. An electron with $n = 1$ has the lowest energy and is bound most firmly to the nucleus. There is a limited number of electrons in an atom which can have the same principal quantum number and is given by $2n^2$, where n is the principal quantum number concerned. Thus,

Principal quantum number	$(n) \longrightarrow$	1	2	3	4
Letter designation	$\longrightarrow$	K	L	M	N
Maximum number of electrons $(2n^2)$	$\longrightarrow$	2	8	18	32

Wave Mechanical Aspects of '*n*'

According to modern quantum theory, the behaviour of an electron is described as that of standing wave and the value of '*n*' tells how many peaks of amplitude (antinodes) exist in that particular standing wave pattern; *the more peaks there are, the higher these energies of the state.*

Azimuthal Quantum Number (*l*)

It is also known as the second, subsidiary, lesser or the orbital quantum number. '*l*' describes the name of subshell and the shape of orbital present in it. It is related to orbital angular momentum by the following relation

$$\text{Orbital angular momentum, } mvr = \frac{h}{2\pi}\sqrt{[l(l+1)]}$$

l can have values ranging from 0 to $(n - 1)$.

(i) When $l = 0$, the subshell is s and orbital is spherical in shape.

(ii) When $l = 1$, the subshell is p and orbital is dumb-bell shaped.

(iii) When $l = 2$, the subshell is d and orbital is double dumb-bell shaped.

(iv) When $l = 3$, the subshell is f and orbital is complicated in shape.

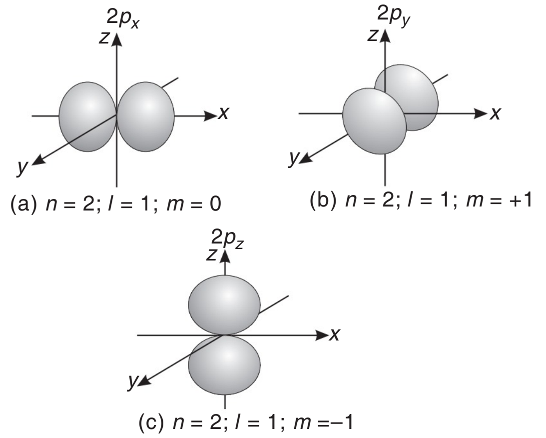
Caution Point *Energy of an electron in an orbit depends on the principal quantum number (n) for systems with only one electron. For multielectron systems, energy depends both on principal quantum number (n) and azimuthal quantum number (l).*

Magnetic Quantum Number (*m*)

This quantum number was introduced to describe the Zeeman effect (*i.e.,* splitting of spectral lines under the influence of an applied magnetic field). The magnetic quantum number is also called **orientation quantum number** because it gives the orientation or distribution of the electron cloud. For each value of azimuthal quantum number, the magnetic quantum number, may assume all the integral values between $+l$ to $-l$ through zero. *e.g.,*

(i) When $l = 0$, m has only one value, *i.e.,* 0; hence, there occur only one spherical orbital for each value of n.

(ii) When $l = 1$, m has 3 values, *i.e.,* +1, 0 and −1; hence, there occur 3 orbitals in p subshell namely p_x, p_y and p_z along the x-axis, y-axis and z-axis respectively.

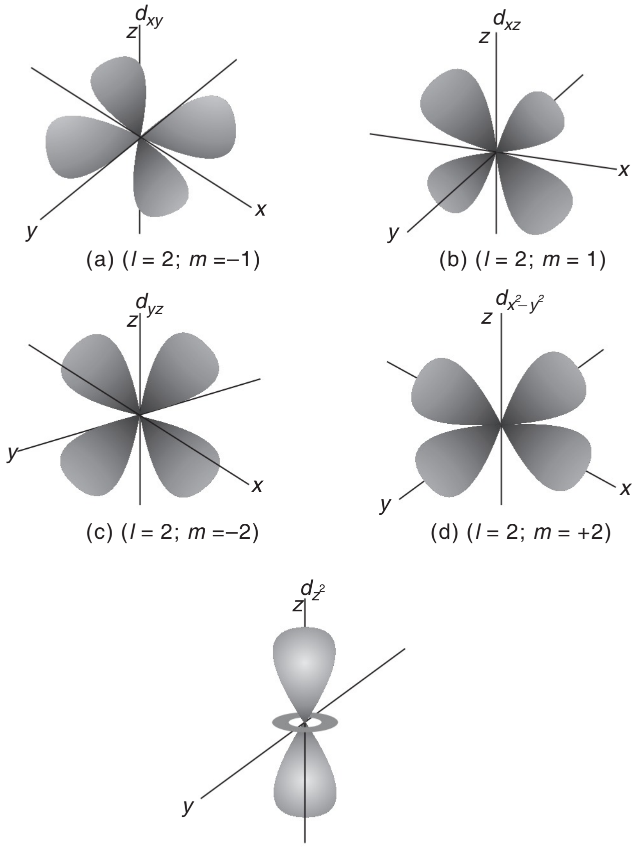


(a) $n = 2$; $l = 1$; $m = 0$ (b) $n = 2$; $l = 1$; $m = +1$ (c) $n = 2$; $l = 1$; $m = -1$

Fig. 3.18 Orientation of p-orbitals along x, y and z axis

These orbitals of a subshell are identical in energy, shape and size and differ only in their direction in space. **Orbitals with identical energy are called degenerate orbitals.**

(iii) For $l = 2$, *i.e.,* d subshell, m has 5 values namely +2, +1, 0, −1, −2 representing 5 such orbitals namely d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$, d_{z^2}. Out of these only d_{xy} and $d_{x^2-y^2}$ lie in xy plane.



(a) ($l = 2$; $m = -1$) (b) ($l = 2$; $m = 1$) (c) ($l = 2$; $m = -2$) (d) ($l = 2$; $m = +2$) (e) ($l = 2$; $m = 0$)

Fig. 3.19 Orientation of d-orbitals

(iv) For l = 3, *i.e.,* *f* subshell, *m* has 7 values namely +3, +2, +1, 0, −1, −2, −3. These orbitals have representation difficulties that's why we consider their shape as "diffused" in generalised way. There is no unique way of representing all the seven orbitals. According to one opinion these orbitals can be represented as f_{z^3}, f_{xz^2}, f_{yz^2}, f_{xyz}, $f_{x(x^2-3y^2)}$, $f_{y(3x^2-y^2)}$ and $f_{z(x^2-y^2)}$, while according to another view these can be represented as f_{x^3}, f_{y^3}, f_{z^3}, $f_{x(z^2-y^2)}$, $f_{y(z^2-x^2)}$, $f_{z(x^2-y^2)}$ and f_{xyz}.

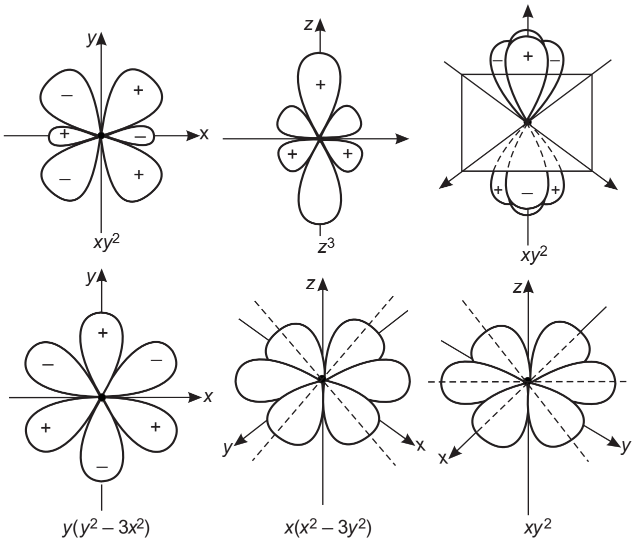


Fig. 3.20 Orientation of *f*-orbitals

Total value of *m* for a given value of $n = n^2$
Total value of *m* for a given value of $l = (2l + 1)$

Spin Quantum Number (*s*)

Spin quantum number arises from the spectral evidence that an electron in its motion around the nucleus in an orbit also rotates or spins about its own axis. The electron can spin clockwise or anti-clockwise. These spinning produces spin angular momentum (*s*) equal to $\sqrt{s(s+1)}\,\frac{h}{2\pi}$. The spin quantum number is either equal to $+\frac{1}{2}$ or $-\frac{1}{2}$.

The positive value of m_l describes orbital angular momentum component which are in the direction of applied magnetic field and the negative value of m_l are for those components which are oriented in direction opposite to that of applied field.

The spin quantum number gives rise to magnetic properties of materials. If there are two electrons in any orbital with opposite spin, their magnetic moments will be cancelled. Presence of magnetic properties indicates the presence of one or more unpaired electrons.

Magnetic moment (μ) can be calculated by the formula $\mu = \sqrt{n(n+2)}$ BM

where, *n* = number of unpaired electrons.

Sample Problem 21 *Which of the following orbitals are degenerate?* [**NCERT Exemplar**]

$$3d_{xy}, 4d_{xy}, 3d_{z^2}, 3d_{yz}, 4d_{z^2},$$

(a) $3d_{xy}$, $3d_{z^2}$, $4d_{xy}$
(b) $4d_{xy}$, $3d_{z^2}$, $4d_{z^2}$,
(c) $3d_{z^2}$, $4d_{z^2}$,
(d) $3d_{xy}$, $3d_{z^2}$, $3d_{yz}$

Interpret (*d*) The orbitals which belongs to same subshell and same shell are called degenerate orbitals. ($3d_{xy}$, $3d_{z^2}$, $3d_{yz}$,) and ($4d_{xy}$, $4d_{yz}$, $4d_{z^2}$) are the two sets of degenerate orbitals.

Hot Spot 2

FINDING QUANTUM Numbers

Many a times questions based on quantum numbers have been seen JEE Main previously AIEEE examination. Which reveals the importance of the topic for the examination. The level of the questions is generally easy.

In order to find all the four quantum number for an electrons follow the following steps

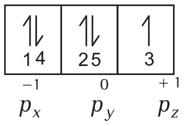
Step I First find the value of n (principal quantum number) for the given, electron from the electronic configuration of the element. *e.g.*. For 17th electron of Cl, configuration is $1s^2, 2s^2, 2p^6, 3s^2, 3p^5$. The 17 electron enters in $3p$ orbital, so $n = 3$

Step II Values of l never be greater than n and possible values of l for a given value of n is 0 to $n - 1$. Thus, possible values of l for $3p$ electrons $= 0, 1, 2$, not 3 ($\because n > l$).

Moreover, value of l is 0, 1, 2 and 3 respectively for s, p, d and f orbitals. Since in case of 17th electron, the orbital is p, so the value of $l = 1$

Step III Values of m varies from $- l$ to $+ l$ including 0.

Thus, for $l = 1$, $m = -1, 0, +1$



Since the fifth electron enters in p_y, $m = 0$

Step IV Value of s may be $+\frac{1}{2}$ or $-\frac{1}{2}$

For 17th electron $s = -\frac{1}{2}$

Thus, the correct set of quantum numbers for 17th electron is

$$n = 3, l = 1, m = 0 \text{ and } s - \frac{1}{2}.$$

Sample **Problem 22** *Which of the following sets of quantum numbers is not possible?*

(*a*) $n = 4, l = 1, m = 0, s = +\frac{1}{2}$

(*b*) $n = 4, l = 3, m = -3, s = -\frac{1}{2}$

(*c*) $n = 4, l = 0, m = 0, s = -\frac{1}{2}$

(*d*) $n = 4, l = 1, m = +2, s = -\frac{1}{2}$

Interpret (*d*) m has values $-l$ to $+l$ including 0. Thus, if $l = 1$, the possible values of $m = -1, 0, +1$ but not $+2$ as given in set (d). Thus, set (d) is not possible.

Sample **Problem 23** *Correct set of four quantum numbers for the valence (outermost) electron of rubidium ($z = 37$) is*

(*a*) $5, 0, 0, +\frac{1}{2}$

(*b*) $5, 1, 0, +\frac{1}{2}$

(*c*) $5, !, 1, . +\frac{1}{2}$

(*d*) $6, 0, 0, +\frac{1}{2}$

Interpret (*a*) The electronic conrfiguration of Rb is [Kr] $5s^1$

Thus, its valence electron enters in 5s orbital.
For 5s orbital, $n = 5$
$l = 0$ (as orbital is s)
$m = -l$ to $+l$ including zero $= 0$, $s = +\frac{1}{2}$

Thus, the correct set of quantum numbers for the valence electron of rubidium is 5, 0, 0, $+\frac{1}{2}$.

3.11 Rules for Filling of Electrons in Orbitals

Following rules have to be followed while filling electrons in orbitals

Aufbau Principle

Aufbau is a German word meaning "building up". The principle related to this word gives us an idea about the filling of orbitals by electrons. The rule states that *orbitals are filled up according to the increase in their energy.'*

The order of increase of energy can be calculated from $(n + l)$ rule which states that

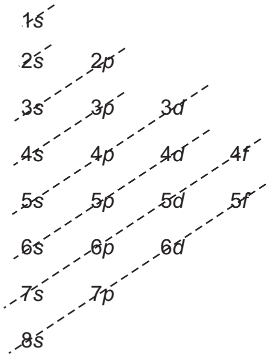
(i) The lower the value of $(n + l)$ for an orbital, the lower is its energy. *e.g.*, between $3d$ and $4s$, the $4s (4 + 0 = 4)$ will be filled before $3d (3 + 2 = 5)$.

Similarly between $4f$ and $6s$, the $6s (6 + 0 = 6)$ will be filled first than $4f (4 + 3 = 7)$.

(ii) If two orbitals have same value of $(n + l)$, the orbital with lower value of n will be filled first. *e.g.*, between $2p$ and $3s$, $2p (2 + 1 = 3)$ will be filled first than $3s (3 + 0 = 3)$.

The order in which electrons are filled in the orbitals, according to this rule is

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p$$



Sample **Problem 24** *Which of the following set of quantum numbers belongs to the highest energy?*

(a) $n = 4, l = 1, m = 1, s = +\frac{1}{2}$

(b) $n = 4, l = 0, m = 0, s = +\frac{1}{2}$

(c) $n = 3, l = 2, m = 1, s = +\frac{1}{2}$

(d) $n = 3, l = 1, m = 0, s = +\frac{1}{2}$

Interpret (a) Higher the value of $(n + l)$, higher is the energy.

(a) $(n + l) = (4 + 1) = 5$

(b) $(n + l) = (4 + 0) = 4$

(c) $(n + l) = (3 + 2) = 5$

(d) $(n + l) = (3 + 1) = 4$

Thus, energy is highest for the electron having $n = 4, l = 1$ quantum numbers.

Pauli Exclusion Principle

Pauli, in 1925 proposed that *no two electrons in an atom can be represented by same values of all the four quantum numbers, i.e.*, an orbital can accommodate a maximum of 2 electrons with opposite spin. These two electrons have same values of principal (n), azimuthal (l) and magnetic quantum numbers (m) but the value of spin quantum number will be different in them always.

For example In oxygen (atomic number 8) : $1s^2, 2s^2, 2p^4$

	$1s$	$2s$	$2p_x$	$2p_y$	$2p_z$
Principal Q.N.	1	2	2	2	2
Azimuthal Q.N.	0	0	1	1	1
Magnetic Q.N.	0	0	+1	−1	0
Spin Q.N.	$+\frac{1}{2} - \frac{1}{2}$	$+\frac{1}{2} - \frac{1}{2}$	$+\frac{1}{2} - \frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$

Hund's Rule of Maximum Multiplicity

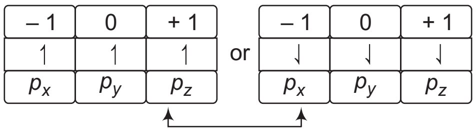
The rule states that *pairing of electrons in the orbitals of a particular sub-shell (p, d, or f) does not take place until all the orbitals of a sub-shell are singly occupied.* Moreover, the singly occupied orbitals must have the electrons with parallel spin.

The basis of this rule is that two electrons in a particular orbital feel greater repulsion and hence, while filling orbitals of equal energy, pairing of electrons is avoided as long as it is possible.

An Illustration of Electron Filling in a Degenerate *p*-Orbital

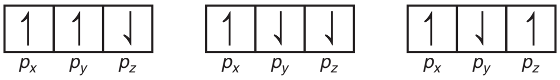
Let us suppose there are three electrons to be filled in a *p*-orbital.

They must obey Hund's rule.



Both are correct electronic representations since both obey the Hund's rule

Other representations are like



All of these are violating Hund's rule of maximum multiplicity *i.e.*, if the orbitals are only singly occupied, all electrons must have same spin quantum number (spinning in the same direction).

3.12 Electronic Configuration of Elements

The arrangement of electrons in various shells, sub-shells and orbitals in an atom is termed as electronic configuration. It is written in terms of nl^x where, n indicates the order of shell, l indicates the subshell and x the number of electrons present in the subshell. Here with the electronic configurations of some elements are given.

Table 3.3 **Electronic Configuration of Some Elements**

Element	Complete electronic configuration	Electronic configuration using inert gas symbol
H (1)	$1s^1$	$1s^1$
He (2)	$1s^2$	$1s^2$
Li (3)	$1s^2, 2s^1$	$[He]\,2s^1$
Be (4)	$1s^2, 2s^2$	$[He]\,2s^2$
B (5)	$1s^2, 2s^2, 2p^1$	$[He]\,2s^2, 2p^1$
C (6)	$1s^2, 2s^2, 2p^2$	$[He]\,2s^2, 2p^2$
N (7)	$1s^2, 2s^2, 2p^3$	$[He]\,2s^2, 2p^3$
O (8)	$1s^2, 2s^2, 2p^4$	$[He]\,2s^2, 2p^4$
F (9)	$1s^2, 2s^2, 2p^5$	$[He]\,2s^2, 2p^5$
Ne (10)	$1s^2, 2s^2, 2p^6$	$[He]\,2s^2, 2p^6$
Na (11)	$1s^2, 2s^2, 2p^6, 3s^1$	$[Ne]\,3s^1$
Cr* (24)	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^5$	$[Ar]\,3d^5, 4s^1$
Cu* (29)	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^{10}$	$[Ar]\,3s^{10}, 4s^1$
Mo* (42)	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6,$ $4s^2, 3d^{10}, 4p^{6,}\ 5s^1, 4d^5$	$[Kr]\,5s^1, 4d^5$
Pd* (46)	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6,$ $4s^2, 3d^{10}, 4p^6, 4d^{10}, 5s^0$	$[Kr]\,4d^{10}, 5s^0$

*The electronic configuration of these elements are exceptional due to half or completely filled orbitals.

3.13 Extra Stability of Completely Filled and Half-Filled Orbitals

The ground state electronic configuration of atom corresponds to the lowest energy state and gives higher stability. The electronic configuration of most of the atoms follows the basic rules. However, certain elements such as Cr or Cu do not follow the rules.

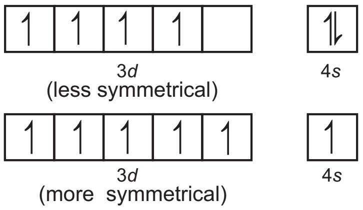
In such elements, the two sub-shells 4*s* and 3*s* slightly differ in energy. *i.e.,* 4*s* is slightly lower in energy than 3*d* orbital. In such case, the electron from lower energy sub-shell may jump to higher energy sub-shell provided such a shift results in all orbitals of the sub-shell of higher energy getting either completely filled or half-filled.

1. **Cr** atomic number 24 — $1s^2, 2\,s^2, 2p^6, 3\,s^2, 3p^6, 3d^5, 4s^1$
2. **Cu** atomic number 29 — $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3\,d^{10}, 4s^1$
3. **Nb** atomic number 41 — $1s^2, 2s^2, 2p^6, 3s^2, 3\,p^6, 3\,d^{10}$ $4s^2, 4p^6, 4d^4, 5s^1$
4. **Mo** atomic number 42 — $1s^2, 2s^2, 2p^6, 3s^2, 3\,p^6, 3\,d^{10}$ $4s^2, 4p^6, 4d^5, 5s^1$
5. **Ru** atomic number 44 — $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3\,d^{10}$ $4s^2, 4\,p^6, 4\,d^7, 5\,s^1$

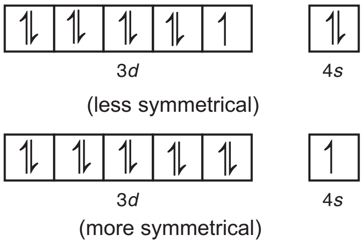
The extra stability of half-filled and fully filled electronic configuration can be explained in terms of symmetry and exchange energy.

Symmetrical Distribution of Electrons

The electronic configurations in which all the orbitals of the same sub-shell are either completely filled or half filled have relatively more symmetrical distribution of electrons. Consequently, their shielding of one another is relatively small and the electrons are more strongly attracted by the nucleus. This leads to more stability of the atom. *e.g.,* the expected configuration of Cr is $3d^4\,4s^2$. But shifting of one electron from 4*s* to 3*d* orbital makes the configuration more symmetrical and hence, more stable.

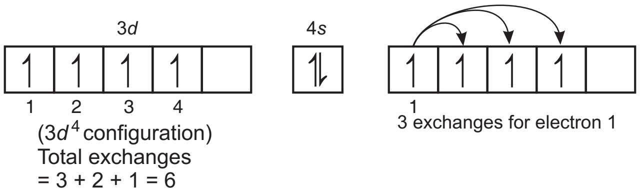


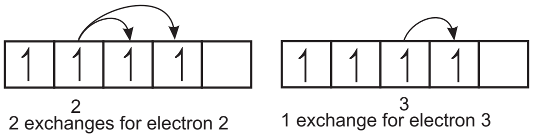
Similarly in copper, shifting of one electron from 4*s* to 3*d* makes the configuration more stable.



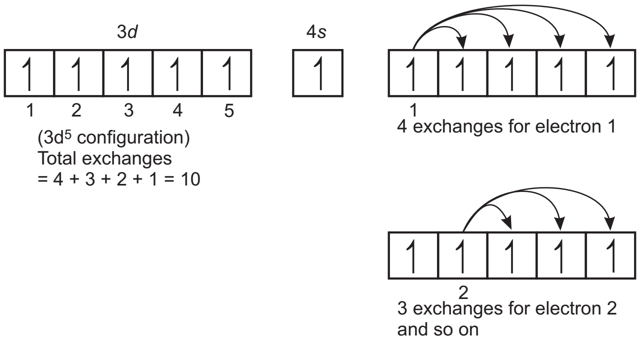
Exchange Energy

For the practical evaluation of this rule, the term "maximum multiplicity" is added in the rule. This term is used to explain the extra stability of half-filled or fully-filled orbitals due to exchange energies. The exchange energy means hypothetical energy evolved on shifting of electrons from one orbital to another within the same sub-shell. Let us compare the number of exchanges in $3d^4 4s^2$ (expected electronic configuration of Cr) and $3d^5 4s^1$ (actual electronic configuration of Cr)





In the above arrangement electron exchanges are six which implies that there are 6 arrangements possible with parallel spin in $3d^4 4s^2$ configuration.



Here, total 10 exchanges are possible, thus it involves more exchange energy and hence, is more stable.

Check Point 3

1. An *f*-orbital can accommodate how many electrons?
2. Hund's rule said that pairing of electrons takes place only when each orbital in a sub-shell is singly occupied. Explain, why?
3. Write down the electronic configuration of Cr in its ground state. (At. no. of Cr = 24)
4. Which properties of elements depend upon the electronic configuration and which do not?

WORKED **OUT** *Examples*

Example 1 *An ion with mass number 56 contains 3 units of positive charge and 30.4% more neutrons than the electrons. Assign the symbol to this ion.* **[NCERT]**

(a) $^{56}_{25}\text{Mn}$ (b) $^{56}_{26}\text{Fe}^{2+}$

(c) $^{56}_{26}\text{Fe}^{3+}$ (d) $^{56}_{25}\text{Mn}^{3+}$

Solution (c) Let the number of electrons in the ion = x

$$\therefore \quad \text{Number of neutrons} = x + \frac{30.4}{100}x = 1.304\,x$$

($\because$ Number of neutrons are 30.4% more than the number of electrons). In the neutral atom, number of electrons $= x + 3$ ($\because$ The ion carries $+3$ charge.)

So, number of protons $= x + 3$

We know that, mass number $= n + p = 1.304\,x + x + 3 = 56$

$$2.304\,x = 53,\ x = \frac{53}{2.304} = 23.003 \approx 23$$

$\therefore$ Number of protons $= 23 + 3 = 26$ = atomic number.

Therefore, the symbol of the ion is $^{56}_{26}\text{Fe}^{3+}$.

Example 2 *The atomic weight of an element is double of its atomic number. If there are four electrons in 2p orbital, the element is isotonic with*

(a) $_{20}\text{Ca}^{40}$ (b) $_{7}\text{N}^{15}$

(c) $_{7}\text{N}^{14}$ (d) $_{8}\text{O}^{17}$

Solution (b) Since, there are four electrons in $2p$ orbital, the outer configuration of the element is $2s^2, 2p^4$. The complete configuration of the element is $1s^2, 2s^2, 2p^4$.

The element contains total 8 electrons, so its atomic number is 8.

Then, the number of neutrons $= 16 - 8 = 8$

It is isotonic with $_{7}\text{N}^{15}$ (as it also contains 8 neutrons).

Example 3 *The radius of first Bohr orbit is x, then de-Broglie wavelength of electron in 3rd orbit is nearly*

(a) $2\pi x$ (b) $6\pi x$

(c) $9x$ (d) $\frac{x}{3}$

Solution (b) The radius of an orbit, $r_n \propto n^2$

Where, n = principal quantum number

$$\Rightarrow \quad \frac{r_1}{r_3} = \frac{1}{3^2}$$

If $\quad r_1 = x$ then $r_3 = 9x$

For third shell, $\quad 2\pi r_3 = 3\lambda$

$$\lambda = \frac{2\pi r_3}{3} = \frac{2\pi 9x}{3} = 6\pi x$$

Example 4 *Photoelectrons are liberated by ultraviolet light of wavelength 3000 Å from a metallic surface for which the photoelectric threshold is 4000 Å. The de-Broglie wavelength of electron emitted with maximum kinetic energy is*

(a) 1.2×10^{-9} m (b) 5.49×10^{-25} m

(c) 7.28×10^{-7} m (d) 1.65×10^{-19} m

Solution (a) KE = quantum energy – threshold energy

$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{3000 \times 10^{-10}} - \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{4000 \times 10^{-10}}$$

$$= 6.626 \times 10^{-19} - 4.9695 \times 10^{-19}$$

$$= 1.6565 \times 10^{-19}\ \text{J}$$

$$\text{KE} = 1.6565 \times 10^{-19} = \frac{1}{2}mv^2$$

$$\therefore \quad m^2v^2 = 2 \times 1.6565 \times 10^{-19} \times 9.1 \times 10^{-31}$$

$$mv = 5.49 \times 10^{-25}$$

$$\text{de-Broglie wavelength, } \lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}}{5.49 \times 10^{-25}}$$

$$= 1.2 \times 10^{-9}\ \text{m}$$

Example 5 *Two hydrogen atoms collide head-on and end up with zero kinetic energy. Each then emits a photon with a wavelength 121.6 nm. The transition that leads to this wavelength and the velocity of hydrogen atoms travelling before the collision are, respectively*

(Given, $R_H = 1.097 \times 10^7\ m^{-1}$ and $m_H = 1.67 \times 10^{-27}$ kg)

(a) $n_2 \to n_1;\ 4.43 \times 10^4$ (b) $n_4 \to n_3;\ 4.43 \times 10^4$

(c) $n_3 \to n_2;\ 2.63 \times 10^7$ (d) $n_2 \to n_3;\ 4.43 \times 10^4$

Solution (a) Wavelength is in UV region, thus n_1 will be 1.

$$\frac{1}{121.6 \times 10^{-9}} = 1.097 \times 10^7 \times 1^2 \times \left(\frac{1}{1^2} - \frac{1}{n_2^2}\right)$$

On solving, $n_2 \approx 2$

$$\frac{1}{2} mv^2 = \frac{hc}{\lambda}$$

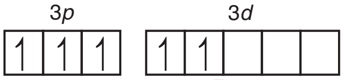
$$\frac{1}{2} \times 1.67 \times 10^{-27} \times v^2 = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{121.6 \times 10^{-9}}$$

$$v = 4.43 \times 10^4 \text{ m s}^{-1}$$

Example 6 *Maximum value of* $(n + l + m)$ *for unpaired electrons in second excited state of chlorine* $_{17}\text{Cl}$ *is*

(a) 28 (b) 25 (c) 20 (d) 18

Solution (b) Configuration in second excited state is written as



n	3	3	3	3	3
l	1	1	1	2	2
m	−1	0	+1	+2	+1

Total $n + l + m = 25$

Example 7 *What is the degeneracy of the nth level of hydrogen atom that has the energy* $\left(-\frac{R_H}{16}\right)$?

(a) 4 (b) 9 (c) 16 (d) 12

Solution (c) Energy of electron in the nth orbit in terms of R_H is

$$E_n = \frac{-R_H Z^2}{n^2}$$

For hydrogen atoms $Z = 1$, thus

$$E_n = -\frac{R_H}{n^2}$$

On comparing the above equation with the given equation, we get

$$n^2 = 16$$

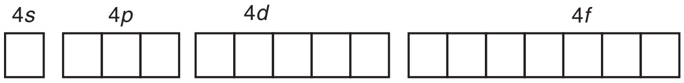
$$n = 4$$

For, $n = 4$ $l = 0(s)$ $m = 0$

$l = 1(p)$ $m = -1, 0, +1$

$l = 2(d)$ $m = -2, -1, 0, +1, +2$

$l = 3(f)$ $m = -3, -2, -1, 0, +1, +2, +3$



Degeneracy = total number of orbitals = 16

Example 8 *The four quantum numbers of the* 19*th electron in* $\text{Ti}(Z = 22)$ *are*

(a) $n = 4, l = 1, m = 0, s = +\frac{1}{2}$

(b) $n = 4, l = 0, m = 0, s = +\frac{1}{2}$

(c) $n = 3, l = 2, m = +2, s = +\frac{1}{2}$

(d) $n = 4, l = 2, m = -1, s = +\frac{1}{2}$

Solution (b) Electronic configuration of $\text{Ti}(Z = 22)$ is

$$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^2$$

19th is in $4s$, therefore,

Hence, $n = 4, l = 0, m = 0, s = +\frac{1}{2}$

Example 9 *The relationship between the* n^{th} *Bohr radius of hydrogen atom and* Li^{2+} *ion is*

(a) $r(\text{H}) = 2r\ (\text{Li}^{3+})$

(b) $r(\text{H}) = 3r\ (\text{Li})^{2+}$

(c) $r(\text{Li}^{2+}) = 3r\ (\text{H})$

(d) $r(\text{Li}^{2+}) = 2r\ (\text{H})$

Solution (b) For hydrogen atom

$$r(\text{H}) = \frac{a_0 n^2}{Z} = a_0 n^2 \qquad (\because Z = 1)$$

For Li^{2+}; $$r(\text{Li}^{2+}) = \frac{a_0 n^2}{Z} = \frac{a_0 n^2}{3} \qquad (\because Z = 3)$$

Now $$\frac{r(\text{H})}{r(\text{Li}^{2+})} = 3$$

$$\Rightarrow \quad r(\text{H}) = 3r(\text{Li}^{2+})$$

Example 10 *A compound of vanadium has a magnetic moment of 1.73 BM. The electronic configuration of the vanadium ion in the compound is*

(a) $1s^2, 2s^2 2p^6, 3s^2 3p^6, 3d^1$

(b) $1s^2, 2s^2 2p^6, 3s^2 3p^6\ 3d^1, 4s^2$

(c) $1s^2, 2s^2 2p^6, 3s^2 3p^6\ 3d^2$

(d) $1s^2, 2s^2 2p^6, 3s^2 3p^6\ 3d^1, 4s^1$

Solution (a) Magnetic moment = $\sqrt{n(n+2)}$

where, n is the number of unpaired electrons.

$$1.73 = \sqrt{n(n+2)}$$

$$\therefore \quad n = 1$$

$\therefore$ Vanadium atom must have one unpaired electron, hence its configuration is $_{23}V^{4+} = 1s^2, 2s^2p^6, 3s^2p^6, 3d^1$

Example 11 *Which of the following has non-spherical shell of electron?*

(a) He (b) B (c) Be (d) Li

Solution (b) The electronic configuration of the given atoms are as

He — $1s^2$

B — $1s^2, 2s^2, 2p^1$

Be — $1s^2, 2s^2$

Li — $1s^2, 2s^1$

Among these atoms, only B has p sub-shell which is a non-spherical shell.

Start Practice for JEE Main

Round I (Topically Divided Problems)

Sub-atomic Particles, Previous Models and Atomic Species

1. Which of the following statements about the electron is incorrect? **[NCERT Exemplar]**

(a) It is a negatively charged particle

(b) The mass of electron is equal to the mass of neutron

(c) It is a basic constituent of all atoms

(d) It is a constituent of cathode rays

2. Which of the following will not show deflection from the path on passing through an electric field? **[NCERT Exemplar]**

(a) Proton (b) Cathode rays

(c) Electron (d) Neutron

3. Which of the following conclusions could not be derived from Rutherford's α-particle scattering experiment? **[NCERT Exemplar]**

(a) Most of the space in the atom is empty

(b) The radius of the atom is about 10^{-10} m while that of nucleus is 10^{-15} m

(c) Electrons move in a circular path of fixed energy, called orbits

(d) Electrons and the nucleus are held together by electrostatic forces of attraction

4. Which of the following statements is incorrect?

(a) The charge on electron and proton are equal and opposite

(b) Neutrons have no charge

(c) The mass of proton and electron are nearly the same

(d) None of the above

5. Find the total mass of neutrons (in kg) in 7 mg of ^{14}C. (Assume that mass of a neutron = 1.675×10^{-27} kg. **[NCERT]**

(a) 2.40×10^{-8} (b) 4.37×10^{-6}

(c) 1.25×10^{-9} (d) 5.36×10^{-7}

6. Find the total number of protons in 34 mg of NH_3 at STP. (Mass of 1 $p = 1.6726 \times 10^{-27}$ kg). **[NCERT]**

(a) 12.044×10^{23} (b) 12.044×10^{22}

(c) 12.044×10^{21} (d) 12.044×10^{20}

7. The diameter of zinc atom is 2.6 Å. Calculate the number of atoms present in a length of 1.6 cm if the zinc atoms are arranged side by side lengthwise. **[NCERT Exemplar]**

(a) 6.023×10^{23} (b) 6.15×10^{7}

(c) 1.62×10^{19} (d) 6.15×10^{12}

8. Two atoms are said to be isobars if **[NCERT Exemplar]**

(a) they have same atomic number but different mass number

(b) they have same number of electrons but different number of neutrons

(c) they have same number of neutrons but different number of electrons

(d) sum of the number of protons and neutrons is same but the number of protons is different

9. Which of the following is isoelectronic with carbon atom?

(a) N^+ (b) O^{2-}

(c) Na^+ (d) Al^{3+}

10. Rutherford scattering formula fails for very small scattering angles because

(a) the kinetic energy of α-particles is larger

(b) the gold foil is very thin

(c) the full nuclear charge of the target atom is partially screened by its electron

(d) All of the above

11. Choose the arrangement which shows the increasing value of e/m for e, p, n and α-particles.

(a) $n < \alpha < p < e$ (b) $e < p < \alpha < n$

(c) $n < p < e < \alpha$ (d) $p < n < \alpha < e$

12. Which of the following pairs have identical values of e/m?

(a) A proton and a neutron
(b) A proton and deuterium
(c) Deuterium and an α-particle
(d) An electron and γ-rays

Nature of EMR and Spectra of Hydrogen

13. Emission transitions in the Paschen series end at orbit $n = 3$ and start from orbit n and can be represented as $\nu = 3.29 \times 10^{15}\ (\text{Hz}) \left[\frac{1}{3^2} - \frac{1}{n^2}\right]$.

Calculate the value of n if the transition is observed at 1285 nm. Find the region of the spectrum. **[NCERT]**

(a) 4, Infra-red (b) 5, Infra-red
(c) 6, Visible (d) 3, Infra-red

14. Yellow light emitted from a sodium lamp has a wavelength (λ) of 580 nm. Calculate the frequency (ν) and wave number $(\bar{\nu})$ of the yellow light. **[NCERT]**

(a) $5.17 \times 10^{14}\ \text{s}^{-1}$, $1.724 \times 10^{4}\ \text{cm}^{-1}$
(b) $4.27 \times 10^{14}\ \text{s}^{-1}$, $3.245 \times 10^{4}\ \text{cm}^{-1}$
(c) $1.26 \times 10^{15}\ \text{s}^{-1}$, $8.37 \times 10^{3}\ \text{cm}^{-1}$
(d) $51.7 \times 10^{14}\ \text{s}^{-1}$, $1.724 \times 10^{5}\ \text{cm}^{-1}$

15. What is the number of photons of light with a wavelength of 4000 pm that provide 1 J of energy? **[NCERT]**

(a) 4.9695×10^{17} (b) 4.9695×10^{8}
(c) 2.0122×10^{15} (d) 2.0122×10^{16}

16. Arrange the following type of radiations in increasing order of frequency. **[NCERT]**

(i) Radiation from microwave oven
(ii) Amber light from traffic signal
(iii) Radiation from FM radio
(iv) Cosmic rays from outer space and
(v) X-rays

The correct order is

(a) (i) < (iii) < (ii) < (iv) < v)
(b) (iii) < (i) < (v) < (ii) < (iv)
(c) (iii) < (i) < (ii) < (v) < (iv)
(d) (iii) < (v) < (i) < (ii) < (iv)

17. A 25 watt bulb emits monochromatic yellow light of wavelength 0.57 μm. The rate of emission of quanta per second is **[NCERT]**

(a) 7.169×10^{20} photon/s
(b) 8.29×10^{19} photon/s
(c) 7.289×10^{21} photon/s
(d) 7.169×10^{19} photon/s

18. Which of the following transitions are not allowed in the normal electronic emission spectrum of an atom?

(a) $2s \rightarrow 1s$ (b) $2p \rightarrow 1s$
(c) $3d \rightarrow 4p$ (d) $5p \rightarrow 3s$

19. The line spectra of two elements are not identical because

(a) the elements do not have the same number of neutrons
(b) they have different mass numbers
(c) their outermost electrons are at different energy levels
(d) All of the above

20. The maximum kinetic energy of the photoelectrons is found to be 6.63×10^{-19} J. When the metal is irradiated with a radiation of frequency 2×10^{15} Hz, the threshold frequency of the metal is about

(a) $2 \times 10^{15}\ \text{s}^{-1}$ (b) $1 \times 10^{15}\ \text{s}^{-1}$
(c) $2.5 \times 10^{15}\ \text{s}^{-1}$ (d) $4 \times 10^{15}\ \text{s}^{-1}$

21. What is the minimum energy that photons must possess in order to produce photoelectric effect with platinum metal? The threshold frequency for platinum is $1.3 \times 10^{15}\ \text{s}^{-1}$

(a) 3.6×10^{-13} erg (b) 8.2×10^{-13} erg
(c) 8.2×10^{-14} erg (d) 8.6×10^{-12} erg

22. An emission transition starts from the orbit having radius 1.3225 nm and ends at 211.6 pm. Name the series to which this transition belongs and the region of the spectrum. **[NCERT]**

(a) Lyman, UV (b) Balmer, visible
(c) Paschen, IR (d) Brackett, IR

23. Which of the following electron transition in hydrogen atom will require largest amount of energy?

(a) From $n = 1$ to $n = 2$ (b) From $n = 2$ to $n = 3$
(c) From $n = \infty$ to $n = 1$ (d) From $n = 3$ to $n = 5$

Bohr and Sommerfeld Models

24. Bohr's theory is applicable to

(a) He (b) Li^{2+}
(c) He^{2+} (d) None of these

25. According to Bohr's model of hydrogen atom

(a) total energy of the electron is quantised
(b) angular momentum of electron is quantised
(c) Both (a) and (b)
(d) None of the above

26. The radius of which of the following orbit is same as that of the first Bohr's orbit of hydrogen atom?

(a) $\text{Li}^{2+}(n = 2)$ (b) $\text{Li}^{2+}(n = 3)$
(c) $\text{Be}^{3+}(n = 2)$ (d) $\text{He}^{+}(n = 2)$

27. According to Bohr's theory, the angular momentum for an electron of 3rd orbit is

(a) $3\ \hbar$ (b) $1.5\hbar$ (c) $9\hbar$ (d) $2\ \dfrac{h}{\pi}$

28. The energy associated with the first orbit in the hydrogen atom is -2.18×10^{-18} J atom^{-1}. What is the energy associated with the fifth orbit? **[NCERT]**

(a) 0.43×10^{-18} J (b) 0.087×10^{-18} J

(c) 2.18×10^{-18} J (d) 3.16×10^{-15} J

29. Electromagnetic radiation of wavelength 242 nm is just sufficient to ionise the sodium atom. Calculate the ionisation energy of sodium in kJ mol^{-1}. **[NCERT]**

(a) 4.945×10^{5} kJ / mol (b) 4.945×10^{4} kJ / mol

(c) 4.945×10^{2} kJ / mol (d) 4.945×10^{3} kJ / mol

30. What is the maximum number of emission lines when the excited electron of a H-atom in $n = 6$ drops to the ground state? **[NCERT]**

(a) 2 (b) 10 (c) 15 (d) 20

31. The potential energy of an electron present in the ground state of Li^{2+} ion is

(a) $+\dfrac{3e^2}{4\pi\varepsilon_0 r}$ (b) $-\dfrac{3e}{4\pi\varepsilon_0 r}$

(c) $-\dfrac{3e^2}{4\pi\varepsilon_0 r}$ (d) $-\dfrac{3e^2}{4\pi\varepsilon_0 r^2}$

32. The velocity of an electron placed in 3rd orbit of H atom, will be

(a) 2.79×10^{7} cm/s (b) 9.27×10^{27} cm/s

(c) 7.29×10^{7} cm/s (d) 92.7×10^{7} cm/s

Modern Structure of Atom
(de-Broglie and Heisenberg's Principle)

33. The wave nature of electron is verified by

(a) de-Broglie (b) Davisson and Germer

(c) Rutherford (d) All of these

34. Table-Tennis ball has a mass 10 g and a speed of 90 m/s. If speed can be measured within an accuracy of 4%, what will be the uncertainty in position? **[NCERT Exemplar]**

(a) 3.6×10^{-23} m (b) 1.46×10^{-33} m

(c) 2.8×10^{-30} m (d) 1.00×10^{-34} m

35. Similar to electron diffraction, neutron diffraction microscope is also used for the determination of the structure of molecules. If the wavelength used here is 800 pm, calculate the characteristics velocity associated with the neutron (mass of neutron $= 1.675\times10^{-27}$ kg). **[NCERT]**

(a) 4.92×10^{2} (b) 2.46×10^{3}

(c) 9.84×10^{2} (d) 0.246×10^{3}

36. According to de-Broglie, matter should exhibit dual behaviour, that is both particle and wave like properties. However, a cricket ball of mass 100 g does not move like a wave when it is thrown by a bowler at a speed of 100 km/h. Calculate the wavelength of the ball. **[NCERT Exemplar]**

(a) 2.385×10^{-36} m (b) 23.85×10^{-36} m

(c) 238.5×10^{-36} m (d) 2385×10^{-36} m

37. Out of electron, proton, neutron and α-particle which one will have a higher velocity to produce matter wave of the same wavelength? **[NCERT Exemplar]**

(a) Electron (b) Proton

(c) Neutron (d) α-particle

38. Which of the following particles moving with same velocity would be associated with smallest de-Broglie wavelength?

(a) Helium molecule (b) Oxygen molecule

(c) Hydrogen molecule (d) Carbon molecule

39. The mass of an electron is m, its charge is e and it is accelerated from rest through a potential difference, V. The velocity of electron will be calculated by formula

(a) $\sqrt{\dfrac{V}{m}}$ (b) $\sqrt{\dfrac{eV}{m}}$

(c) $\sqrt{\left(\dfrac{2eV}{m}\right)}$ (d) None of these

40. What is the wavelength of an α-particle having mass 6.6×10^{-27} kg moving with a speed of 10^{5} cm s^{-1}? ($h = 6.6\times10^{-34}$ kg m^{2}- s)

(a) 2×10^{-12} m (b) 3×10^{-10} m

(c) 1×10^{-10} m (d) 2×10^{-10} m

41. The de-Broglie wavelength relates to applied voltage for α-particles as

(a) $\lambda = \dfrac{12.3\ \text{Å}}{\sqrt{V}}$ (b) $\lambda = \dfrac{0.286}{\sqrt{V}}\ \text{Å}$

(c) $\lambda = \dfrac{0.101}{\sqrt{V}}\ \text{Å}$ (d) $\lambda = \dfrac{0.856}{\sqrt{V}}\ \text{Å}$

42. The uncertainty in momentum of an electron is 1×10^{-5} kg m / s. The uncertainty in its position will be ($h = 6.62\times10^{-34}$ kg m^{2} / s)

(a) 2.36×10^{-28} m (b) 5.25×10^{-28} m

(c) 2.27×10^{-30} m (d) 5.27×10^{-30} m

43. If the kinetic energy of an electron is increased four times, the wavelength of the de-Broglie wave associated with it would becomes

(a) half times (b) $\dfrac{1}{4}$ times

(c) four times (d) two times

Wave Mechanical Model and Quantum Numbers

44. The two electrons in K-subshell will differ in
(a) principal quantum number
(b) azimuthal quantum number
(c) magnetic quantum number
(d) spin quantum number

45. Which of the following arrangement of orbitals is in the increasing order of energy? **[NCERT Exemplar]**
(a) $1s, 2s, 2p, 3s$ (b) $4s, 3s, 3p, 4d$
(c) $5p, 4d, 5d, 4f, 6s$ (d) $5f, 6d, 7s, 7p$

46. What is the lowest value of n that allows g orbitals to exist? **[NCERT]**
(a) 3 (b) 4
(c) 5 (d) 6

47. The number of spherical nodes in $3p$ orbital is
(a) 0 (b) 1
(c) 2 (d) 3

48. Which of the following sets of quantum numbers are not possible? **[NCERT]**

I. $n = 0, l = 0, m_l = 0, m_s = +\frac{1}{2}$
II. $n = 1, l = 0, m_l = 0, m_s = -\frac{1}{2}$
III. $n = 1, l = 1, m_l = 0, m_s = +\frac{1}{2}$
IV. $n = 2, l = 1, m_l = 0, m_s = -\frac{1}{2}$
V. $n = 3, l = 3, m_l = -3, m_s = +\frac{1}{2}$
VI. $n = 3, l = 1, m_l = 0, m_s = +\frac{1}{2}$

(a) I, II and III (b) I, III and V
(c) I, IV and VI (d) I, II, III and V

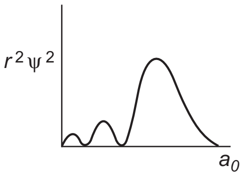
49. Total number of orbitals associated with third shell will be **[NCERT Exemplar]**
(a) 2 (b) 4
(c) 9 (d) 3

50. Number of angular nodes for $4d$ orbital is **[NCERT Exemplar]**
(a) 4 (b) 3
(c) 2 (d) 1

51. The Z-component of angular momentum of an electron in an atomic orbital is governed by the
(a) magnetic quantum number
(b) azimuthal quantum number
(c) spin quantum number
(d) principal quantum number

52. Which of the following statements regarding an orbital is correct?
(a) An orbital is a definite trajectory around the nucleus in which electron can move
(b) An orbital always has spherical trajectory
(c) An orbital is the region around the nucleus where there is a 90 – 95% probability of finding all the electrons of an atom
(d) An orbital is characterised by 4 quantum numbers n, l, m and s

53. Which of the following radial distribution graphs correspond to $n = 3, l = 2$ for an atom?

(a)


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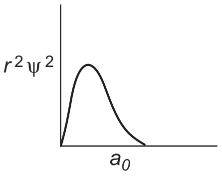

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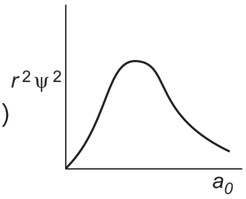

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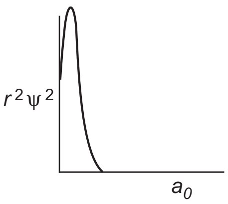


54. For a particular value of azimuthal quantum number, the total number of magnetic quantum number values are given by
(a) $l = \frac{m+1}{2}$ (b) $l = \frac{m-1}{2}$
(c) $l = \frac{2m+1}{2}$ (d) $m = \frac{2l+1}{2}$

55. Among the following sets of quantum numbers, which one is incorrect for $4d$-electron?
(a) $4, 3, 2, +\frac{1}{2}$ (b) $4, 2, 1, +\frac{1}{2}$
(c) $4, 2, -2, +\frac{1}{2}$ (d) $4, 2, 1, -\frac{1}{2}$

56. The quantum numbers $+\frac{1}{2}$ and $-\frac{1}{2}$ for an electron represent
(a) rotation of electron in clockwise and anticlockwise direction respectively
(b) rotation of electron in anticlockwise and clockwise direction respectively
(c) magnetic moment of electron pointing up and down respectively
(d) two quantum mechanical spin states which have no classical analogue

57. For an electron in a hydrogen atom, the wave function ψ is proportional to $\exp^{-t/a_0}$, where a_0 is the Bohr's radius. What is the ratio of the probability of finding the electron at the nucleus to the probability of finding it at a_0?

(a) e (b) e^2 (c) $\frac{1}{e^2}$ (d) Zero

58. Consider the following statements.

1. Electron density in xy plane in $3d_{x^2-y^2}$ orbital is zero
2. Electron density in xy plane in $3d_{z^2}$ orbital is zero
3. 2s orbital has only one spherical node
4. For $2p_z$ orbital yz is the nodal plane

The correct statements are

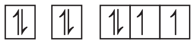
(a) 2 and 3 (b) 1, 2, 3, 4

(c) Only 2 (d) 1 and 3

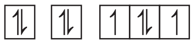
Filling of Electrons in Orbitals and Related Principles

59. The distribution of electrons in oxygen atom (atomic number 8) is shown by **[NCERT Exemplar]**

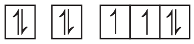
(a)



(b)



(c)



(d) All of these

60. For the electrons of oxygen atom, which of the following statements is correct? **[NCERT Exemplar]**

(a) Z_{eff} for an electron in a 2 s orbital is the same as Z_{eff} for an electron in a 2p orbital

(b) An electron in the 2s orbital has the same energy as an electron in the 2p orbital

(c) Z_{eff} for an electron in 1s orbital is the same as Z_{eff} for an electron in a 2s orbital

(d) The two electrons present in the 2s orbital have spin quantum numbers m_s but of opposite sign

61. The pair of ions having same electronic configuration is **[NCERT Exemplar]**

(a) Cr^{3+}, Fe^{3+} (b) Fe^{3+}, Mn^{2+}

(c) Fe^{3+}, Co^{3+} (d) Sc^{3+}, Cr^{3+}

62. Find the electronic configuration of the O^{2-} ion **[NCERT]**

(a) $1s^2, 2s^2, 2p^4$ (b) $1s^2, 2s^2, 2p^6$

(c) $1s^2, 2s^2, 2p^5$ (d) $1s^2, 2s^2$

63. Which of the following options does not represent ground state electronic configuration of an atom? **[NCERT Exemplar]**

(a) $1s^2 2s^2 2p^6, 3s^2 3p^6, 3d^8, 4s^2$

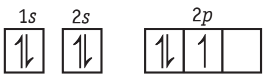
(b) $1s^2 2s^2 2p^6, 3s^2 3p^6 3d^9, 4s^2$

(c) $1s^2 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^1$

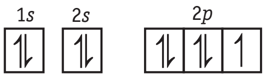
(d) $1s^2 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^1$

64. Which of the following will violates aufbau principle as well as Pauli's exclusion principle?

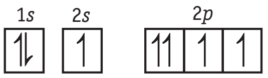
(a)



(b)



(c)



(d) None of the above

65. The atomic number of an element is 35 and its mass is 81. The number of electrons in its outermost shell is

(a) 3 (b) 5 (c) 7 (d) 9

66. How many unpaired electrons are present in Ni^{2+} cation? (At. no. = 28)

(a) 0 (b) 2 (c) 4 (d) 6

67. The electronic configuration with maximum exchange energy will be

(a) $3d^1_{xy}, 3d^1_{yz}, 3d^1_{zx}, 4s^1$

(b) $3d^1_{xy}, 3d^1_{yz}, 3d^1_{zx}, 3d^1_{x^2-y^2}, 3d^1_{z^2}, 4s^1$

(c) $3d^2_{xy}, 3d^2_{yz}, 3d^2_{zx}, 3d^2_{x^2-y^2}, 3d^1_{z^2}, 4s^1$

(d) $3d^2_{xy}, 3d^2_{yz}, 3d^2_{zx}, 3d^2_{x^2-y^2}, 3d^2_{z^2}, 4s^1$

68. A Mo atom in its ground state has $4d^5, 5s^1$ configuration and a Ag atom has $4d^{10}, 5s^1$ configuration. This is because a shell which is half-filled or completely filled is particularly

(a) strongly exchange stabilised

(b) weakly exchange stabilised

(c) weakly exchange destabilised

(d) strongly exchange destabilised

69. In a set of degenerate orbitals, the electrons distribute themselves to retain like spins as far as possible. This statement belongs to

(a) Pauli's exclusion principle

(b) Aufbau principle

(c) Hund's rule of maximum multiplicity

(d) Slater's rule

70. An f-shell containing 6 unpaired electrons can exchange

(a) 6 electrons (b) 9 electrons

(c) 12 electrons (d) 15 electrons

Round II (Mixed Bag)

Only One Correct Option

1. The work function (ϕ) of some metals is listed below. The number of metals which will show photoelectric effect when light of 300 nm wavelength falls on the metal is

Metal	Li	Na	K	Mg	Cu	Ag	Fe	Pt	W
ϕ (eV)	2.4	2.3	2.2	3.7	4.8	4.3	4.7	6.3	4.75

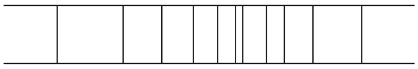
(a) 2 (b) 4 (c) 6 (d) 8

2. Which transition in the hydrogen atomic spectrum will have the same wavelength as the Balmer transition, $n = 4$ to $n = 2$ of He^+ spectrum? [**NCERT**]

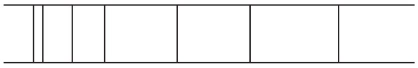
(a) $n = 4$ to $n = 3$
(b) $n = 3$ to $n = 2$
(c) $n = 4$ to $n = 2$
(d) $n = 2$ to $n = 1$

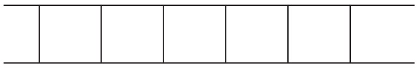
3. Which diagram best represents the appearance of the line spectrum of atomic hydrogen in the visible region?

Increasing wavelength

(a)


(b)


(c)


(d)


4. The electronic configuration of the oxide ion is much most similar to the electronic configuration of the

(a) sulphide ion
(b) nitride ion
(c) oxygen atom
(d) nitrogen atom

5. The number of photons emitted per second by a 60 W source of monochromatic light of wavelength 663 nm is ($h = 6.63 \times 10^{-34}$ Js).

(a) 4×10^{-20}
(b) 1.54×10^{20}
(c) 3×10^{-20}
(d) 2×10^{20}

6. The work function for caesium atom is 1.9 eV. If the caesium element is irradiated with a wavelength 500nm, the velocity of the ejected photoelectron is [**NCERT**]

(a) 4.527×10^5
(b) 3.258×10^5
(c) 1.892×10^6
(d) 2.329×10^5

7. The ejection of the photoelectron from the silver metal in the photoelectric effect experiment can be stopped by applying the voltage of 0.35 V when the radiation 256.7 nm is used. Calculate the work function for silver metal. [**NCERT**]

(a) 4.83 eV
(b) 4.48 eV
(c) 4.45 eV
(d) 4.34 eV

8. The quantum numbers of six electrons are given below. Arrange them in the order of increasing energies.

I. $n = 4, l = 2, m_l = -2, m_s = -\frac{1}{2}$
II. $n = 3, l = 2, m_l = 1, m_s = +\frac{1}{2}$
III. $n = 4, l = 1, m_l = 0, m_s = +\frac{1}{2}$
IV. $n = 3, l = 2, m_l = -2, m_s = -\frac{1}{2}$
V. $n = 3, l = 1, m_l = -1, m_s = +\frac{1}{2}$
VI. $n = 4, l = 1, m_l = 0, m_s = +\frac{1}{2}$ [**NCERT**]

(a) $1 < 2 = 4 < 3 = 6 < 5$
(b) $5 < 2 = 6 < 3 = 4 < 1$
(c) $5 < 3 = 6 < 2 = 4 < 1$
(d) $5 < 2 = 4 < 3 = 6 < 1$

9. An electron, a proton and an alpha particle have KE of $16E$, $4E$ and E respectively. What is the qualitative order of their de-Broglie wavelengths?

(a) $\lambda_e > \lambda_p > \lambda_\alpha$
(b) $\lambda_p = \lambda_\alpha > \lambda_e$
(c) $\lambda_p < \lambda_e < \lambda_\alpha$
(d) $\lambda_\alpha < \lambda_e \approx \lambda_p$

10. Suppose 10^{-17} J of light energy is needed by the interior of a human eye to see an object. Calculate the number of photons of green light ($\lambda = 550$ nm) needed to generate this minimum amount of energy.

(a) 26 (b) 27 (c) 28 (d) 29

11. The incorrect statement about Bohr's orbit of hydrogen atom is

(a) $r = n^2 \dfrac{h^2}{4\pi^2 m \left(\dfrac{e^2}{4\pi\varepsilon_0}\right)}$

(b) KE of electron = PE of electron

(c) $E = -\dfrac{1}{n^2} \dfrac{2\pi^2 m \left(\dfrac{e^2}{4\pi\varepsilon_0}\right)^2}{h^2}$

(d) None of the above is incorrect

12. If the photon of the wavelength 150 pm strikes an atom and one of its inner bound electrons is ejected out with a velocity of 1.5×10^7 ms^{-1}, the energy with which it is bound to the nucleus is **[NCERT]**

(a) 1.222×10^{-16} J (b) 7.63×10^{3} eV
(c) 1.22×10^{-19} kJ (d) All of these

13. An electron beam is accelerated through a potential difference of 10,000 volt. The de-Broglie wavelength of the electron beam is

(a) 0.123 Å (b) 0.356 Å
(c) 0.186 Å (d) 0.258 Å

14. I_2 molecule dissociates into atoms after absorbing light of 4500 Å. If one quantum of energy is absorbed by each molecule, the KE of iodine atoms will be (BE of I_2 = 240 kJ/mol)

(a) 240×10^{-19} J
(b) 0.216×10^{-19} J
(c) 2.16×10^{-19} J
(d) 2.40×10^{-19} J

15. A particle A moving with a certain velocity has the de-Broglie wavelength of 1 Å. For particle B with mass 25% of A and velocity 75% of A, calculate the de-Broglie wavelength.

(a) 3 Å (b) 5.33 Å
(c) 6.88 Å (d) 0.48 Å

16. Lifetimes of the molecules in the excited states are often measured by using pulsed radiation source of duration nearly in the nanosecond range. If the radiation source has the duration of 2*ns* and the number of photons emitted during the pulse source is 2.5×10^{15}, calculate the energy of the source. **[NCERT]**

(a) 8.28×10^{-10} J (b) 8.28×10^{-10} kJ
(c) 8.28×10^{-10} eV (d) All of these

17. If the shortest wavelength of H-atom in Lyman series is x, the longest wavelength in Balmer series of He^+ is

(a) $\frac{36x}{5}$ (b) $\frac{5x}{9}$
(c) $\frac{x}{4}$ (d) $\frac{9x}{5}$

18. If uncertainties in the measurement of position and momentum of an electron are equal, the uncertainty in the measurement of velocity is

(a) 8.0×10^{12} ms^{-1}
(b) 4.2×10^{10} ms^{-1}
(c) 8.5×10^{10} ms^{-1}
(d) 6.2×10^{10} ms^{-1}

19. An ion with mass number 37 possesses one unit of negative charge. If the ion contains 11.1% more neutrons than the electrons, find the symbol of the ion. **[NCERT]**

(a) $^{35}_{17}Cl$ (b) $^{37}_{17}Cl^-$
(c) $^{37}_{19}K^+$ (d) None of these

20. Chlorophyll present in green leaves of plants absorbs light at 4.620×10^{14} Hz. Which part of the electromagnetic spectrum does it belong to? **[NCERT Exemplar]**

(a) UV (b) IR (c) Far IR (d) Visible

21. Some energy is required to ionize a H-atom if the electron occupies $n = 5$ orbit. The ratio of the ionization enthalpy of H-atom (energy required to remove the electron from $n = 1$ orbit) with the energy required to ionise H-atom if electron occupies $n = 5$ orbit is **[NCERT]**

(a) 1 : 25 (b) 25 : 1 (c) 1 : 5 (d) 5 : 1

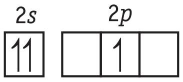
22. What is the colour of light emitted when the electron in a hydrogen atom undergoes transition from an energy level with $n = 4$ to an energy level with $n = 2$? **[NCERT]**

(a) Blue (b) White (c) Green (d) Red

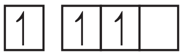
23. Which of the following is correctly matched?

(a) Momentum of H- atom when electrons return from $n = 2$ to $n = 1$: $\frac{3Rh}{4}$
(b) Momentum of photon : Independent of wavelength of light
(c) e/m ratio of anode rays : Independent of gas in the discharge tube
(d) Radius of nucleus : $(\text{Mass no.})^{1/2}$

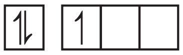
24. Which among the following is correct for $_5B$ in normal state?

(a) 

: Against Hund's rule

(b) 
: Against Aufbau principle as well as Hund's rule

(c) 
: Violation of Pauli's exclusion principle and not Hund's rule

(d) 
: Against Aufbau principle

25. The uncertainty in position for a dust particle ($m = 10^{-11}$ g; diameter = 10^{-4} cm and velocity = 10^{-4} cm/s) will be (The error in measurement of velocity is 1%)

(a) 5.27×10^{-4} cm (b) 5.27×10^{-5} cm
(c) 5.27×10^{-6} cm (d) 5.27×10^{-7} cm

26. If an electron has spin quantum number of $+\frac{1}{2}$ and a magnetic quantum number of -1, it cannot be represented in an

(a) s-orbital
(b) p-orbital
(c) d-orbital
(d) f-orbital

27. How many electrons in an atom may have the following quantum number? **[NCERT]**

(i) $n = 4, m_s = \frac{1}{2}$ (ii) $n = 3, l = 0$

(a) 32 and 2 respectively
(b) 16 and 2 respectively
(c) 16 and 1 respectively
(d) 32 and 1 respectively

28. In the ground state of Cu^+, the number of shell occupied, sub-shells occupied, filled orbitals and unpaired electrons respectively are

(a) 4, 8, 15, 0
(b) 3, 6, 15, 1
(c) 3, 6, 14, 0
(d) 4, 7, 14, 2

29. Following results are observed when sodium metal is irradiated with different wavelengths. Calculate threshold wavelength **[NCERT]**

λ (nm)	500	450	400
$v \times 10^5$ (ms^{-1})	2.55	4.35	5.20

(a) 4.28×10^{-6} m
(b) 5.31×10^{-7} m
(c) 3.29×10^{-9} m
(d) 2.48×10^{-7} m

30. Match the following species with their corresponding ground state electronic configuration.

	Atom/Ion		Electronic configuration
A.	Cu	1.	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}$
B.	Cu^{2+}	2.	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2$
C.	Zn^{2+}	3.	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^1$
D.	Cr^{3+}	4.	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^9$
		5.	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^3$

Codes **[NCERT Exemplar]**

	A	B	C	D
(a)	1	2	3	4
(b)	2	3	4	5
(c)	3	4	2	5
(d)	3	4	1	5

31. The frequency of revolution of an electron in the second Bohr orbit in hydrogen atom is

(a) 8.18×10^{14} Hz
(b) 2.39×10^{15} Hz
(c) 3.29×10^{16} Hz
(d) 9.25×10^{14} Hz

32. Determine the Bohr orbit of Li^{2+} ion in which electron is moving at speed equal to the speed of electron in the first Bohr orbit of H-atom.

(a) 1
(b) 2
(c) 3
(d) 4

33. A mixture contains atoms of fluorine and chlorine. The removal of an electron from each atom of sample absorbs 284 kJ while the addition of an electron to each atom of mixture releases 68.89 kJ. Determine the percentage composition of the F in the mixture, given that the ionization energies of F and Cl are 27.91×10^{-22} and 20.77×10^{-22} kJ, respectively, and electron affinities are 5.53×10^{-22} and 5.78×10^{-22} kJ respectively.

(a) 62.19%
(b) 37.8%
(c) 12.1%
(d) 40.2%

More than One Correct Option

34. Which of the following statements concerning the quantum numbers are correct? **[NCERT Exemplar]**

(a) Angular quantum number determines the three dimensional shape of the orbital
(b) The principal quantum number determines the orientation and energy of the orbital
(c) Magnetic quantum number determines the size of the orbital
(d) Spin quantum number of an electron determines the orientation of the spin of electron relative to the chosen axis

35. Which of the following statement/s is/are correct?

(a) The oxidation state of nitrogen in HN_3 is 3
(b) The electronic configuration of Cr is $3d^5 4s^1$
(c) In silver atom, 23 electrons have a spin of one type and 24 of the opposite type (At. no. 47)
(d) The magnetic quantum number may have negative values

36. Which of the following sets of quantum numbers are correct? **[NCERT Exemplar]**

	n	l	m_l		n	l	m_l
(a)	1	1	+ 2	(b)	2	1	+1
(c)	3	2	− 2	(d)	3	4	− 2

37. In which of the following pairs, the ions are iso-electronic? **[NCERT Exemplar]**

(a) Na^+, Mg^{2+}
(b) Al^{3+}, O^-
(c) Na^+, O^{2-}
(d) N^{3-}, Cl^-

38. Out of the following pairs of electrons, identify the pairs of electrons present in degenerate orbitals : **[NCERT Exemplar]**

(a) (i) $n = 3, l = 2, m_l = -2, m_s = -\frac{1}{2}$

(ii) $n = 3, l = 2, m_l = -1, m_s = -\frac{1}{2}$

(b) (i) $n = 3, l = 1, m_l = 1, m_s = +\frac{1}{2}$

(ii) $n = 3, l = 2, m_l = 1, m_s = +\frac{1}{2}$

(c) (i) $n = 4, l = 1, m_l = 1, m_s = +\frac{1}{2}$

(ii) $n = 3, l = 2, m_l = 1, m_s = +\frac{1}{2}$

(d) (i) $n = 3, l = 2, m_l = +2, m_s = -\frac{1}{2}$

(ii) $n = 3, l = 2, m_l = +2, m_s = +\frac{1}{2}$

Assertion and Reason

Directions (Q. No. 39 to 43) *Each of these questions contains two statements : Statement* I (*Assertion*) *and Statement* II (*Reason*). *Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes* (*a*), (*b*), (*c*), (*d*) *given below :*

(a) Statement I is true; Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true; Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

39. **Statement I** The charge to mass ratio of the particles in anode rays depends on nature of the gas taken in the discharge tube.

Statement II The particles in anode rays carry positive charge.

40. **Statement I** It is impossible to determine the exact position and exact momentum of an electron simultaneously.

Statement II The path of an electron in an atom is clearly defined. **[NCERT Exemplar]**

41. **Statement I** Black body is an ideal body that emits and absorbs radiations of all frequencies.

Statement II The frequency of radiation emitted by a body goes from a lower frequency to higher frequency with an increase in temperature. **[NCERT Exemplar]**

42. **Statement I** The radius of second orbit of He^+ is equal to that of first orbit of hydrogen.

Statement II The radius of an orbit in hydrogen like species is directly proportional to n^2 and inversely proportional to Z.

43. **Statement I** Only principal quantum number determines the energy of an electron in an orbital in sodium atom.

Statement II For one electron system, the expression of energy is the same as that obtained in Bohr's theory.

Comprehension Based Questions

Directions (Q. Nos. 44 and 45) For a single electron atom or ion the wave number of radiation emitted during the transition of electron from a higher energy state ($n = n_2$) to a lower energy state ($n = n_1$) is given by the expression

$$\bar{\nu} = \frac{1}{\lambda} = R_H \cdot Z^2 \left\{\frac{1}{n_1^2} - \frac{1}{n_2^2}\right\} \quad \text{... (i)}$$

where $R_H = \frac{2\pi^2\, m\, k^2\, e^4}{h^3 C}$ = Rydberg constant for H-atom

where the terms have their usual meanings.

For Lyman series $n_1 = 1$ (fixed for all the lines) while $n_2 = 2, 3, 4, \ldots$ for successive lines *i.e.*, Ist, 2nd, 3rd ... lines, respectively. For Balmer series : $n_1 = 2$ (fixed for all the lines) while $n_2 = 3, 4, 5 \ldots$ for successive lines.

44. The ratio of the wave numbers for the highest energy transition of electron in Lyman and Balmer series of H-atom is

(a) 4:1 (b) 6:1 (c) 9:1 (d) 3:1

45. If proton in H-nucleus be replaced by positron having the same mass as that of proton but same charge as that of proton, then considering the nuclear motion, the wavenumber of the lowest energy transition of He^+ ion in Lyman series will be equal to

(a) $2\,R_H$ (b) $3\,R_H$
(c) $4\,R_H$ (d) R_H

Directions (Q. Nos. 46 to 48) According to the uncertainty principle, it is impossible to know simultaneously both the conjugate properties accurately. Both the position and the momentum of the particle at any instant can't be determined with absolute exactness or certainty. The uncertainty in measurement of position, Δx and the uncertainty of determination of momentum, ΔP are related by Heisenberg's relationship as

$$\Delta x \times \Delta P \geq \frac{h}{4\pi}$$

or

$$\Delta x \times m\Delta v \geq \frac{h}{4\pi}$$

If position is known quite accurately *i.e.,* Δx is very small, the uncertainty regarding velocity, Δv becomes immensely large and *vice-versa*. It is therefore, very clear that the uncertainty principle is only important in considering measurements of small particles comprising an atomic system.

46. If uncertainty in the position of electron is zero, the uncertainty in its momentum would be

(a) $< \frac{h}{4\pi}$ (b) $\geq \frac{h}{4\pi}$
(c) zero (d) infinite

47. The uncertainty in position of an electron ($m = 9.1 \times 10^{-28}$ g) moving with a velocity 3×10^4 cm/s accurate upto 0.001% will be

(a) 3.84 cm
(b) 1.92 cm
(c) 7.68 cm
(d) 5.76 cm

48. If the light of wavelength, λ is used to observe an electron then uncertainty in position of the electron would be

(a) less than λ
(b) more than λ
(c) equal to λ
(d) equal to or greater than λ

Previous Years' Questions

49. The electrons identified by quantum numbers n and l

(1) $n = 4, l = 1$
(2) $n = 4, l = 0$
(3) $n = 3, l = 2$
(4) $n = 3, l = 1$

can be placed in the order of increasing energy as **[AIEEE 2012]**

(a) $3 < 4 < 2 < 1$
(b) $4 < 2 < 3 < 1$
(c) $2 < 4 < 1 < 3$
(d) $1 < 3 < 2 < 4$

50. A gas absorbs photon of 355 nm and emits at two wavelengths. If one of the emission is at 680 nm, the other is at **[AIEEE 2011]**

(a) 1035 nm
(b) 325 nm
(c) 743 nm
(d) 518 nm

51. The frequency of light emitted for the transition $n = 4$ to $n = 2$ of He^+ is equal to the transition in H atom corresponding to which of the follwing? **[AIEEE 2011]**

(a) $n = 3$ to $n = 1$
(b) $n = 2$ to $n = 1$
(c) $n = 3$ to $n = 2$
(d) $n = 4$ to $n = 3$

52. The energy required to break one mole of Cl — Cl bonds in Cl_2 is 242 kJ mol^{-1}. The longest wavelength of light capable of breaking a single Cl — Cl bond is **[AIEEE 2010]**

(a) 594 nm
(b) 640 nm
(c) 700 nm
(d) 494 nm

53. Ionisation energy of He^+ is 19.6×10^{-18} J atom^{-1}. The energy of the first stationary state ($n = 1$) of Li^{2+} is **[AIEEE 2010]**

(a) 4.41×10^{-16} J atom^{-1}
(b) -4.41×10^{-17} J atom^{-1}
(c) -2.2×10^{-15} J atom^{-1}
(d) 8.82×10^{-17} J atom^{-1}

54. Calculate the wavelength (in nanometer) associated with a proton moving at 1.0×10^3 ms^{-1} (mass of proton = 1.67×10^{-27} kg and $h = 6.63 \times 10^{-34}$ Js) **[AIEEE 2009]**

(a) 0.032 nm
(b) 0.40 nm
(c) 2.5 nm
(d) 14.0 nm

55. In an atom, an electron is moving with a speed of 600 m/s with an accuracy of 0.005%. Certainity with which the position of the electron can be located is ($h = 6.6 \times 10^{-34}$ kg m^2 s^{-1}, mass of electron, $e_m = 9.1 \times 10^{-31}$ kg) **[AIEEE 2009]**

(a) 1.52×10^{-4} m
(b) 5.10×10^{-3} m
(c) 1.92×10^{-3} m
(d) 3.84×10^{-3} m

56. The ionisation enthalpy of hydrogen atom is 1.312×10^6 J mol^{-1}. The energy required to excite the electron in the atom from $n = 1$ to $n = 2$ is **[AIEEE 2008]**

(a) 8.51×10^5 J mol^{-1}
(b) 6.56×10^5 J mol^{-1}
(c) 7.56×10^5 J mol^{-1}
(d) 9.84×10^5 J mol^{-1}

57. Which of the following sets of quantum numbers represents the highest energy of an atom? **[AIEEE 2007]**

(a) $n = 3, l = 1, m = 1, s = +1/2$
(b) $n = 3, l = 2, m = 1, s = +1/2$
(c) $n = 4, l = 0, m = 0, s = +1/2$
(d) $n = 3, l = 0, m = 0, s = +1/2$

58. Which one of the following sets of ions represents a collection of isoelectronic species? **[AIEEE 2006]**

(a) K^+, Cl^-, Ca^{2+}, Sc^{3+}
(b) Ba^{2+}, Sr^{2+}, K^+, S^{2-}
(c) N^{3-}, O^{2-}, F^-, S^{2-}
(d) Li^+, Na^+, Mg^{2+}, Ca^{2+}

59. According to Bohr's theory, the angular momentum of an electron in 5th orbit is **[AIEEE 2006]**

(a) $25\frac{h}{\pi}$
(b) $1.0\frac{h}{\pi}$
(c) $10\frac{h}{\pi}$
(d) $2.5\frac{h}{\pi}$

60. Which one of the following statements in relation to the hydrogen atom is correct? **[AIEEE 2005]**

(a) 3s, 3p and 3d orbitals all have the same energy
(b) 3s and 3p orbitals are of lower energy than 3d orbital
(c) 3p orbital is lower in energy than 3d orbital
(d) 3s orbital is lower in energy than 3p orbital

Answers

Round I

1. (b)	**2.** (d)	**3.** (c)	**4.** (c)	**5.** (b)	**6.** (c)	**7.** (b)	**8.** (d)	**9.** (a)	**10.** (c)
11. (a)	**12.** (c)	**13.** (b)	**14.** (a)	**15.** (d)	**16.** (c)	**17.** (d)	**18.** (c)	**19.** (c)	**20.** (b)
21. (d)	**22.** (b)	**23.** (a)	**24.** (b)	**25.** (c)	**26.** (c)	**27.** (a)	**28.** (b)	**29.** (c)	**30.** (c)
31. (c)	**32.** (c)	**33.** (b)	**34.** (b)	**35.** (a)	**36.** (c)	**37.** (a)	**38.** (b)	**39.** (c)	**40.** (c)
41. (c)	**42.** (d)	**43.** (a)	**44.** (d)	**45.** (a)	**46.** (c)	**47.** (b)	**48.** (b)	**49.** (c)	**50.** (c)
51. (b)	**52.** (c)	**53.** (c)	**54.** (b)	**55.** (a)	**56.** (d)	**57.** (d)	**58.** (a)	**59.** (d)	**60.** (d)
61. (b)	**62.** (b)	**63.** (b)	**64.** (c)	**65.** (c)	**66.** (b)	**67.** (d)	**68.** (a)	**69.** (c)	**70.** (d)

Round II

1. (b)	**2.** (d)	**3.** (c)	**4.** (b)	**5.** (d)	**6.** (a)	**7.** (b)	**8.** (d)	**9.** (a)	**10.** (c)
11. (b)	**12.** (b)	**13.** (a)	**14.** (b)	**15.** (b)	**16.** (a)	**17.** (d)	**18.** (a)	**19.** (b)	**20.** (d)
21. (b)	**22.** (a)	**23.** (a)	**24.** (c)	**25.** (c)	**26.** (a)	**27.** (b)	**28.** (c)	**29.** (b)	**30.** (d)
31. (a)	**32.** (c)	**33.** (b)	**34.** (a,d)	**35.** (b,c,d)	**36.** (b,c)	**37.** (a,c)	**38.** (a,d)	**39.** (b)	**40.** (c)
41. (b)	**42.** (d)	**43.** (d)	**44.** (a)	**45.** (b)	**46.** (d)	**47.** (b)	**48.** (a)	**49.** (b)	**50.** (c)
51. (b)	**52.** (d)	**53.** (b)	**54.** (b)	**55.** (c)	**56.** (d)	**57.** (b)	**58.** (a)	**59.** (d)	**60.** (a)

the Guidance

Round I

1. Mass of electron = 9.1×10^{-31} kg

Mass of neutron = 1.67×10^{-27} kg

2. Neutron being neutral will not show deflection from the path on passing through an electric field.

5. 1 mol^{14} C $= 14$ g $= 6.022 \times 10^{23}$ carbon atoms

Number of neutrons in 1 carbon atom

$$= \text{mass number} - \text{atomic number} = 14 - 6 = 8 \text{ neutrons}$$

$\because 6.023 \times 10^{23}$ carbon atoms will contain $6.023 \times 10^{23} \times 8$ neutrons

$\therefore$ 14 g carbon-14 have $6.023 \times 10^{23} \times 8$ neutrons

and 7 mg or 7×10^{-3} g carbon-14 will have

$$\frac{7 \times 10^{-3} \times 6.023 \times 10^{23} \times 8}{14} \text{ neutrons}$$

$$= 24.092 \times 10^{20} \text{ neutrons} = 2.4092 \times 10^{21} \text{ neutrons}$$

Mass of 1 neutron $= 1.675 \times 10^{-27}$ kg

Mass of 2.4092×10^{21} neutrons

$$= 2.4092 \times 10^{21} \times 1.675 \times 10^{-27} \text{ kg}$$

$$= 4.0347 \times 10^{-6} \text{ kg}$$

6. 1 mole of NH_3 contains protons $= 7 + 3 = 10$ moles of protons (7 in N and 1 in each H atom) $= 6.023 \times 10^{23} \times 10$ protons

$= 6.023 \times 10^{24}$ protons 34 mg or 34×10^{-3} g NH_3 will contain

$$\frac{34 \times 10^{-3} \times 6.023 \times 10^{24}}{17} = 12.046 \times 10^{21} \text{ protons}$$

7. Diameter of Zn atom $= 2.6$ Å $= 2.6 \times 10^{-10}$ m

Given, length $= 1.6$ cm $= 1.6 \times 10^{-2}$ m

Number of Zn atoms in 1.6×10^{-2} m

$$= \frac{1.6 \times 10^{-2} \text{ m}}{2.6 \times 10^{-10} \text{ m}} = 0.6154 \times 10^{8} \text{ atoms}$$

$$= 6.154 \times 10^{7} \text{ atoms}$$

8. Isobars have the same mass number (*i.e.*, sum of protons and neutrons) but different atomic number (*i.e.*, number of protons).

10. According to Rutherford

$$\text{Scattering angle} \propto \frac{1}{\sin^4 (\theta/2)}$$

It fails for very small scattering angles because the full nuclear charge of the target atom is partially screened by its electron.

11. Mass of electron $= 9.1 \times 10^{-31}$ kg,

Mass of proton $= 1.67 \times 10^{-27}$ kg

Mass of neutron $= 1.675 \times 10^{-27}$ kg

Mass of α-particle $= 6.67 \times 10^{-27}$ kg

So, increasing order of e/m for e, p, n and α-particle is $e > p > \alpha > n$ (∵ neutron has no charge).

12. $$\frac{\frac{e}{m_d}}{\frac{2e}{m_{\alpha-p}}} = \frac{4m_{\alpha-p}}{4m_d} = 1$$

So, deuterium and an α-particle have identical value of e/m.

13. Given, frequency $\nu = \dfrac{c}{\lambda} = 3.29 \times 10^{15}\,\text{Hz}\left(\dfrac{1}{3^2} - \dfrac{1}{n^2}\right)$

$$\nu = \frac{3.0 \times 10^8 \text{ms}^{-1}}{1285 \times 10^{-9}\,\text{m}} = 3.29 \times 10^{15}\,\text{Hz}\left(\frac{1}{9} - \frac{1}{n^2}\right)$$

$$\frac{3.0 \times 10^8 \text{ms}^{-1}}{1285 \times 10^{-9}\,\text{m} \times 3.29 \times 10^{15}\,\text{Hz}} = \left(\frac{1}{9} - \frac{1}{n^2}\right)$$

$$0.0709 = 0.1111 - \frac{1}{n^2}$$

$$\frac{1}{n^2} = 0.1111 - 0.0709 = 0.0402 \approx 0.04 = \frac{1}{25}$$

$$n^2 = 25 \text{ or } n = 5$$

∴ The electron jumps from $n = 5$ to $n = 3$ *i.e.*, the transition occurs in Paschen series and lies in infrared region.

Note The radiation 1285 nm lies in the infrared region.

14. Frequency, $\nu = \dfrac{c}{\lambda}$

$$[1 \text{ nm} = 10^{-9} \text{ m}]$$

$580 \text{ nm} = 580 \times 10^{-9}\,\text{m} = 580 \times 10^{-7}$ cm

$$\nu = \frac{3.0 \times 10^8 \text{ ms}^{-1}}{580 \times 10^{-9}\,\text{m}} = 5.17 \times 10^{14}\,\text{s}^{-1}$$

(∴ Velocity of light $= 3 \times 10^8 \text{ ms}^{-1}$)

Wave number, $\bar{\nu} = \dfrac{1}{\lambda} = \dfrac{1}{580 \times 10^{-7}\text{ cm}}$

$$= 1.724 \times 10^4 \text{ cm}^{-1}$$

15. Energy of one photon,

$$E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34}\text{Js} \times 3.0 \times 10^8 \text{ ms}^{-1}}{4000 \times 10^{-12}\,\text{m}}$$

$$(1\text{pm} = 10^{-12} \text{ m})$$

$$= 4.9695 \times 10^{-17}\text{J}$$

Number of photons,

$$N = \frac{1\text{J}}{4.9695 \times 10^{-17}\text{J}} = 2.0122 \times 10^{16} \text{ photons}$$

16. The order of frequency is radiation from FM radio < microwaves < amber colour < X-rays < cosmic rays.

17. 25 watt $= 25 \text{ Js}^{-1}$ $\quad (1 \text{watt} = 1 \text{Js}^{-1})$

Wavelength, $\lambda = 0.57\,\mu\text{m} = 0.57 \times 10^{-6}$ m $\quad (1\mu\text{m} = 10^{-6}\,\text{m})$

Energy of one photon,

$$E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34}\text{Js} \times 3.0 \times 10^8 \text{ ms}^{-1}}{0.57 \times 10^{-6} \text{ m}}$$

$$E = 34.87 \times 10^{-20} \text{ J}$$

Number of photons emitted per second

$$= \frac{\text{Total energy per second}}{\text{Energy of photon}}$$

$$= \frac{25 \text{ Js}^{-1}}{34.87 \times 10^{-20}} = 0.7169 \times 10^{20} \text{ photons per second}$$

$$= 7.169 \times 10^{19} \text{ photon per second}$$

18. Atoms corresponds to different transitions from higher energy levels to lower energy levels.

20. Kinetic energy $= h(\nu - \nu_0)$

$$\text{KE} = h\nu - h\nu_0$$

$$\nu_0 = \nu - \frac{\text{KE}}{h} = 2 \times 10^{15} - \frac{6.63 \times 10^{-19}}{6.63 \times 10^{-34}}$$

$$= 1 \times 10^{15} \text{ s}^{-1}$$

21. The threshold frequency (ν_0) is the lowest frequency that photons may possess to produce the photoelectric effect. The energy corresponding to this frequency is the minimum energy (E).

$$E = h\nu_0$$

$$= (6.626 \times 10^{-27} \text{ erg-}s)\,(1.3 \times 10^{15} \text{ s}^{-1})$$

$$= 8.6 \times 10^{-12} \text{ erg}$$

22. Radius of nth orbit of H like species,

$$r_n = \frac{52.9\,(n^2)}{Z}\,\text{pm}$$

$$r_1 = 1.3225\,\text{nm} = 1322.5\,\text{pm} = \frac{52.9\,n_1^2}{Z}$$

$$r_2 = 211.6 \text{ pm} = \frac{52.9\,n_2^2}{Z}$$

$$\frac{r_1}{r_2} = \frac{1322.5}{211.6} = \frac{n_1^2}{n_2^2}$$

$$\frac{n_1^2}{n_2^2} = 6.25 \text{ or } \frac{n_1}{n_2} = 2.5$$

If $n_1 = 5$, $n = 2$, so, the transition (emission transition) is from 5th orbit to 2nd orbit and it belongs to Balmer series.

$$\bar{\nu} = \frac{1}{\lambda} = 1.09677 \times 10^7 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \text{m}^{-1}$$

$$\frac{1}{\lambda} = 1.09677 \times 10^7 \left[\frac{1}{2^2} - \frac{1}{5^2}\right] \text{m}^{-1}$$

$$\frac{1}{\lambda} = 1.09677\times 10^{7} \times \frac{21}{100} = 2.303\times 10^{6}\ \text{m}^{-1}$$

$$\lambda = 0.434\times 10^{-6}\text{m} = 434\times 10^{-9}\text{m} = 434\,\text{nm}$$

It belongs to visible region.

Note In the above Rydberg formula if $n_1 = 1, 2\ldots$ then $n_2 = n_1 + 1$, $n_1 + 2\ldots$ For Balmer series, spectral region is visible.

23. $E \propto \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ or $E \propto \frac{1}{n^2}$

26. $r_{\text{H}} = 0.529$ Å

$$r_n = r_{\text{H}} \times \frac{n^2}{Z}$$

For Li^{2+} $(n = 2)$,

$$r_{\text{Li}^{2+}} = r_{\text{H}} \times \frac{(2)^2}{3} = \frac{r_{\text{H}} \times 4}{9}$$

For $\text{Li}^{2+} (n = 3)$,

$$r_{\text{Li}^{2+}} = r_{\text{H}} \times \frac{(3)^3}{3} = 3r_{\text{H}}$$

For $\text{Be}^{3+} (n = 2)$

$$r_{\text{Be}^{3+}} = r_{\text{H}} \times \frac{(2)^2}{4} = r_{\text{H}}$$

For $\text{He}^{+} (n = 2)$

$$r_{\text{He}^{+}} = r_{\text{H}} \times \frac{(2)^2}{2} = 2r_{\text{H}}$$

Thus, $\text{Be}^{3+} (n = 2)$ has same radius as that of the first Bohr's orbit of H-atom.

27. Angular momentum, $mvr = \frac{nh}{2\pi} = \frac{3\times h}{2\pi} = \frac{1.5h}{\pi}$

$$= 3\hbar \qquad \left[\because\ \hbar = \frac{h}{2\pi}\right]$$

28. Energy in nth orbit, $E_n = \frac{-2.18\times 10^{-18}}{n^2}$ J

Energy in fifth orbit, $E_5 = \frac{-2.18\times 10^{-18}}{5^2}\text{ J} = -0.0872\times 10^{-18}\text{ J}$

29. Given, wavelength, $\lambda = 242\,\text{nm} = 242\times 10^{-9}$ m

Energy, $E = h\nu = \frac{hc}{\lambda} = \frac{6.626\times 10^{-34}\,\text{Js}\times 3.0\times 10^{8}\ \text{ms}^{-1}}{242\times 10^{-9}\ \text{m}}$

$$E = 0.0821\times 10^{-17}\ \text{J/atom}$$

This energy is sufficient for ionization of one Na atom, so it is the ionization energy of Na.

$$E = 6.02\times 10^{23}\times 0.0821\times 10^{-17}\ \text{J/mol}$$

$$E = 4.945\times 10^{5}\ \text{J/mol} = 4.945\times 10^{2}\ \text{kJ/mol}$$

30. Number of lines produced when electron from nth shell drops to ground state $= \frac{n(n-1)}{2}$

When $n = 6$, number of lines produced

$$= \frac{6(6-1)}{2} = \frac{6\times 5}{2} = 15$$

31. $E = \frac{1}{4\lambda\varepsilon_0}\frac{Ze^2}{r}$

For Li^{2+}, $Z = 3$ so $E = \frac{3e^2}{4\lambda\varepsilon_0 r}$

32. $v = \frac{2.18\times 10^{8}\times Z}{n}$ cm s^{-1}

For H atom, $Z = 1$ and third orbit, $n = 3$,

$$v_3 = \frac{2.18\times 10^{8}\times 1}{3}$$

$$= 7.26\times 10^{7}\ \text{cm s}^{-1}$$

34. $m = 10\,\text{g} = 10\times 10^{-3}$ kg

Uncertainty in speed $(\Delta\nu)$ = 4% of 90 ms^{-1} $= \frac{4\times 90}{100}$

$$= 3.6\ \text{ms}^{-1}$$

From Heisenberg uncertainty principle,

$$\Delta x\cdot\Delta\nu = \frac{h}{4\pi m} \text{ or } \Delta x = \frac{h}{4\pi m\Delta\nu}$$

Uncertainty in position,

$$\Delta x = \frac{6.626\times 10^{-34}\ \text{kg m}^2\text{s}^{-1}}{4\times 3.14\times 10\times 10^{-3}\ \text{kg}\times 3.6\,\text{ms}^{-1}}$$

$$= 1.46\times 10^{-33}\ \text{m}$$

35. Wavelength, $\lambda = \frac{h}{mv}$

Mass of neutron, $m = 1.675\times 10^{-27}$kg

$$\lambda = 800\ \text{pm} = 800\times 10^{-12}\text{m} = \frac{6.626\times 10^{-34}\ \text{kg m}^2\ \text{s}^{-1}}{1.675\times 10^{-27}\ \text{kg}\times v}$$

$$v = \frac{6.626\times 10^{-34}\,\text{kg m}^2\ \text{s}^{-1}}{1.675\times 10^{-27}\ \text{kg}\times 800\times 10^{-12}\text{m}}$$

$$= 0.494\times 10^{3}\ \text{ms}^{-1} = 4.94\times 10^{2}\text{ms}^{-1}$$

36. Given, $m = 100\,\text{g} = 0.1\text{kg}$

$$v = 100\text{km/h} = \frac{100\times 1000}{60\times 60} = \frac{1000}{36}\ \text{ms}^{-1}$$

From de-Broglie equation, wavelength, $\lambda = \frac{h}{mv}$

$$\lambda = \frac{6.626\times 10^{-34}\ \text{kg m}^2\ \text{s}^{-1}}{0.1\ \text{kg}\times\frac{1000}{36}\ \text{ms}^{-1}} = 238.5\times 10^{-36}\ \text{m}$$

(As the wavelength is very small so wave nature cannot be detected)

37. From de-Broglie equation, wavelength, $\lambda = \frac{h}{mv}$

For same wavelength of different particles, *i.e.,* electron, proton, neutron and α-particle, $m_1v_1 = m_2v_2$ as (h is constant). Lesser the mass of the particle, greater will be the velocity. Hence, electron will have higher velocity.

38. de-Broglie wavelength,

$$\lambda = \frac{h}{mv}$$

or $$\lambda \propto \frac{1}{m} \qquad \text{If } v = \text{constant (same)}$$

39. We know that kinetic energy = eV

or $$= \frac{1}{2} mv^2$$

So, $$\frac{1}{2} mv^2 = eV$$

$$v^2 = \frac{2eV}{m}$$

$$\therefore \qquad v = \sqrt{\frac{2eV}{m}}$$

40. $\lambda = \dfrac{h}{mv} = \dfrac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{6.6 \times 10^{-27} \text{ kg} \times 10^3 \text{ ms}^{-1}} = 1 \times 10^{-10} \text{ m}$

41. The de-Broglie wavelength associated with the charged particles as

For electron, $\lambda = \dfrac{12.27}{\sqrt{V}}$ Å

For proton, $\lambda = \dfrac{0.286}{\sqrt{V}}$ Å

For α-particles, $\lambda = \dfrac{0.101}{\sqrt{V}}$ Å

42. $\Delta x \cdot \Delta P = \dfrac{h}{4\pi}$

$$\Delta x = \frac{6.63 \times 10^{-34}}{4 \times 3.14 \times 10^{-5}}$$

$$= \frac{5.27 \times 10^{-35}}{1 \times 10^{-5}}$$

$$= 5.27 \times 10^{-30} \text{ m}$$

43. $\lambda = \dfrac{h}{\sqrt{2Em}}$

When kinetic energy of electron becomes four times, the de-Broglie wavelength will become half.

45. The arrangement of orbitals is based upon $(n + l)$ rule. According to which,lower the value of $(n + l)$, lower is the energy. For the orbitals having similar value of $(n + l)$ lower the value of n, lower is the energy. Thus, the correct order of arrangement are

(a) $1s < 2s < 2p < 3s$
(b) $3s < 3p < 4s < 4d$
(c) $4d < 5p < 6s < 4f < 5d$
(d) $7s < 5f < 6d < 7p$

46. For g subshell $l = 4$ and to have $l = 4$ minimum value of $n = 5$ [because the value of $l = 0$ to $(n - 1)$]

47. Number of spherical nodes in $3p$ orbital

$$= n - l - 1 = 3 - 1 - 1 = 1$$

48. (I) is not possible as $n \neq 0$

(II) is possible ($1s$)
(III) is not possible because if $n = 1, l = 0$ only $l \neq 1$
(VI) is possible ($2p$)
(V) is not possible because if $n = 3, l = 0\ 1$ and $2\ (l \neq 3)$
(VI) is possible ($3p$)

49. Total number of orbitals associated with nth shell = n^2

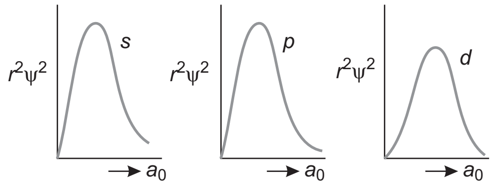
∴ Total number of orbitals associated with 3rd shell = $(3)^2 = 9$

50. Number of angular nodes = l

For 4th orbital, $(n = 4)$ and $l = 2$ for d orbital

∴ Number of angular nodes = 2

53. The electron density is directly proportional to ψ^2. The larger the electron density, the larger the value of ψ^2 and more is the probability of finding the electrons.



54. For a particular value of azimuthal quantum number, the total number of magnetic quantum number,

$$m = 2l + 1 \quad \text{or} \quad 2l = m - 1$$

$$l = \frac{m - 1}{2}$$

55. For $4d$ electron,

$$n = 4, l = 2, m = -2, -1, 0, +1, +2$$

$$s = +\frac{1}{2} \text{ or } -\frac{1}{2}$$

56. $+\dfrac{1}{2}$ and $-\dfrac{1}{2}$ spinning produces angular momentum equal to Z-component of angular momentum which is given as $m_s(h/2\pi)$.

57. Higher values of ψ^2 means greater probability for finding electron and a zero value of ψ^2 means the probability for finding the electron is zero (at nucleus).

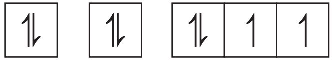
58. The four lobes of $d_{x^2 - y^2}$ orbital are lying along x and y axes, while the two lobes of d_{z^2} orbital are lying along z-axis, and contain a ring of negative charge surrounding the nucleus in xy plane.

$2s$ orbital has only one spherical node, where electron density is zero.

p-orbital have directional character.

$$\text{orbital} \longrightarrow \; p_z \quad p_x \quad p_y$$
$$m \longrightarrow \; 0 \quad \pm 1 \quad \pm 1$$
$$\text{Nodal plane} \longrightarrow \; xy \quad yz \quad zx$$

59. $_8O = 1s^2 \quad 2s^2 \quad 2p^4$



60. (a) Z_{eff} of $2s >$ Z_{eff} of $2p$

(b) energy of $2s$ orbital $<$ energy of $2p$ orbital

(c) Z_{eff} of $1s \neq$ Z_{eff} of $2s$

(d) For the two electrons of $2s$ orbital,

the value of m_s is $+\frac{1}{2}$ and $-\frac{1}{2}$

61. $Cr_{24} = [Ar]3d^5, 4s^1$

$Cr^{3+} = [Ar]3d^3$

$Fe_{26} = [Ar]3d^6, 4s^2$

$Fe^{3+} = [Ar]3d^5$

$Mn_{25} = [Ar]3d^5, 4s^2$

$Mn^{2+} = [Ar]3d^5$

$Co_{27} = [Ar]3d^7, 4s^2$

$Co^{3+} = [Ar]3d^6$

$Sc_{21} = [Ar]3d^1, 4s^2$

$Sc^{3+} = [Ar]$

Thus, Fe^{3+} and Mn^{2+} have the same electronic configuration.

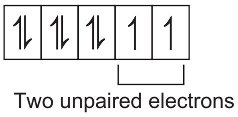
62. (i) (c) $_8O = 1s^2, 2s^2, 2p^4$; $O^{2-} = 1s^2, 2s^2, 2p^6$

65. $35 = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^5$

Thus, it contains 7 electrons in 4th or outermost shell.

66. $_{28}Ni = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^8$

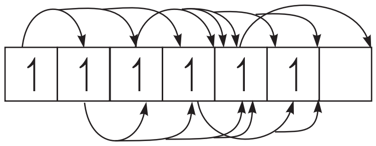
$Ni^{2+} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^8$



67. The energy of electrons in the same orbital is the same. For $3d$ orbitals, $3d_{xy}, 3d_{yz}, 3d_{zx}, 3d_{z_2^2}, 3d_{x^2-y^2}$, are at the same level of energy, irrespective of their orientation. The electronic configuration $3d^2_{xy}, 3d^2_{yz}, 3d^2_{zx}, 3d^2_{x^2-y^2}, 3d^2_{z^2}, 4s^1$ has maximum exchange energy.

68. A subshell having nearly half-filled or nearly completely filled configurations tends to acquire exactly half-filled or exactly completely filled nature to have lower energy level in order to attain extra stability.

70.



$5 + 4 + 3 + 2 + 1 = 15$

Round II

1. Energy of photon $= \frac{hc}{\lambda}\text{J} = \frac{hc}{e\lambda}\text{eV}$

$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{300 \times 10^{-9} \times 1.602 \times 10^{-19}}$$

$$= 4.14 \text{ eV}$$

For photoelectric effect to occur, energy of incident photons must be greater than work functions of metal and only Li, Na, K and Mg have work functions less than 4.14 V.

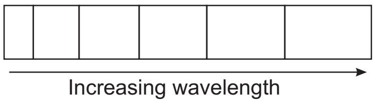
2. $\frac{1}{\lambda} = Z^2 \cdot R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$

For He^+, $\frac{1}{\lambda} = 2^2 \cdot R_H \left[\frac{1}{2^2} - \frac{1}{4^2} \right] = 4 \times \frac{3}{16} = \frac{3}{4}$

For $H, \frac{1}{\lambda} = 1^2 \cdot R_H \left[\frac{1}{1^2} - \frac{1}{2^2} \right] = \frac{3}{4}$

Hence, for hydrogen the given transition corresponds to $n = 2$ to $n = 1$ transition,

3. Line spectrum of atomic hydrogen in the visible region is as



4. Species having the same number of electrons as in oxide ion, has the same electronic configuration as oxide ion. O^{2-} or N^{3-} both species have same number of electrons (10 electrons).

5. Energy, $E = \frac{nhc}{\lambda}$

$$\Rightarrow \quad 60 \times 1\text{Js} = \frac{n \times 6.63 \times 10^{-34} \text{ Js} \times 3 \times 10^{8} \text{ m}}{663 \times 10^{-9} \text{m}}$$

$$\left[\because \text{Power} = \frac{\text{energy}}{\text{time}} \right]$$

$$\because \quad n = \frac{60 \times 1 \times 663 \times 10^{-9}}{6.63 \times 10^{-34} \times 3 \times 10^{8}} = 2 \times 10^{20}$$

6. Work function $W_0 = h\nu_0$

$$W_0 = 1.9 \text{ eV} = 1.9 \times 1.602 \times 10^{-19} \text{ J}$$

Threshold frequency,

$$\nu_0 = \frac{W_0}{h} = \frac{1.9 \times 1.602 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ Js}}$$

$$\nu_0 = 4.59 \times 10^{14} \text{ s}^{-1}$$

KE of ejected photoelectron $= h(\nu - \nu_0)$

λ of striking radiation $= 500 \text{ nm} = 500 \times 10^{-9}$ m

$$\nu = \frac{c}{\lambda} = \frac{3.0\times 10^{8}\ \text{ms}^{-1}}{500\times 10^{-9}\ \text{m}} = 6.0\times 10^{14}\ \text{s}^{-1}$$

$$\text{KE} = 6.626\times 10^{-34}\ \text{Js}\ (6.0\times 10^{14}\ \text{s}^{-1} - 4.59\times 10^{14}\ \text{s}^{-1})$$

$$= 9.34\times 10^{-20}\ \text{J}$$

$$\text{KE} = \frac{1}{2}mv^2\ (\text{Mass of an electron} = 9.11\times 10^{-31}\ \text{kg})$$

$$9.34\times 10^{-20}\ \text{J} = \frac{1}{2}\times 9.11\times 10^{-31}\ \text{kg}\times v^2$$

$$\therefore \quad v^2 = 2.050\times 10^{11}\ \text{m}^2\text{s}^{-2} \qquad (\because 1\,\text{J} = 1\,\text{kg m}^2\text{s}^{-2})$$

$$\text{or} \quad v = \sqrt{20.50\times 10^{10}}\ \text{m}^2\text{s}^{-2}$$

$$\text{or} \quad v = 4.527\times 10^{5}\ \text{ms}^{-1}$$

Note Minimum energy required to eject an electron is also known as work function, W_0 ($W_0 = h\nu_0$).

7. Energy of incident radiation, $h\nu = h\nu_0 + \text{KE}$

$$E = h\nu = \frac{hc}{\lambda} = \frac{6.626\times 10^{-34}\ \text{Js}\times 3.0\times 10^{8}\ \text{ms}^{-1}}{256.7\times 10^{-9}\ \text{m}}$$

$$= 7.74\times 10^{-19}\ \text{J} = \frac{7.74\times 10^{-19}\ \text{eV}}{1.602\times 10^{-19}} = 4.83\ \text{eV}$$

Applied potential gives the kinetic energy to electron, *i.e.*,

$$\text{eV}_0 = \frac{1}{2}mv_{\text{max}}^2 = \text{KE}$$

$$= \frac{1}{2}mv_{\text{max}}^2 = 1.6\times 10^{-19}\times 0.35 = 0.56\times 10^{19}\ \text{J}$$

$$= \frac{0.56\times 10^{-19}}{1.6\times 10^{-19}}\ \text{eV} = 0.35\ \text{eV}$$

$$\therefore \quad \text{KE} = 0.35\ \text{eV}$$

Work function, W_0 or $h\nu_0 = h\nu - \text{KE}$

$$= 4.83\ \text{eV} - 0.35\ \text{eV} = 4.48\ \text{eV}$$

8.

	Subshell notation	***n* + *l***
1. $n = 4, l = 2, m_l = -2, m_s = -\frac{1}{2}$	$4d$	$4 + 2 = 6$
2. $n = 3, l = 2, m_l = 1, m_s = +\frac{1}{2}$	$3d$	$3 + 2 = 5$
3. $n = 4, l = 1, m_l = 0, m_s = +\frac{1}{2}$	$4p$	$4 + 1 = 5$
4. $n = 3, l = 2, m_l = -2, m_s = -\frac{1}{2}$	$3d$	$3 + 2 = 5$
5. $n = 3, l = 1, m_l = -1, m_s = +\frac{1}{2}$	$3p$	$3 + 1 = 4$
6. $n = 4, l = 1, m_l = 0, m_s = +\frac{1}{2}$	$4p$	$4 + 1 = 5$

$$5 < 2 = 4 < 3 = 6 < 1$$

$$3p < 3d = 3d < 4p = 4p < 4d$$

(Arrangement of orbitals in order of their increasing energies.)

9. $\lambda = \frac{h}{mv}$, *i.e.*, $\lambda \propto \frac{1}{\sqrt{mE}}$ and $m >>> E$

Thus, correct order is $\lambda_e > \lambda_p > \lambda_\alpha$.

10. Energy of one photon, $E = \frac{hc}{\lambda}$

$$= \frac{6.626\times 10^{-34}\times 3\times 10^{8}}{550\times 10^{-9}\ \text{m}} = 3.61\times 10^{-19}\ \text{J}$$

$$\therefore \quad \text{Number of photons} = \frac{\text{energy required}}{\text{energy of one photon}}$$

$$= \frac{10^{-17}}{3.61\times 10^{-19}} = 27.67 \approx 28$$

11. In Bohr orbit,

$$\text{KE of} \quad e^- = \frac{1}{2}\frac{Zke^2}{r_n}$$

$$\text{PE of} \quad e^- = \frac{Zke^2}{r_n}$$

$$\text{Thus,} \quad \text{KE} = -\frac{1}{2}\ \text{PE}$$

12. Energy of incident radiation, $h\nu = h\nu_0 + \frac{1}{2}mv^2$

$$E = h\nu = \frac{hc}{\lambda} = \frac{6.626\times 10^{-34}\ \text{Js}\times 3.0\times 10^{8}\ \text{ms}^{-1}}{150\times 10^{-12}\ \text{m}}$$

$$(1\ \text{pm} = 10^{-12}\ \text{m})$$

$$E = 13.25\times 10^{-16}\ \text{J}$$

$$\text{KE of ejected electron} = \frac{1}{2}mv^2$$

$$= \frac{1}{2}\times 9.11\times 10^{-31}\ \text{kg}\ \times (1.5\times 10^{7}\ \text{ms}^{-1})^2$$

$$= 1.025\times 10^{-16}\ \text{J}$$

$$W_0 = h\nu_0 = h\nu - \frac{1}{2}mv^2$$

$$= 13.25\times 10^{-16}\ \text{J} - 1.025\times 10^{-16}\ \text{J}$$

$$= 12.225\times 10^{-16}\ \text{J}$$

$$= \frac{12.225\times 10^{-16}}{1.602\times 10^{-19}}\ \text{eV} = 7.63\times 10^{3}\ \text{eV}$$

Note Energy with which the electron was bound to the nucleus = work function for the metal.

13. $\lambda = \frac{h}{\sqrt{2eVm_e}}$

$$e = 1.6\times 10^{-19}\ \text{C}, V = 10{,}000\ \text{V}, m_e = 9.1\times 10^{-31}\ \text{kg}$$

$$\lambda = \frac{6.63\times 10^{-34}}{\sqrt{2\times 1.6\times 10^{-19}\times 10{,}000\times 9.1\times 10^{-31}}} = 0.123\ \text{Å}$$

14. Energy given to I_2 molecule $= \frac{hc}{\lambda}$

$$= \frac{6.626\times 10^{-34}\times 3\times 10^{8}}{4500\times 10^{-10}} = 4.4\times 10^{-19}\ \text{J}$$

Energy of I_2 molecule $= 240\times 10^{3}$ J/mol

$$= \frac{240\times 10^{3}}{6.023\times 10^{23}}\ \text{J/atom} = 3.98\times 10^{-19}\ \text{J/atom}$$

$$\text{KE} = (4.4\times 10^{-19}) - (3.98\times 10^{-19}) = 0.42\times 10^{-19}\ \text{J/atom}$$

$$\text{KE of I atoms} \quad = \frac{0.42}{2}\times 10^{-19} = 0.21\times 10^{-19}$$

15. $\lambda_A = \dfrac{h}{m_A v_A}$ and $\lambda_B = \dfrac{h}{m_B v_B}$

$$\frac{\lambda_A}{\lambda_B} = \frac{m_B v_B}{m_A v_A}$$

$$\frac{1\times10^{-10}}{\lambda_B} = \frac{m_A \times 3v_A}{m_A \times 4 \times v_A \times 4}$$

$$\lambda_B = \frac{16\times10^{-10}}{3} = 5.33\ \text{Å}$$

16. Frequency, $\nu = \dfrac{1}{\text{period}} = \dfrac{1}{2ns} = \dfrac{1}{2\times 10^{-9}\text{s}} = 0.5\times 10^{-9}\ \text{s}^{-1}$

Energy of the source = Energy of 1 photon × number of photons produced

$$E_{\text{source}} = h\nu \times N$$

$$= 6.626\times 10^{-34}\ \text{Js}\times 0.5\times 10^{9}\ \text{s}^{-1}\times 2.5\times 10^{15}$$

$$= 8.28\times 10^{-10}\ \text{J}$$

17. $\bar{\nu} = \dfrac{1}{\lambda} = R' Z^2 \left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]$

For shortest wavelength (maximum energy) in Lyman series of hydrogen $Z = 1, n_1 = 1, n_2 \to \infty$ and

$$\lambda = x$$

$$\frac{1}{x} = R'$$

For longest wavelength (minimum energy) in Balmer series of He^+, $Z = 2$ and $n_1 = 2, n_2 = 3$.

$$\frac{1}{\lambda} = R' 2^2 \left[\frac{1}{2^2} - \frac{1}{3^2}\right]$$

$$\frac{1}{\lambda} = \frac{4}{x}\left[\frac{1}{4} - \frac{1}{9}\right]$$

$$\frac{1}{\lambda} = \frac{4}{x}\,\frac{5}{36}$$

$$\lambda = \frac{9x}{5}$$

18. Given, $\Delta x = \Delta P$ or $\Delta x = m\cdot\Delta v$

From Heisenberg's uncertainty principle,

$$\Delta x \cdot m \cdot \Delta v = \frac{h}{4\pi}$$

$$m\cdot\Delta v\cdot m\Delta v = \frac{h}{4\pi}$$

$$(\Delta v)^2 = \frac{h}{4\pi m^2}$$

$$\Delta v = \frac{1}{2m}\sqrt{\frac{h}{\pi}}$$

$$= \frac{1}{2\times 9.1\times 10^{-31}}\sqrt{\frac{6.63\times 10^{-34}}{3.14}}$$

$$= 7.98\times 10^{12}\ \text{ms}^{-1} \approx 8\times 10^{12}\ \text{ms}^{-1}$$

19. Let the number of electrons in an ion = x

$\therefore$ Number of neutrons, $n = x + \dfrac{11.1}{100}x = 1.111x$

(As the number of neutrons are 11.1% more than the number of electrons.)

In the neutral atom, number of electrons, $e^- = x - 1$

(as the ion carries – 1 charge)

Similarly, number of protons, $p = x - 1$

we know that, mass number = $n + p = 37$

or $1.111x + x - 1 = 37$

$$2.111x = 37 + 1 = 38$$

$$x = \frac{38}{2.111} = 18.0009 \approx 18$$

Number of protons = atomic number = 18 − 1 = 17

Therefore, the symbol of the ion is ${}^{37}_{17}\text{Cl}^-$.

20. $\lambda = \dfrac{c}{\nu} = \dfrac{3.0\times 10^8 \text{ms}^{-1}}{4.620\times 10^{14}\ \text{Hz}} = 0.6494\times10^{-6}\ \text{m} = 649.4\ \text{nm};$

Thus, it belongs to visible region.

21. Energy change, $\Delta E = E_f - E_i$

$$\Delta E = 2.18\times10^{-18}\ \text{J}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

When $n_i = 5$ and $n_f = \infty$,
Energy change,

$$\Delta E = 2.18\times 10^{-18}\ \text{J}\left(\frac{1}{5^2} - \frac{1}{\infty}\right) = 0.0872\times 10^{-18}\ \text{J}$$

When $n_i = 1$ and $n_f = \infty$, energy change,

$$\Delta E' = 2.18\times 10^{-18}\ \text{J}\left(\frac{1}{1^2} - \frac{1}{\infty}\right)$$

$$\Delta E' = 2.18\times 10^{-18}\ \text{J}$$

$$\frac{\Delta E'}{\Delta E} = \frac{2.18\times 10^{-18}}{0.0872\times 10^{-18}} = 25$$

Hence, energy required to remove an electron from first orbit is 25 times than that required to remove an electron from fifth orbit.

22. Wave number, $\bar{\nu} = \dfrac{1}{\lambda} = R\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right)$

(Rydberg constant, $R = 109677\ \text{cm}^{-1}$)

$$\frac{1}{\lambda} = 109677\left(\frac{1}{2^2} - \frac{1}{4^2}\right)\ \text{cm}^{-1}$$

$$\frac{1}{\lambda} = 109677\left(\frac{3}{16}\right)\ \text{cm}^{-1}$$

$$\frac{1}{\lambda} = 20564.4\ \text{cm}^{-1}$$

$$\lambda = \frac{1}{20564.4}\ \text{cm} = 486\times 10^{-7}\ \text{cm}$$

$$= 486\times 10^{-9}\ \text{m} = 486\ \text{nm}$$

The colour corresponding to this wavelength is blue.

23. $\frac{1}{\lambda}=R\left[\frac{1}{1^2}-\frac{1}{2^2}\right]=\frac{3R}{4}$

$$\lambda=\frac{h}{P}$$

$$P=\frac{h}{\lambda}=h\times\frac{3R}{4}=\frac{3Rh}{4}$$

24. Option (c) is correct as in it Pauli's exclusion principle is violated but Hund's rule does not.

25. Use, $\Delta v\times\Delta x=\frac{h}{4\pi m}$ or $\Delta x=\frac{h}{4\pi m\cdot\Delta v}$

26. $m=-1$ is not possible for s-orbital ($l=0$).

27. (a) Total electrons if $n=4=2n^2=2\times4^2=32$

Half of the total electrons, *i.e.*, 16 electrons have $m_s=-\frac{1}{2}$

(b) $n=3, l=0$ it is 3s-orbital and it can have two electrons.

28. ${}_{29}\text{Cu}=1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^{10}$

$\text{Cu}^+=1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^0$

Total number of shells occupied = 3

Number of sub-shells occupied = 6

Number of orbitals filled = 14

Number of unpaired electrons = 0

29. Kinetic energy, KE $=h(\nu-\nu_0)=\frac{1}{2}mv^2$

On substituting the given results of the three experiments, we get

For Ist experiment, $\lambda=500\text{ nm}=500\times10^{-9}\text{ m}$;

$$\nu=\frac{c}{\lambda}=\frac{3.0\times10^8\text{ ms}^{-1}}{500\times10^{-9}\text{ m}}=6\times10^{14}\text{ s}^{-1}$$

$$h(6\times10^{14}\text{ s}^{-1}-\nu_0)=\frac{1}{2}m(2.55\times10^5\text{ ms}^{-1})^2 \quad \text{...(i)}$$

For 2nd experiment, $\lambda=450\text{ nm}=450\times10^{-9}\text{ m}$;

$$\nu=\frac{c}{\lambda}=\frac{3.0\times10^8\text{ ms}^{-1}}{450\times10^{-9}\text{ m}}=6.67\times10^{14}\text{ s}^{-1}$$

$$h(6.67\times10^{14}\text{s}^{-1}-\nu_0)=\frac{1}{2}\text{m}(4.35\times10^5\text{ ms}^{-1})^2 \quad \text{...(ii)}$$

For 3rd experiment, $\lambda=400\text{ nm}=400\times10^{-9}\text{ m}$;

$$v=\frac{c}{\lambda}=\frac{3.0\times10^8\text{ ms}^{-1}}{400\times10^{-9}\text{ m}}=7.5\times10^{14}\text{ s}^{-1}$$

$$h(7.5\times10^{14}\text{ s}^{-1}-\nu_0)=\frac{1}{2}m(5.20\times10^5\text{ ms}^{-1})^2 \quad \text{...(iii)}$$

On dividing Eq. (ii) by Eq. (i), we get

$$\frac{h(6.67\times10^{14}\text{s}^{-1}-\nu_0)=\frac{1}{2}m(4.35\times10^5\text{ ms}^{-1})^2}{h(6\times10^{14}\text{ s}^{-1}-\nu_0)=\frac{1}{2}m(2.55\times10^5\text{ ms}^{-1})^2}$$

$$\frac{6.67\times10^{14}\text{ s}^{-1}-\nu_0}{6\times10^{14}\text{ s}^{-1}-\nu_0}=\frac{(4.35)^2}{(2.55)^2}=2.91$$

$$6.67\times10^{14}\text{ s}^{-1}-\nu_0=17.46\times10^{14}\text{s}^{-1}-2.91\,\nu_0$$

$$2.91\nu_0-\nu_0=17.46\times10^{14}\text{ s}^{-1}-6.67\times10^{14}\text{ s}^{-1}$$

$$1.91\nu_0=10.79\times10^{14}\text{s}^{-1}$$

$$\nu_0=\frac{10.79\times10^{14}\text{s}^{-1}}{1.91}=5.649\times10^{14}\text{ s}^{-1}$$

$$\lambda_0=\frac{c}{\nu_0}=\frac{3.0\times10^8\text{ ms}^{-1}}{5.649\times10^{14}\text{ s}^{-1}}=5.31\times10^{-7}\text{ m}$$

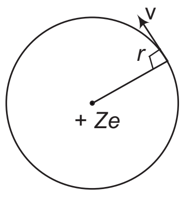
30. $\text{Cu}_{29}=1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^1$

$\text{Cu}^{2+}=1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^9$

$\text{Zn}^{2+}=1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}$

$\text{Cr}^{3+}=1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^3$

31. The frequency of revolution of an electron is given by



$$\text{Frequency}=\frac{1}{\text{Time period}}$$

$$\text{Time period}=\frac{\text{Total distance covered in one revolution}}{\text{Velocity}}$$

$$=\frac{2\pi r}{v}$$

$$\therefore\quad \text{Frequency}=\frac{v}{2\pi r}$$

Calculate the velocity (v_2) and radius (r_2) of the electron in the second Bohr orbit in H atom

$Z=1$ for H atom

Using $r_n=0.529\frac{n^2}{Z}$ Å

We get,

$$r_2=0.529\times10^{-10}\frac{(2)^2}{1}\text{ m}=2.12\times10^{-10}\text{m}$$

$$v_n=2.18\times10^6\,(1/n)\text{ m s}^{-1}$$

$$v^2=2.18\times10^6(1/2)=1.09\times10^6\text{ m s}^{-1}$$

$$\therefore\quad \text{Frequency}=\frac{v_2}{2\pi r_2}=\frac{1.09\times10^6}{2(\pi)(2.12\times10^{-10})}$$

$$v=8.18\times10^{14}\text{Hz}$$

Note Frequency of revolution $(f)=\frac{1}{T}$

where $T=\frac{2\pi r}{v}\propto\frac{n^3}{Z^2}$ $\left[\because r\propto\frac{n^2}{Z}\text{ and } v\propto\frac{Z}{n}\right]$

32. In the 1st Bohr orbit of H

$$v=2.18\times10^6\text{ ms}^{-1}$$

Now, let us consider that in Li^{2+} the electron is in nth orbit. Speed of electron in nth Bohr orbit of Li^{2+} is

$$v\,(\text{Li}^{2+}) = 2.18\times 10^{6}\times\frac{3}{n}$$

Now, applying the condition of equal speed

$$2.18\times 10^{6}\times\frac{3}{n} = 2.18\times 10^{6}$$

$$\Rightarrow \qquad n = 3$$

33. Let atoms of chlorine and fluorine in the mixture be x and y respectively

∴ Energy absorbed 284 kJ

$$= (x)\times 20.77\times 10^{-22} + (y)\times 27.91\times 10^{-22} \qquad \ldots\text{(i)}$$

Energy released

$$= 68.8\text{ kJ} = (x)\times 5.78\times 10^{-22} + (y)\times 5.53\times 10^{-22} \qquad \ldots\text{(ii)}$$

On solving equation (i) and (ii) we can get the values of x and y respectively.

% of Cl = 62.19

% of F = 37.81

34. Angular quantum number determines the three dimensional shape of the orbital.

Principal quantum number shows the energy of orbital but not orientation, which is shown by magnetic quantum number.

Spin quantum number is related with the spinning of electrons.

35. The choice (a) is incorrect as the oxidation state of nitrogen in HN_3 is $-\frac{1}{3}$ and not –3.

36. When $n = 1 \;\; l \neq 1 \;\; (\because l < n)$

When $n = 3 \;\; l \neq 4 \;\; (\because l < n)$

37.

$$\text{Na}^{+} = 11 - 1 = 10$$

$$\text{Mg}^{2+} = 12 - 2 = 10$$

$$\text{Al}^{3+} = 13 - 3 = 10$$

$$\text{O}^{-} = 8 + 1 = 9$$

$$\text{O}^{2-} = 8 + 2 = 10$$

$$\text{N}^{3-} = 7 + 3 = 10$$

$$\text{Cl}^{-} = 17 + 1 = 18$$

Thus, Na^{+} is isoelectronic with Mg^{2+} and O^{2-}.

38. The orbitals of same energy are called degenerate orbitals.

(a) (i) $3d_{xy}$ (ii) $3d_{yz}$

(b) (i) $3p_x$ (ii) $3d_{xy}$

(c) (i) $4s$ (ii) $3d_{xy}$

(d) (i) $3d_{x^2-y^2}$ (ii) $3d_{x^2-y^2}$

Thus, $3d_{xy}$ and $3d_{yz}$, $3d_{x^2-y^2}$ and $3d_{x^2-y^2}$ represent pair of degenerate orbitals.

39. The particles in anode rays are positive ions formed by loss of one or more electrons by atoms of the gas in the discharge tube.

40. According to Heisenberg's uncertainty principle, the exact position and exact momentum of an electron cannot be determined simultaneously. Thus, the path of electron in an atom is not clearly defined.

41. A body which absorbs and emits all radiations falling on it is called perfect black body. With rise in temperature, frequency increases.

42. The radius of second orbit of He^{+} is twice that of the first orbit of hydrogen. Bohr expression for radius of the electron in a particular orbit in hydrogen and hydrogen like species is

$$r_n = \frac{n^2h^2}{4\pi^2 kmZe^2}$$

43. In a multi-electron atom such as sodium atom energy of the electron is determined by both n and l.

44. For highest energy transition,

$$\bar{v} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

here, for Lyman series $n_1 = 1$ and $n_2 = \infty$

For Balmer series, $n = 2$ and $n_2 = \infty$

$$\frac{\bar{v}_{\text{Lyman}}}{\bar{v}_{\text{Balmer}}} = \frac{1\times(2)^2}{(1)^2\times 1} = 4:1$$

45. For lowest energy transition in Lyman series,

$$n_1 = 1, n_2 = 2$$

$$\bar{v} = R_H Z^2\left[\frac{1}{(1)^2} - \frac{1}{(2)^2}\right]$$

$$= R_H(2)^2\left[\frac{1}{1} - \frac{1}{4}\right]$$

$$= R_H\frac{4\times 3}{4} = 3R_H$$

46. $\Delta x\cdot\Delta P \geq \frac{h}{2\pi}$

when, $\Delta x = 0$ ΔP becomes infinite.

47. Uncertainty in velocity $= 3\times 10^{4}\times\frac{0.001}{100} = 0.3$ cm/s

$$\Delta x\cdot\Delta v = \frac{h}{4\pi m} = \frac{6.6\times 10^{-27}}{4\times 3.14\times 9.1\times 10^{-28}}$$

$$\Delta x = \frac{6.6\times 10^{-27}}{4\times 3.14\times 9.1\times 10^{-28}\times 0.3}$$

$$= 1.92 \text{ cm}$$

48. The uncertainty in the position of electron would be less than λ.

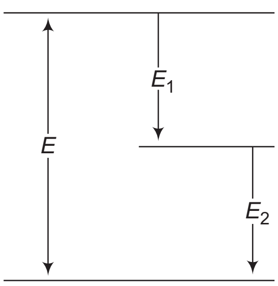
49.

	n	l	nl (suborbit)	$n+l$
(a)	4	1	$4p$	5
(b)	4	0	$4s$	4
(c)	3	2	$3d$	5
(d)	3	1	$3p$	4

Higher the value of $(n+l)$, higher the energy. If for two electrons the value of $(n+l)$ is same, suborbit with lower value of n has lower energy, Thus

$$3p < 4s < 3d < 4p$$
$$4 < 2 < 3 < 1$$

50. Energy values are always additive.



$$E_{\text{total}} = E_1 + E_2$$
$$\frac{hc}{\lambda} = \frac{hc}{\lambda_1} + \frac{hc}{\lambda_2}$$
$$\frac{1}{\lambda} = \frac{1}{\lambda_1} + \frac{1}{\lambda_2}$$
$$\frac{1}{355} = \frac{1}{680} + \frac{1}{\lambda_2}$$
$$\lambda_2 = 742.77 \text{ nm} \approx 743 \text{ nm}$$

51. $\Delta E = hv = \dfrac{2\pi^2 mZ^2e^4k^2}{h^2}\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]$

If electron falls from n_2 level to n_1 level.

$\therefore$ In He$^+$ for the $n_2 = 4$ to $n_1 = 2$ transition

$$v(\text{He}^+) = \text{constant }(4)\left[\frac{1}{2^2} - \frac{1}{4^2}\right] \qquad [\because Z_{\text{He}^+} = 2]$$
$$= \text{constant} \times 4\left[\frac{3}{16}\right] = \frac{3}{4}\text{ constant}$$
$$v(\text{H}) = \text{constant }(1)^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$
$$= \text{constant} \times \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

(a) For $n_2 = 3$ and $n_1 = 1$

$$v(\text{H}) = \text{constant}\left[\frac{1}{1} - \frac{1}{9}\right]$$
$$= \frac{8}{9}\text{ constant}$$
$$\neq \frac{3}{4} \times \text{constant}$$

(b) For $n_2 = 2$ and $n_1 = 1$

$$v(\text{H}) = \text{constant} \times \left[\frac{1}{1} - \frac{1}{4}\right]$$
$$= \frac{3}{4} \times \text{constant}$$
$$= v(\text{He}^+)$$

52. Energy required for 1 Cl_2 molecule $= \dfrac{242 \times 10^3}{N_A}$ J

$$E = \frac{hc}{\lambda}$$

or $$\lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8 \times 6.02 \times 10^{23}}{242 \times 10^3}$$
$$= 494 \times 10^{-9} \text{ m} = 494 \text{ nm}$$

53. IE $= -E_1$

$$E_1 \text{ for He}^+ = -19.6 \times 10^{-18} \text{ J atom}^{-1}$$
$$\frac{(E_1)_{\text{He}^+}}{(E_1)_{\text{Li}^{2+}}} = \frac{(Z_{\text{He}^+})^2}{(Z_{\text{Li}^{2+}})^2}$$
$$\frac{-19.6 \times 10^{-18}}{(E_1)_{\text{Li}^{2+}}} = \frac{4}{9}$$

or $$E_1(\text{Li}^{2+}) = \frac{-19.6 \times 9 \times 10^{-18}}{4} = -4.41 \times 10^{-17} \text{ J atom}^{-1}$$

54. $\lambda = \dfrac{h}{mv} = \dfrac{6.63 \times 10^{-34}}{1.67 \times 10^{-27} \times 1 \times 10^3}$

$$= 3.97 \times 10^{-10} \text{m} \sim 0.40 \text{ nm}$$

55. By Heisenberg's uncertainty principle,

$$\Delta x \cdot m\Delta v = \frac{h}{4\pi}$$
$$\Delta v = 0.005\% \text{ of } 600 \text{ m/s} = \frac{600 \times 0.005}{100} = 0.03$$
$$\Delta x \times 9.1 \times 10^{-31} \times 0.03 = \frac{6.6 \times 10^{-34}}{4 \times 3.14}$$

Hence, $$\Delta x = \frac{6.6 \times 10^{-34}}{4 \times 3.14 \times 0.03 \times 9.1 \times 10^{-31}}$$
$$= 1.92 \times 10^{-3} \text{ m}$$

56. Ionisation enthalpy of hydrogen at 1.312×10^6 J mol^{-1}. It suggests that the enegy of electron in the ground state (first orbit) is -1.312×10^6 J mol^{-1}

$$\Delta E = E_2 - E_1$$
$$= \frac{1.312 \times 10^6}{2^2} - \left(\frac{-1.312 \times 10^6}{1}\right)$$
$$= -9.84 \times 10^5 \text{ J mol}^{-1}$$

57. $n + l = 5$ (maximum), thus has the highest energy.

58. Isoelectronic means having same number of electrons.

K$^+$, Cl$^-$, Ca^{2+}, Sc^{3+} (all are having 18 electrons).

59. Angular momentum of an electron

$$mvr = \frac{nh}{2\pi} \text{ (n is orbit number)}$$

$$\text{In 5th orbit} = \frac{5h}{2\pi} = \frac{2.5h}{\pi}$$

60. Hydrogen atom is in $1s^1$ and the $3s$, $3p$ and $3d$ orbitals will have the same energy.

4

Chemical Bonding and Molecular Structure

JEE Main MILESTONE

- Bond
- Theories of Chemical Bonding
- Ionic Bonding or Electrovalent Bonding
- Covalent Bonding
- Coordinate Bonding
- Quantum Mechanical Approach to Covalent Bonding
- Valence Bond Theory
- Hybridisation
- Resonance
- Molecular Orbital Theory
- Metallic Bonding
- Hydrogen Bonding

4.1 Bond

"A bond is a kind of inter-atomic, inter-molecular, or inter-ionic attraction which holds two or more constituents (atoms, molecules or ions) *together*." The combining capacity of different constituents is called their **valency**. In case of elements of I A and II A group it is equal to their group number *i.e.*, + 1 and + 2 respectively.

For other elements it varies from group number to group number – 8 *i.e.*,

Valency = group number to (group number – 8)

(Here, group number are in accordance with modern Periodic Table). *e.g.*, Nitrogen, an element of group V A, has valency from + 5 to – 3 (= 5 – 8).

Depending upon the nature of combining constituents (atoms, ions), the bonds can be of following two types.

"Chemical bonding is the phenomenon of union of two or more atoms by redistribution of electrons, so that each atom involved in bonding acquires stable configuration to gain stability or to achieve a state of lower energy".

1. Chemical Bonds

These involves redistribution of electrons *i.e.,* the electrons are either transferred or shared to achieve a state of lower energy. Here, the lowering of energy exceed 40 kJ mol^{-1}.

A chemical bond is further classified into following types

(a) Electrovalent or ionic bond
(b) Covalent bond
(c) Coordinate bond

2. Physical Bonds

In this case, the atoms within molecules are held together by chemical bonds, but various molecules attract each other by physical forces like hydrogen bonding, van der Waals' forces. These bonds are weaker than chemical bonds. Here, lowering of energy is less than 40 kJ mol^{-1}.

Lewis Symbols

The simple notations that represent the valence electrons in an atom is called Lewis symbol *e.g.,*

$$\underset{(2\text{ valence }e^-)}{\cdot\text{Be}\cdot}\ ,\quad \underset{(3\text{ valence }e^-)}{\cdot\dot{\text{B}}\cdot}\ ,\quad \underset{(5\text{ valence }e^-)}{\cdot\ddot{\text{N}}:}$$

Lewis dot structure can also be written for molecules also. *General steps that you have to follow to write the Lewis structure are*

(i) Calculate the total number of valence electrons of all the atoms.

(ii) If species is charged, add or subtract the number of electrons equal to negative or positive charge of the ion.

(iii) Select the central atom (which is generally the least electronegative atom) and draw the skeletal structure by making an intelligent guess to indicate which atom is linked to which atom.

For example in CO

Number of valence electrons = 4 (C) + 6 (O) = 10

In skeletal structure of CO the octet of C can be completed by sharing two more electron pairs from oxygen.

$$:\text{C}\,\vdots\vdots\,\text{O}: \quad \text{or} \quad :\text{C}\equiv\text{O}:$$

[In Lewis dot structure, the electrons may be represented by dot, cross or any other symbol]

In Lewis representation number of bonds = $\dfrac{n_1 - n_2}{2}$

where, n_1 = number of atoms (other than H) $\times 8$ + no. of H atoms $\times 2$

n_2 = number of valence electrons of all isolated atom + (negative charge) − (positive charge)

e.g., In N_2, $n_1 = 2 \times 8 + 0 = 16$; $n_2 = 5 \times 2 + 0 - 0 = 10$

$$\text{Number of bonds} = \frac{n_1 - n_2}{2} = \frac{16 - 10}{2} = 3$$

$$\therefore \qquad N_2 = \ddot{\text{N}} \equiv \ddot{\text{N}}$$

4.2 Theories of Chemical Bonding

As formation of chemical compounds takes place as a result of combination of atoms of various elements in different way, it raises many questions like why do atoms combine? Why are only certain combinations possible? etc. In order to answer such questions different theories and concepts have been put forward from time to time, out of which two important are as follows

Kossel-Lewis Approach (Octet Rule)

In 1961, Kossel and Lewis proposed a concept on the basis of electronic configuration of elements. Thus, this concept was called **electronic concept of valency** or **octet rule.** Langmuir later on, extended it.

The main points of this concepts are as

1. The outer most shell of an atom is called the **valence shell** and the electrons present in it are called **valence electrons**.
2. It was assumed that inert gases (rare gases) are stable or chemically inert due to their stable configuration, *i.e.,* due to the presence of eight electrons (except He) in their valence shell. On this basis, Kossel and Lewis proposed that elements having eight electrons (except H which has 2 electrons in their valence shell) *i.e.,* having complete octet, are chemically inert.
3. Elements that do not have complete octet (or 8 electrons in their valence shell) have a high tendency to attain this configuration either by losing or gaining or sharing electrons to the atoms of same or other elements.

Violation of Octet Rule

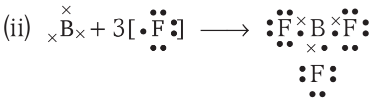
However, the octet rule is violated in a significant number of cases.
These are

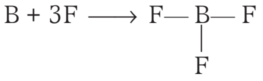
1. Be and B have less than 4 valence electrons, hence their octet cannot be completed even if they bind with their full strength *e.g.,*

(i) $_\times\text{Be}_\times + 2[\cdot\ddot{\underset{\cdot\cdot}{\text{F}}}:] \longrightarrow :\ddot{\underset{\cdot\cdot}{\text{F}}}\overset{\times}{\cdot}\ \text{Be}\ \overset{\times}{\cdot}\ddot{\underset{\cdot\cdot}{\text{F}}}:$

or $\quad \text{Be} + 2\text{F} \longrightarrow \text{BeF}_2$

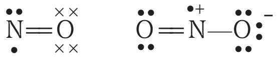
(Total 4 electrons in octet)

(ii)

$_\times\overset{\times}{\text{B}}_\times + 3[\cdot\ddot{\underset{\cdot\cdot}{\text{F}}}:] \longrightarrow :\ddot{\underset{\cdot\cdot}{\text{F}}}\overset{\times}{\cdot}\underset{:\ddot{\text{F}}:}{\text{B}}\overset{\times}{\cdot}\ddot{\underset{\cdot\cdot}{\text{F}}}:$

or

$\text{B} + 3\text{F} \longrightarrow \text{F—}\underset{\substack{|\\ \text{F}}}{\text{B}}\text{— F}$

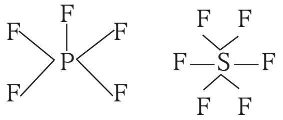
(Total 6 electrons in octet)

2. In molecules with an odd number of electrons, the octet rule is not satisfied for all the atoms, *e.g.,* in molecules like NO, NO_2, ClO_2^- etc., as they have $2c-3e^-$ bond (2 centre three electron bond)

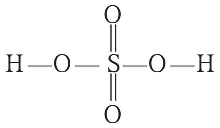

$$\ddot{\underset{\cdot}{\text{N}}}{=}\overset{\times\times}{\underset{\times\times}{\text{O}}} \qquad \ddot{\underset{\cdot\cdot}{\text{O}}}{=}\overset{\cdot+}{\text{N}}{-}\ddot{\underset{\cdot\cdot}{\text{O}}}:^{-}$$

(Total 7 electrons in nitrogen octet)

3. In a number of compounds there are more than 8 valence electrons present in the central atom. This is termed as **expanded octet.** This tendency is seen in elements beyond the 3rd period of the Periodic Table as they have vacant *d*-orbitals for bonding. Obviously octet rule is not applicable in such cases. Some of the examples of such compounds are PF_5, SF_6, H_2SO_4, etc.

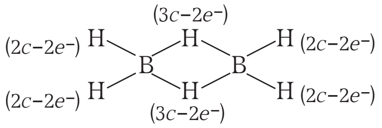


10 electrons in valence shell of P, 12 electrons in valence shell of S



12 electrons in valence shell of S

4. It also does not explain the formation of $3c-2e^-$ bonds as found in B_2H_6.



The other drawbacks of octet rule include

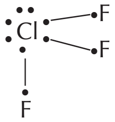
1. The shape of the molecule is not clear
2. It is totally silent about the energy of the molecule *i.e.*, relative stability.

Sample Problem 1 *Which of the following compounds does not follow octet rule?*

(*a*) ICl (*b*) ClF_3

(*c*) PCl_3 (*d*) CO_2

Interpret (*b*)



In this molecule, Cl has 10 electrons, thus it does not follow octet rule.

Modern Theory

The cause or basis of attractive forces or chemical bond, can be easily understood if we look at structure of an atom having positive nucleus and negative electrons. When two atoms come closer to combine, the attractive and repulsive forces begin to operate between them as

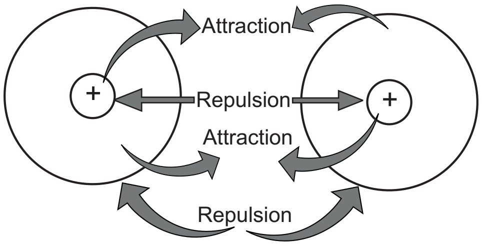
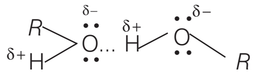


Fig 4.1 Attractive and repulsive forces between two atoms

The net result of these forces may be either attraction or repulsion between the atoms. A bond is formed if the net result of interaction is in the form of attraction. Now the agency *i.e.*, basis for a chemical bond is same in all cases thatswhy these attractive forces are called by different names? Here, the answer lies in one sentence and that is *"the different names to bonds are assigned due to difference in the intensities of these forces"*. These difference are summarized in the following table.

Table 4.1 **Various Attractive Electric Forces**

S. No.	Electric force	Relative strength	Type	Example
1.	Cation-anion (in a crystal) or ionic bond	Very strong	+ −	Lithium fluoride crystal lattice
2.	Covalent bonds	Strong (140-523 kJ mol^{-1})	Shared electron pairs δ + δ −	H—H (435 kJ mol^{-1}) $CH_3—CH_3$ (370 kJ mol^{-1}) I — I (150 kJ mol^{-1})
3.	Coordinate bond	Moderate	Shared electrons but given by one atom	$NH_3 \longrightarrow BH_3$
4.	Ion-dipole	Moderate	δ + δ − + δ − δ +	Na^+ in water
5.	Dipole-dipole (including hydrogen bonds)	Moderate to weak (4-38 kJ mol^{-1})	$\overset{\delta-}{—Z:}\ldots\overset{\delta+}{H}—$	 and $\overset{\delta+}{CH_3}—\overset{\delta-}{Cl}\ \overset{\delta+}{CH_3}—\overset{\delta-}{Cl}$

4.3 Ionic Bonding or Electrovalent Bonding

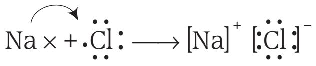
The attractive forces of ionic bond (*i.e.*, electrostatic force of attraction) are developed between an electropositive atom (*i.e.,* an atom with tendency to loose electron and convert into a cation) and an electronegative atom (*i.e.,* an atom with tendency to gain electron and convert into an anion) due to complete transfer of electrons from former to later. It is generally formed between the atoms having large difference in their electronegativity.

e.g., (i) Consider the formation of the compound "NaCl"

$$\underset{(1s^2, 2s^2, 2p^6, 3s^1)}{\text{Na}} \longrightarrow \underset{(1s^2, 2s^2, 2p^6)}{\text{Na}^+} \qquad \text{(cation formation)}$$

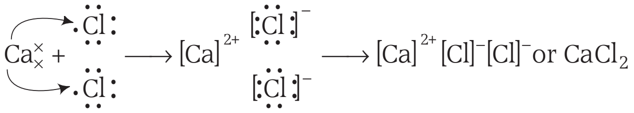
$$\underset{(1s^2, 2s^2, 2p^6, 3s^2, 3p^5)}{\text{Cl}} + e^- \longrightarrow \underset{(1s^2, 2s^2, 2p^6, 3s^2, 3p^6)}{\text{Cl}^-} \qquad \text{(anion formation)}$$

$$\text{Na}^+ + \text{Cl}^- \longrightarrow \text{NaCl} \qquad \text{(molecule formation)}$$



$$\text{Na}\times + \cdot\ddot{\underset{\cdot\cdot}{\text{Cl}}}: \longrightarrow [\text{Na}]^+ [:\ddot{\underset{\cdot\cdot}{\text{Cl}}}:]^-$$ (Lewis diagram)

e.g., (ii) Formation of "$CaCl_2$"



$$\text{Ca}^{\times}_{\times} + 2\,\cdot\ddot{\underset{\cdot\cdot}{\text{Cl}}}: \longrightarrow [\text{Ca}]^{2+} \, 2[:\ddot{\underset{\cdot\cdot}{\text{Cl}}}:]^- \longrightarrow [\text{Ca}]^{2+}[\text{Cl}]^-[\text{Cl}]^- \text{or } \text{CaCl}_2$$

Transfer of electron is not the necessary condition for this type of bonding, rather it is considered as a generalized condition. Such attractive forces can be seen between any two oppositely charged atoms or ions even from different sources, *e.g.,*

$$\text{H}^+\text{Cl}^-(l) + \text{Na}^+\text{OH}^-(l) \longrightarrow \text{Na}^+\text{Cl}^- + \text{H}_2\text{O}$$

In the above reaction Cl^- was formed after gaining an electron from H^+ and Na^+ is formed after losing an electron to OH^-.

If the difference between electronegativity is around 1.9 and more the bond is generally ionic, meaning that one atom has gained complete control of the electron pair in the bond.

Electrovalency

The number of electrons lost (or gained) by an atom during the formation of ionic bond is called the electrovalency of that atom.

For most of the atoms, its value is fixed and depends upon the number of valence electrons. However, certain elements (metals) show more than one electrovalency in their electrovalent compounds. The atoms of these elements lose different number of electrons under different conditions, thereby showing variable electrovalency. The following are two reasons for variable electrovalency.

(a) Instability of the Core

The residue configuration left after the loss of valency electrons (electrons present in the outermost energy level) is called the **core** or **kernel**. In case of transition elements, ions formed after the loss of valency electrons do not possess a stable core as the configuration of outermost shell is not ns^2np^6, but $ns^2np^6d^{1\text{ to }10}$. The outer shell generally loses one or more electrons giving rise to metal ions of higher valencies *e.g.,* Iron

$$\text{Fe }(26) = 2, 8, 8, 6, 2 \quad 3s^2 \quad 3p^6 \quad 3d^6, \quad 4s^2$$
$$\text{Fe}^{2+} (24) = 2, 8, 8, 6 \quad 3s^2 \quad 3p^6 \quad 3d^6 \quad \text{(Not stable)}$$
$$\text{Fe}^{3+} (23) = 2, 8, 8, 5 \quad 3s^2 \quad 3p^6 \quad 3d^5 \quad \text{(Stable)}$$

Thus, iron exhibits + 2 and + 3 valencies. *The compounds of* Fe^{3+} (ferric ion) *are more stable than the compounds of* Fe^{2+} (ferrous ion).

The only electron present in the outermost shell of copper atom is lost by it to get converted into Cu^+ (cuprous) ion.

$$\text{Cu}(29) = 2, 8, 18, 1 \quad 3s^23p^63d^{10}, 4s^1$$
$$\text{Cu}^+(28) = 2, 8, 18 \quad 3s^23p^63d^{10}$$

The $s^2p^6d^{10}$ configuration is not as stable as s^2p^6 configuration and the nuclear charge is not sufficiently strong to hold all the electrons intact in their positions. Thus, Cu^+ ion loses one more electron to form Cu^{2+} (cupric) ion. The Cu^{2+} ion is quite stable as the nuclear charge is sufficient to hold 27 electrons intact.

$$\text{Cu}^{2+} = 2, 8, 17 \text{ or } 3s^2 \ 3p^6 \ 3d^9$$

Thus, cupric (Cu^{2+}) *compounds are more stable than cuprous* (Cu^+) *compounds.*

The above two explanations fail to account why

(i) Co^{2+} ion cannot be easily converted into Co^{3+} ion like Fe^{2+} ion.

(ii) Zn^{2+} ion does not lose one more electron as its configuration ($3s^2\ 3p^6\ 3d^{10}$) is similar to Cu^+ ion.

In general, we can say that whenever the core is unstable, it loses one or more electrons to show higher valency and if the core is comparatively stable it always resists the loss of more electrons.

The cores of Co^{2+} ion and Zn^{2+} ion are comparatively stable as the nuclear charges are sufficient to hold all the electrons intact in their positions. Co^{2+} ion changes into Co^{3+} ion in the presence of an oxidising agent, but cobaltous compounds are comparatively more stable than cobaltic compounds.

(b) Inert Pair Effect

In case of heavier p-block elements, the outer ns^2 electrons penetrate to some extent to penultimate orbit consisting 18 electrons thereby attracted strongly towards nucleus. Due to this they (ns^2 electrons) do not take part in bond formation. *"The reluctance of s-electrons to take part in bond formation is called inert pair effect". e.g.,*

Pb	(IV group)	2,8,18,32,18, $6s^2 6p^2$	
Pb^{2+}		2,8,18,32,18, $6s^2$	Only $6p$ electrons are lost
Bi	(V group)	2,8,18,32,18, $6s^2 6p^3$	
Bi^{3+}		2,8,18,32,16, $6s^2$	Only $6p$ electrons are lost

When sufficient energy is available, the s-electrons also enter into bond formation and higher valencies are observed *e.g.,* Pb^{4+} = 2, 8, 18, 32, 18. This tendency to show higher valencies is less in the case of Tl, Pb and Bi but more in the case of comparatively lighter elements such as In, Sn, Sb, etc.

Factors Affecting the Formation of Ionic Bonds

The formation of an ionic bond is related to the ease of formation of cations and anions, which depends upon the ionisation energy of metal atom and electron affinity of non-metallic atom. Thus, these two also affects the formation of ionic bond.

For the formation of ionic bond

1. The ionisation energy of the electropositive element should be low *i.e.,* the metal atoms form a low charged positive ion easily.
2. The quantitative value of electron affinity of electronegative element should be high *i.e.,* the non-metal atom is small and give rise to low charged negative ion easily.
3. Lattice enthalpy should be high.

Lattice Enthalpy

The energy given off when gaseous positive and negative ions come together to form 1 mole of the solid ionic compound is called **lattice enthalpy** (U). *e.g.,*

$$Na^+(g) + Cl^-(g) \longrightarrow NaCl(s), \qquad \Delta H = -U$$

For the reverse process,

$$NaCl(s) \longrightarrow Na^+(g) + Cl^-(g), \qquad \Delta H = +U$$

Lattice enthalpy varies directly with the charge of ions and inversely with the size of ions. Thus,

$$\text{Lattice enthalpy} \propto \text{charge of ions}$$
$$\propto \frac{1}{\text{size of ions}}$$

Lattice energy can be calculated using Born-Haber cycle.

Sample Problem 2 *Which shows the highest lattice energy?*

(a) RbF (b) CsF (c) NaF (d) KF

Interpret (c) In all the given molecules, anion (*i.e.,* F^-) is common, thus lattice energy depends upon the size of cations. The order of size is

$$Na^+ < K^+ < Rb^+ < Cs^+$$

$$\text{Lattice energy} \propto \frac{1}{\text{size of ion}}$$

Thus, the order of lattice energy is

$$NaF > KF > RbF > CsF$$

Born-Haber Cycle

The fundamental of this cycle is based upon the fact that the formation of an ionic crystal may occur either by direct combination of the elements or by an alternate process in which

(i) The reactants are vaporized to convert into gaseous state.

(ii) The gaseous atoms are converted into ions.

(iii) The gaseous ions are combined to form ionic lattice of molecules.

e.g., $$M(s) + \frac{1}{2}X_2(g) \longrightarrow MX(s), \qquad \Delta H_1 = Q$$

Alternatively

(i) $M(s) \longrightarrow M(g), \qquad \Delta H = S$

(ii) $M(g) \longrightarrow M^+(g) + e^-, \qquad \Delta H = I$

(iii) $\frac{1}{2}X_2(g) \longrightarrow X(g), \qquad \Delta H = \frac{D}{2}$

(iv) $X(g) + e^- \longrightarrow X^-(g), \qquad \Delta H = -E$

(v) $M^+(g) + X^-(g) \longrightarrow MX(s), \qquad \Delta H = -U$

$$\Delta H_2 = S + I + \frac{D}{2} - E - U$$

where, S = heat of sublimation
I = ionisation energy
D = dissociation energy
E = electron affinity

ΔH_1 and ΔH_2 represent the enthalpy change for same chemical change. Hence,

$$\Delta H_1 = \Delta H_2$$

$$\therefore \quad Q = S + I + \frac{D}{2} - E - U$$

$$\therefore \quad U = S + I + \frac{D}{2} - E - Q$$

Sample Problem 3 *Calculate the lattice energy (in kJ mol $^{-1}$) of the salt MX(s) from the following data*

Heat of formation of $MX(\Delta H) = -550\ kJ\ mol^{-1}$

Heat of sublimation of metal, $M = 80\ kJ\ mol^{-1}$

Heat of dissociation of $X_2 = 155\ kJ\ mol^{-1}$

Ionisation energy of $M = 374\ kJ\ mol^{-1}$

Electron affinity of $X = -343\ kJ\ mol^{-1}$

(a) 738.5 (b) −324.5 (c) −816 (d) 402

Interpret (a) $U = S + I + \frac{D}{2} - E - Q$

$$= 80 + 374 + \frac{155}{2} - 343 - (-550) = +\ 738.5$$

Sample Problem 4 *If the ionisation potential of* Na *is* 495.8 *kJ mol* $^{-1}$*, the electron affinity of* Cl *is* 349.4 *kJ mol* $^{-1}$ *and lattice energy is* 776 *kJ mol* $^{-1}$*, the true statement for the formation of ionic bond in* NaCl *is*

(a) *total energy released per mole of* NaCl *formed is* 628.6 *kJ*
(b) *the ionic bond formed is unstable*
(c) *the total energy absorbed per mole of* NaCl *formed is* 1125.4 *kJ*
(d) *net energy released in this process is* 629.6 *kJ*

Interpret (d) $Na(g) + 495.8 \longrightarrow Na^+(g) + e^-$ ...(i)

$$Cl(g) + e^- \longrightarrow Cl^-(g) + 349.4$$

$$Na^+(g) + Cl^-(g) \longrightarrow NaCl(s) + 776\ kJ\ mol^{-1}$$

Total energy released per mole of NaCl formed

$$= 776 + 349.4 = 1125.4\ kJ$$

Total energy absorbed in step (i) = 495.8 kJ

Net energy released = 629.6 kJ

Thus, a stable ionic bond is formed between NaCl.

Lattice enthalpy (or lattice energy) **play an important role in deciding the solubility of ionic solids.** *It affects the solubility in the following manner*

1. If the anion and the cation are of comparable size, the cationic radius will influence the lattice energy. Since, lattice energy decreases much more than the hydration energy with increasing ionic size, solubility will increase as we go down the group.
2. If the anion is large compared to the cation, the lattice energy will remain almost constant within a particular group. Since, the hydration energies decrease down a group, solubility will decrease as found for alkaline earth metal carbonates and sulphates.

Characteristics of Ionic Compounds

The main characteristics of ionic compounds are as follows

1. These are usually crystalline in structure. Thus, at normal temperature and pressure, these are solids with **low volatility, high stability** and **high density.**
2. Due to strong forces of attraction, these possess high melting and boiling points.
3. These are **very hard** and **brittle** as the crystal planes can be separated very easily.
4. These are soluble in polar solvents like water because polar solvent molecules interact very strongly with the ions of crystal (solvation or hydration) and the high solvation or hydration energy released, is sufficient to break the lattice structure. In addition, ions in solution acquire greater degree of motion.

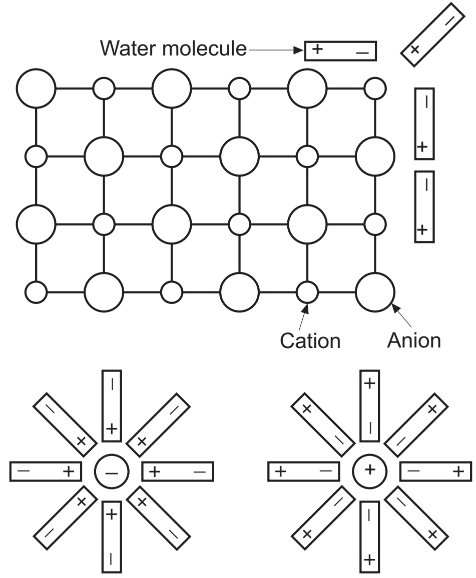


Fig 4.2 Solubility of ionic compounds in polar solvent

Note for dissolution solvation energy > lattice energy and dissolution is also favoured by high dielectric constant of solvent, *e.g.,*

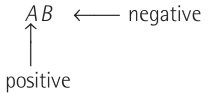
Solvent	H_2O	CH_3OH	C_2H_5OH	CH_3COCH_3	CH_3OCH_3
Dielectric constant	81	35	27	21	4.1

—capacity for dissolving ions decreases ⟶

5. Ionic compounds do not conduct electricity in solid state but these are very good conductors when fused or dissolved in a solvent of high dielectric constant due to the presence of mobile ions.
6. Compounds with same electronic configuration are isomorphous to each other. (Isomorphous = structurally same).
7. Ionic compounds undergo very fast reactions in solution which are of simple ion exchange type. The reactions are so fast because ions of the ionic compound maintain their indivisibility, thus easily separated from each other in the presence of polar molecules like water as polar molecules interfere with the attractive forces between the ions.
8. The ionic bond power is never saturated in a crystal, therefore, ionic bonds are always **non-rigid** and **non-directional,** and thus, do not exhibit space isomerism.

Steps to be Followed While Writing Formula of an Ionic Compound

***Step* 1.** Write the symbols of the ions side by side in such a manner so that the positive ion is at the left and negative ion is at the right as

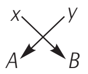


***Step* 2.** Write their electrovalencies in figure on the top of each symbol as

$A^x B^y$.

***Step* 3.** Divide their valencies by HCF

***Step* 4.** Now apply cross-cross rule as



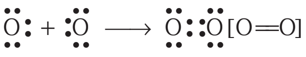
Thus, the formula is $A_y B_x$.

4.4 Covalent Bonding

A "covalent bond" is formed between atoms of comparable electronegativity. The attractive forces are developed due to the sharing of electron pair with each atom contributing one electron to the pair.

Example (Lewis structure)

(i) $H\bullet + \bullet H \longrightarrow H:H\ [H—H]$

(ii)


$\ddot{\underset{\cdot\cdot}{O}}: + :\ddot{\underset{\cdot\cdot}{O}} \longrightarrow \ddot{\underset{\cdot\cdot}{O}}::\ddot{\underset{\cdot\cdot}{O}}\ [O{=}O]$

(iii)


$\bullet\dot{\underset{\bullet}{C}}\bullet + 2\,\ddot{\underset{\cdot\cdot}{O}}: \longrightarrow \ddot{\underset{\cdot\cdot}{O}}::C::\ddot{\underset{\cdot\cdot}{O}}\ [O{=}C{=}O]$

(iv)


$2[H\bullet] + 2[\bullet\dot{\underset{\bullet}{C}}\bullet] \longrightarrow H:C\underset{\cdot\cdot}{\vdots}C:H\ [H—C\equiv C—H]$

Formal Charge (FC)

The atoms of a molecule or ion are usually neutral, *i.e.*, carry no charge but for some purposes, such as to find reaction mechanisms, assigning of formal charge of atoms in a molecule or ion is important. Formal charge (FC) is calculated as

$$FC = V - \left[lp + \frac{1}{2}bp\right]$$

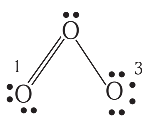
where,

V = total number of valence electrons in the free atom

lp = total number of non-bonding electrons or lone pairs

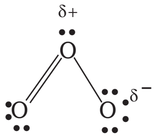
bp = total number of bondpair of electrons

e.g., formal charge of O atoms in ozone molecule is calculated as



$$\text{FC of } O^1 = 6 - \left(4 + \frac{1}{2} \times 4\right)$$
$$= 6 - 6 = 0$$
$$\text{FC of } O^2 = 6 - \left(2 + \frac{1}{2} \times 6\right)$$
$$= 6 - 5 = +1$$
$$\text{FC of } O^3 = 6 - \left(6 + \frac{1}{2} \times 2\right)$$
$$= 6 - 7 = -1$$

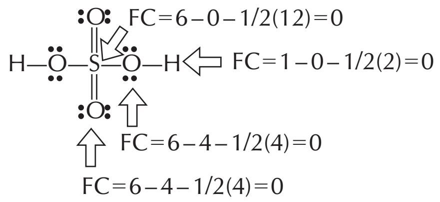
Thus, the correct representation of ozone molecule is



Sample **Problem 5** *The formal charge of each atom in sulphuric acid is equal to*

(*a*) 0 (*b*) 1 (*c*) 2 (*d*) 3

Interpret (*a*)



Types of Covalent Bonds

The covalent bond can be of following two types

(a) Non-polar Covalent Bond

If the covalent bond is formed between two homonuclear atoms, *i.e.*, between atoms of exactly equal electronegativity, the electron pair is equally shared between them. Such a bond is called non-polar covalent bond, *e.g.*, H_2, Cl_2, F_2, Br_2, etc.

(b) Polar Covalent Bond

If the bond forming entities are dissimilar *i.e.*, heteronuclear or with different electronegativity, the bond formed has partial ionic character as the electron pair is attracted by more electronegative entity. Such a bond is called polar covalent bond. *e.g.*,

$$\overset{\delta+}{H}\cdots\overset{\delta-}{O}\cdots\overset{\delta+}{H} \quad \overset{\delta+}{H}\cdots\overset{\delta-}{Cl}$$

The greater the difference in electronegativity, higher is the polar nature. The relative order of electronegativity of some important elements is

	F	> O	> Cl ≈ N	> Br	> S ≈ C ≈ I	> H
Max. of all the elements known	4.0	3.5	3.0	2.8	2.5	2.1

The ionic character in a polar bond can be calculated by the following methods

1. Pauling gave the following equation to calculate the percentage ionic character of a polar bond by using electronegativity difference $(x_A - x_B)$

Amount of ionic character in $A-B$ bond

$$= [1 - e^{0.25(x_A - x_B)}]\%$$

or $$[18(x_A - x_B)^{1.4}]\%$$

With the help of this equation, **Pauling** established the following relation

$(x_A - x_B)$	—	0.6	1.0	1.4	1.7	2.0	2.4	3.0	3.2
% ionic character	—	9	22	39	51	63	76	91	92

↑ At about midway between covalent and ionic character

2. **Hannary** and **Smith** also used the electronegativity difference $(x_A - x_B)$ to find the percentage ionic character by the following expression.

Ionic character in $A-B$ bond

$$= [16(x_A - x_B) + 3.5\,(x_A - x_B)^2]\%$$

3. There is an another method also which is based upon dipole moment.

Dipole Moment

The polarity of covalent bonds results in the formation of electric dipole possessing a permanent dipole moment, μ which is defined as the product of net charge and the distance between the two charged ends (bond length).

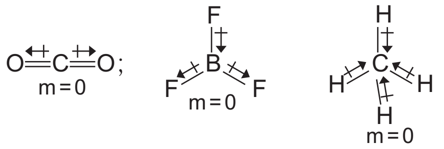
$$\mu = \text{charge}\,(e) \times \text{bond length}\,(d)$$

The units of dipole moment in CGS system is **debye** (*D*) and in SI system is **coulomb-metre.**

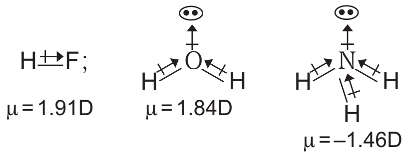
Dipole moment is a vector quantity, thus indicated by the symbol (⟶) pointing towards the negative end. *e.g.,*

$$\overset{\delta+}{\mathrm{H}} \overset{\longmapsto}{—} \overset{\delta-}{\mathrm{Cl}}$$

For symmetrical molecules, dipole moment is zero but unsymmetrical molecules have some dipole moment. *e.g.,* CO_2, BF_3, CH_4 etc. Being symmetrical have zero dipole moment.



However, unsymmetrical molecules like HF, H_2O, NH_3 have some dipole moment as



By using dipole moment, the percentage ionic character of a polar bond $(A-B)$ can be calculated as,

$$\text{Percentage ionic character} = \frac{\mu_{\text{exp}}}{\mu_{\text{cal}}} \times 100 = \frac{\mu_{\text{exp}}}{d_{A-B} \times e} \times 100$$

here, μ_{exp} = experimental (or observed) value of dipole moment of *AB* molecule,

$(\mu_{\text{cal}})_{\text{ionic}}$ = calculated (theoretical) value of dipole moment of *AB* molecule when molecule was assumed to be completely ionic. This value can be calculated as

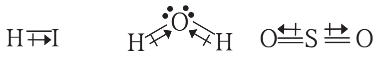
$d \times e$, *i.e.,* bond length × charge

Sample **Problem 6** *Polarity in a molecule and hence, the dipole moment depends primarily on electronegativity of the constituent atoms and shape of a molecule. Which of the following has the highest dipole moment?* **[NCERT Exemplar]**

(a) CO_2	(b) HI
(c) H_2O	(d) SO_2

Interpret (c) CO_2 being symmetrical has zero dipole moment.

Among HI, SO_2 and H_2O, dipole moment is highest for H_2O as in it the central atom contains 2 lone pairs.



Sample **Problem 7** *The bond length of* HCl *bond is* 2.29×10^{-10} *m. The percentage ionic character of* HCl*, if measured dipole moment is* 6.226×10^{-30} *C-m, is*

(a) 8%	(b) 20%
(c) 17%	(d) 50%

Interpret (c) $\mu_{\text{cal}} = e \times d$

$$= 1.6 \times 10^{-19} \times 2.29 \times 10^{-10}$$
$$= 3.664 \times 10^{-29}\ \text{C - m}$$

$$\%\ \text{ionic character} = \frac{\mu_{\text{exp}}}{\mu_{\text{cal}}} \times 100$$

$$= \frac{6.226 \times 10^{-30}}{3.664 \times 10^{-29}} \times 100 = 17\%$$

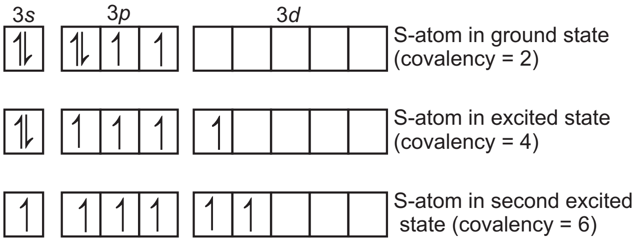
Covalency

The number of electrons contributed by an atom for sharing with other atoms to achieve inert gas configuration is called its **covalency. The usual covalency of an atom** (except hydrogen-covalency 1) **is equal to 8– number of the group to which element belongs. This is applicable for non-metals of *p*-block only.**

Generally, the covalency of an element is equal to the total number of unpaired electrons present in *s* and *p*-orbitals. The elements having vacant *d*-orbitals in their valence shell (*e.g.,* P, S, Cl, As, Sn etc) show variable covalency by increasing the number of unpaired electrons during excited conditions. The maximum covalency of the elements in different periods is

1. 4 for the elements of second period,
2. 6 for the elements of 3rd and 4th period,
3. 8 for the elements of 5th period onwards.

Such a variation in maximum covalency can be explained on the basis of absence of vacant *d*-orbitals in 2nd period elements and their availability in 3rd and subsequent period elements. *e.g.,* in case of sulphur



On this basis we can explain why compounds like OF_6, NCl_5 or ion like CF_6^{2-}, NF_6^{3-} do not exist and compounds like ICl, ICl_3, IF_5, IF_7 or ion like SiF_6^{3-}, PF_6^{3-} can be formed.

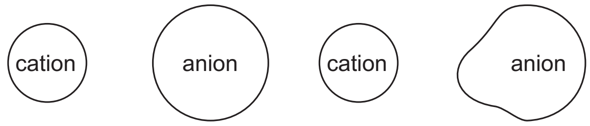
Characteristics of Covalent Compounds

The main characteristics of covalent compounds are as

1. Normal covalent compounds are **gases** or **liquids** under ordinary conditions of temperature and pressure. Some of the compounds are soft solids also if molecular weights are high. *e.g.,* Cl_2 (mol. wt. = 71) is a gas, Br_2 (mol. wt. = 160) is a liquid, I_2 (mol. wt. = 254) is a volatile solid.
2. With a few exceptions (like diamond, carborundum, silica) covalent compounds have relatively low values of their melting and boiling points.
3. In solid state crystals of covalent compounds are of three types mainly
   - (i) Soft, easily fusible, volatile crystals in which molecules are held by weak van der Waals' forces. *e.g.,* crystals of organic compounds, sulphur, iodine etc.
   - (ii) Very hard crystals in which every atom is bonded with the other atoms resulting in the formation of a **giant molecule.** *e.g.,* diamond crystal.
   - (iii) The crystals which consists of separate **lattice layers.** *e.g.,* graphite. These crystals are very soft and of lubricating nature.
4. The covalent bond is rigid and directional hence, different spatial arrangements of atoms are possible. Thus, these compounds exhibit structural as well as space isomerism.
5. In general, covalent compounds are bad conductors of electricity in fused as well as in solid state. However, graphite can conduct electricity as it possess free electrons in its layers.
6. In general, covalent compounds are insoluble in polar solvents like water but dissolve in non-polar solvents like benzene, CCl_4, ether etc. However, some of them like alcohols are miscible with water due to intermolecular H-bonding.
7. The reaction of covalent compounds are slow and complex as these involve fission of older bonds and formation of new bonds.

Fajan's Rule

When two oppositely charged ions of unequal size approach each other closely, the ion smaller in size attracts outermost electrons of the other ion and repel its nuclear charge. The net result of this is distortion or polarisation of the bigger ion which is generally the anion. This distortion is usually done by the cation as its size is smalller than the anion. The electron cloud of anion no longer remains symmetrical but is elongated towards the cation. The ability of a cation to polarize the nearby anion is called its **polarizing power** and the tendency of an anion to get distorted or deformed or polarized by the cation is called its **polarisability**. Due to polarization, sharing of electrons occur between two ions to some extent and the bond show some covalent character.



(a) No polarisation (b) Polarised anion

Fig 4.3 Representation of polarisation

Fajan gave the following rules to decide the magnitude of polarisation or covalent character in an ionic bond

(a) Higher Charge on Cation or Anion

As the charge on the cation increases, its tendency to polarise the anion increases. This brings more and more covalent nature in the electrovalent compound *e.g.,* in case of NaCl, $MgCl_2$ and $AlCl_3$, the polarisation increases from NaCl to $AlCl_3$, thereby covalent character becomes more and more as the charge on the cation increases. (Na^+, Mg^{2+}, Al^{3+})

A larger anion is polarised more and thus, also result in increased covalent character. *e.g.,* $CaSO_4$ is more covalent than $Ca(NO_3)_2$.

(b) Smaller Size of Cations

The charge possessed by a small cation will be more concentrated, thus causing more polarisation of anion. Hence, we can say that ionic compounds having smaller cations show more covalent nature.

(c) Larger Size of Anions

In such anions, the outer electrons will be at a greater distance from the nucleus, hence, more easily influenced by the attractive forces of cation. As a result larger anions will be more easily polarised in comparison to smaller anions.

(d) Non-inert Gas Configuration

The polarising power of those cations which don't have inert gas configuration will be more in comparison to cations having inert gas configuration. *e.g.,* polarising power of Cu^+ ion (electronic configuration 2, 8, 18) is more in comparison with polarising power of Na^+ ion (electronic configuration 2, 8).

Generally, electrovalent compound having high values of polarisation (more covalent character) are found to be less soluble in water but more soluble in organic solvents. This can be seen in the following examples

(i) Sulphides are less soluble in water than oxides of the same metal.
(ii) Lithium salts are soluble in organic solvents.
(iii) Beryllium compounds are less soluble than corresponding other alkaline earth metal compounds.
(iv) The solubility of aluminium halides decreases from AlF_3 to AlI_3.

Sample **Problem 8** *Which compound is most covalent?*

(*a*) LiF (*b*) LiCl
(*c*) LiBr (*d*) LiI

Interpret (*d*) Covalent character ∝ size of anion

[∵ In the given compounds, same cation, Li^+ is present.]

The order of size of anions is

$$F^- < Cl^- < Br^- < I^-$$

Thus, the order of covalent character is

$$LiF < LiCl < LiBr < LiI$$

Variation of Polarising Power/Polarisability in the Periodic Table

(i) On moving down a group, the polarising power of the cations decreases.
(ii) Polarising power of the cations increase on moving from left to right in a period.
(iii) The polarisability of the anions by a given cation decreases on moving from left to right in a period.
(iv) The polarisability of the anions by a given cation increases on moving down a group.

Valence Shell Electron Pair Repulsion Theory (VSEPR Theory)

This theory was given by "**Gillespie** and **Nyholm**" and is helpful in predicting the geometric arrangement of atoms in molecules. It includes all molecules which may or may not obey octet rule.

The main postulates of this theory are

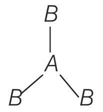
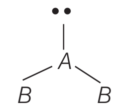
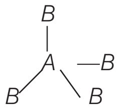
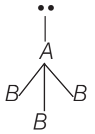
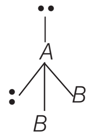
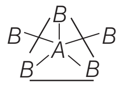
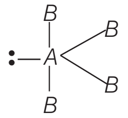
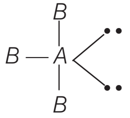
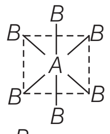
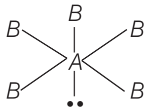
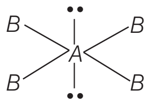
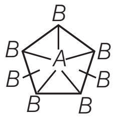
1. The shape of the molecule is determined by repulsions between all the electrons pairs present in the valence shell.
2. A lone pair of electrons takes up more space around the central atom than a bond pair, since the lone pair is attracted to only one nucleus whilst the bond pair is shared by two nuclei. It follows that repulsion between two lone pair is greater than repulsion between a lone pair and a bond pair, which in turn is greater than, the repulsion between two bond pairs. Thus, the presence of lone pairs on the central atom causes slight distortion of the bond angles from the ideal shape calculated from hybridization.

   Thus, repulsion among pairs increases as

   $$bp - bp < bp - lp < lp - lp.$$
3. The magnitude of repulsions between bonding pairs of electrons depends on the electronegativity difference between the central atom and the other atoms.
4. Double bonds cause more repulsion than single bonds and triple bonds cause more repulsion than double bonds.

A brief summary of molecular shapes resulting from different configurations of electrons pairs is presented below

Table 4.2 **Geometry of Molecules According to VSEPR Theory**

S. No.	Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electron pairs	Shape (Geometry)	Examples
1.	AB_2	2	0	B—A—B	Linear	BeF_2
2.	AB_3	3	0		Trigonal planar	BF_3
3.	AB_2E	2	1	 Trigonal planar	Bent	SO_2,O_3
4.	AB_4	4	0		Tetrahedral	CH_4,
5.	AB_3E	3	1	 Tetrahedral	Trigonal pyramidal	NH_3
6.	AB_2E_2	2	2	 Tetrahedral	Bent or V-shape	H_2O
7.	AB_5	5	0		Trigonal bipyramidal	PF_5
8.	AB_4E	4	1	 Trigonal bipyramidal	See-saw	SF_4
9.	AB_3E_2	3	2	 Trigonal bipyramidal	T-shaped	ClF_3
10.	AB_6	6	0		Octahedral	SF_6
11.	AB_5E	5	1	 Octahedral	Square pyramid	BrF_5
12.	AB_4E_2	4	2	 Octahedral	Square planar	XeF_4
13.	AB_7	7	0		Pentagonal bipyramidal	IF_7

Note With very few exceptions, the predictions based on the VSEPR theory have been shown to be correct.

Hot Spot 1

FINDING Shapes of Molecules

It is very important topic for JEE Main examination as questions are frequently asked from this topic. By following some simple steps, the geometry of a molecule can be obtained easily.

To find the shape of a molecule, follow the steps given below.

Step I *Identify the central atom and count the number of valence electrons. e.g.,* In PCl_3, P being less electronegative is the central atom.
No. of valence electrons of P = 5

Step II *Find the number of electron pairs shared.*
e.g., In PCl_3, there are 3Cl atoms, so total no. of shared electrons $= \underset{\text{from P}}{3} + \underset{\text{from Cl}}{3} = 6e^-$

$$\text{Use, No. of bond pairs} = \frac{\text{total no. of shared electrons}}{2}$$

$$\text{and No. of lone pairs} = \frac{\text{Valence } e^- - \text{bond pair}}{2}$$

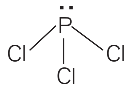
$$\therefore \text{No. of bond pairs} = \frac{6}{2} = 3$$

$$\text{and No. of lone pairs} = \frac{5-3}{2} = \frac{2}{2} = 1$$

Step III *While counting the number of electron pairs for ion, value of negative charge is added and positive charge is subtracted* (with/from the valence e^- of central atom). In PCl_3, no charge is there, so we left this step.

Step IV *On the basis of total number of electron pairs (bond pairs + lone pairs) predict the geometry of the molecule with the help of the above table.*

Note Learn the table mainly *lp*, *bp* and geometry for examination
e.g., The shape of PCl_3 with 3*bp* + 1*lp* is pyramidal.



Sample Problem 9 *The shape of* BrF_5 *is* **[NCERT]**

(*a*) *octahedral* (*b*) *pentagonal bipyramidal*
(*c*) *trigonal bipyramidal* (*d*) *square pyramidal*

Interpret (*d*) In BrF_5^-, Br being less electronegative is the central atom.

In Br, no. of valence $e^- = 7$

5 F atoms shaped with 5 Br atoms.

So, no. of electrons shared = 5 + 5 = 10

$$\therefore \text{No. of bond pairs} = \frac{10}{2} = 5$$

$$\text{No. of lone pairs} = \frac{7-5}{2} = 1$$

Thus, the shape of BrF_5 with 5 *bp* and 1 *lp* is square pyramidal.

Sample Problem 10 *In* NO_3^- *ion, the number of bond pairs and lone pairs of electrons on nitrogen atom are* **[NCERT Exemplar]**

(*a*) 2,2 (*b*) 3,1 (*c*) 1,3 (*d*) 3,0

Interpret (*d*) In N atom,
No. of valence electrons = 5
Due to the presence of one negative charge
No. of valence electrons = 5 + 1 = 6
One O atom forms two bond (═ bond), thus, each O atom shared with two e^-s of N atom.
Thus, 3 O atoms shared with 6 e^-s of N atom.
$\therefore$ No. of bond pairs (or shared pairs) = 3
No. of lone pairs = 0

Important Characteristics of Covalent Bonds

Covalent bonds are characterised by the some parameters which are as follows

(a) **Bond Length**

The average distance between the centre of nuclei of the two bonded atoms in a molecule is known as bond length. It depends upon the size of atoms, hybridization, steric effect, resonance etc.

Usually bond length of polar bond is smaller as compared to a non-polar bond. Bond length increases as the size of atom or orbital increases.

(b) **Bond Enthalpy**

Bond enthalpy is the amount of energy required to break a particular bond in one mole of gaseous molecule.

$$\text{Bond enthalpy} \propto \text{electronegativity}$$
$$\propto \frac{1}{\text{size of atoms}}$$
$$\propto \frac{1}{\text{number of lone pair of electrons}}$$

(c) Bond Order

It is the number of covalent bonds present between the two atoms in a molecule.

$$\text{Bond order} \propto \text{Bond enthalpy} \propto \frac{1}{\text{bond length}}$$

(d) Bond Angles

It is the angle between the bonded orbitals. Presence of lone pair of electrons greatly affects the bond angle.

Some examples are given below.

1. As the number of lone pairs of electrons increased, bond angle decreased, *e.g.,* The bond angle order for CH_4, NH_3 and H_2O is

   $CH_4 > NH_3 > H_2O$, *i.e.,* 109°28′, 106°51′ and 104°31′ respectively.

2. Bond angle increases as the electronegativity of the central atom increases. *e.g.*,

   in hydrides of oxygen family, order of bond angle is.

   $$\underset{(104.5)}{H_2O} > \underset{(92)}{H_2S} > \underset{(91)}{H_2Se} > \underset{(89)}{H_2Te}$$

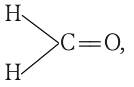
   However, in molecule having same central atom, bond angle increases as the electronegativity of surrounding atoms decreases, *e.g.,* the order of bond angle for PI_3, PBr_3 and PCl_3 is as

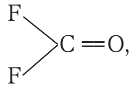
   $$\underset{(102)}{PI_3} > \underset{(101.5)}{PBr_3} > \underset{(100)}{PCl_3}$$

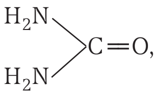
   ∵ The order of electronegativity is Cl > Br > I

   Similarly, NF_3 and NH_3 both have structure based on a tetrahedron with one corner occupied by a lone pair. The high electronegativity of F push the bonding electrons further away from N than in NH_3. Hence, the lone pair in NF_3 causes a greater distortion from tetrahedral and gives a F — N — F bond angle of 102°30′ as compared with 107°48′ in NH_3. The same effect is found in H_2O (bond angle 104°27′) and F_2O (bond angle 102°).

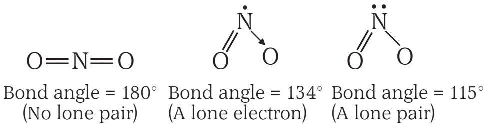
3. pi (π) bonds do not affect the stereochemistry of a molecule. However, multiple bond orbitals repel other orbitals more strongly than single bond orbital, thus the bond angle will increase.

   (i) 
   $H_2C{=}O$, $\angle H—C—H \Rightarrow 116°$ and $\angle H—C{=}O \Rightarrow 122°$.

   (ii) 
   $F_2C{=}O$, $\angle F—C—F \Rightarrow 108°$ and $\angle F—C{=}O \Rightarrow 126°$

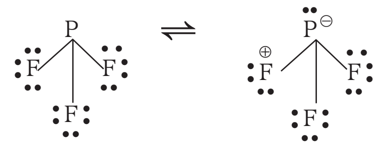
   (iii) 
   $(H_2N)_2C{=}O$, $\angle N—C—N \Rightarrow 118°$ and $\angle N—C—O \Rightarrow 121°$

4. A lone pair and double bond repulsion is much greater than a lone electron and double bond repulsion.

   Bond angle = 180° (No lone pair) Bond angle = 134° (A lone electron) Bond angle = 115° (A lone pair)

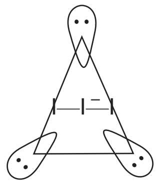
5. The bond angle of $PF_3 > PCl_3$. The PF_3 molecule has lone pair of electrons on F atom and P has vacant *d*-orbitals. The small size of F-atom leads to *pπ-dπ* bonding in PF_3 as shown below

   The double bond formation increases bond pair-bond pair repulsion to result in an increase in bond angle in PF_3. In PCl_3, the Cl-atom being larger in size does not show *pπ-dπ* bonding. Similarly, bond angle in arsenic halides are:

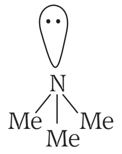
   $$\underset{102°}{AsF_3} > \underset{98.4°}{AsCl_3}$$

6. The lone pairs always occupy the equatorial positions (in an triangle), rather than the axial positions (up and down). Thus in I_3^- ion, the central I atom has five electron pairs in the outer shell, made of two bond pairs and three lone pairs. The lone pairs occupy all the three equatorial positions and the two I atoms occupy the top, and bottom positions in the bipyramid, thus giving a linear arrangement with a bond angle of exactly 180°.

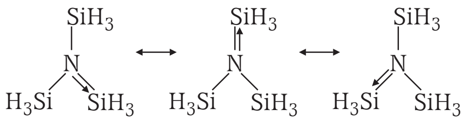
   

7. The interaction between an empty orbital and lone pair of electrons known as **back bonding.**

   e.g., the nitrogen in trimethyl amine and trisilyl amine has a lone pair of electrons at nitrogen but nitrogen in trimethyl amine has pyramidal shape while in trisilyl amine nitrogen has planar shape because in trimethyl amine there is repulsion between lone pair and bond pair that's why the shape becomes pyramidal.

   In trisilyl amine, there is vacant *d*-orbital at silicon which overlaps with lone pair of nitrogen, called *pπ – dπ* back bonding, hence geometry becomes planar.

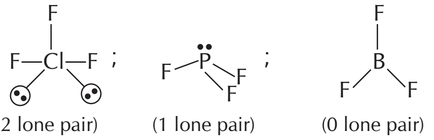
   

Sample **Problem 11** *The correct increasing bond angle among* BF_3, PF_3 *and* ClF_3 *follows the order*

(*a*) $BF_3 > PF_3 > ClF_3$ (*b*) $PF_3 < BF_3 < ClF_3$

(*c*) $BF_3 = PF_3 = ClF_3$ (*d*) $ClF_3 < PF_3 < BF_3$

Interpret (*d*) Bond angle $\propto \dfrac{1}{\text{number of lone pairs}}$

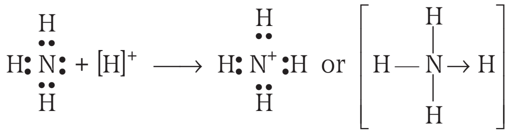


Thus, the order of bond angle is $ClF_3 < PF_3 < BF_3$.

4.5 Coordinate Bonding

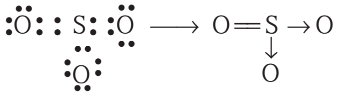
Coordinate covalent bond or **dative bond** is a special type of covalent bond, which involves sharing of a pair of electrons. The speciality in this bonding is that the shared electron pair is donated by one atom (called donor) and shared by both the atoms (the other atom being called acceptor) *e.g.,*

(i) **Formation of** NH_4^+

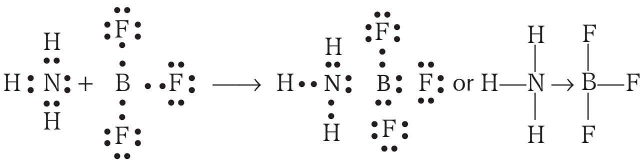


(ii) **Formation of** SO_2

(iii) **Formation of** SO_3



(iv) **Formation of** $NH_3 \rightarrow BF_3$



Characteristics of Dative Bond or Coordination Compounds

The important characteristics of dative compounds are as follows

1. The compounds exist in all the three states *i.e.,* solids, liquids and gases under ordinary conditions.
2. The melting and boiling points of these compounds are higher as compared to covalent compounds but lower than those of ionic compounds.
3. Like covalent compounds these are also poor conductors of electricity in solid as well as in fused state.
4. These compounds are sparingly soluble in polar solvents like water, however, these are readily soluble in organic solvents.
5. These compounds are generally as stable as covalent compounds. The addition compounds are not very stable.
6. **Coordinate linkage is rigid and directional, thus they exhibit isomerism.** Due to its directional nature the coordinate bond is shown as (under classical approach)

   Donor atom $\longrightarrow$ Acceptor atom

   But under modern approach, this bond can also be shown as

   Donor atom $\overset{+\;-}{\longrightarrow}$ Acceptor atom
7. Dative compounds show molecular reactions just like covalent compounds.
8. The dielectric constants for these compounds are higher.

Check Point 1

1. Why does a molecule is more stable in terms of energy than the uncombined atoms?
2. Why are zero group elements chemically inert?
3. Cu and Fe exhibits variable electrovalency, explain, why?
4. Sodium chloride does not conduct electricity in solid state but does so in molten and liquid state. Give reason.
5. Which out of NH_3 and NF_3 has the higher dipole moment and why?
6. Why the repulsion between non-bonding orbitals are greater than between the bonded orbitals?
7. Bond angle in ammonia is 107° 28′ while that in water is 104° 20′, however both are sp^3 hybridised. Explain, why?

4.6 Quantum Mechanical Approach to Covalent Bonding

Electronic theory of covalent bonding was not capable to explain correct shape of molecules, nature of bonds, and formation of bonds. Thus, new theories, called collectively the quantum mechanical theory have been proposed, which includes dual nature of electrons. Electronic theory however gives an impression that electrons are located very precisely in a molecule.

Two theories based on quantum mechanical treatment are

1. Valence bond theory
2. Molecular orbital theory

4.7 Valence Bond Theory (VBT)

It was put forward by **Heitler** and **London** in 1927 and was extended by **Pauling** and **Slater** in 1931.

According to this theory, atoms with unpaired electrons tend to combine with other atoms which also have unpaired electrons. In this way the unpaired electrons are paired up, and the atoms involved, all attain a stable electronic arrangement. This is usually a full shell of electrons (*i.e.,* a noble gas configuration). **Two electrons shared between two atoms constitute a bond**. The number of bonds formed by an atom is usually the same as the number of unpaired electrons in the ground state, *i.e.,* the lowest energy state.

However, in some cases the atoms may form more bonds than this. This occurs by excitation of the atom (*i.e.,* providing it with energy) when electrons, which were paired in the ground state, are unpaired and promoted into suitable empty orbitals. This increases the number of unpaired electrons and hence, increase the number of bonds which can be formed.

The theory can be summarised as

1. A covalent bond is formed when the orbital of one atom overlaps with the orbital of another atom, each of the orbital containing one unpaired electron.
2. The two atomic orbital in such a case, merge to form a single **bond orbital** or **a localized molecular orbital,** which is occupied by both the electrons.
3. The two electrons occupying the bond orbital must have opposite spins. **(Pauli principle)**
4. Each electron may be considered to belong to both the atomic nuclei.
5. As a result of overlapping, there is maximum electron density somewhere between the two atoms. The electrostatic attraction between the nuclei and the accumulated electron clouds between them provides a large part of the binding force of covalent bond.
6. The neutralization of spin magnetic moments of the two electrons taking part in the bond formation also contributes to the binding force.

The modifications suggested by Pauling and Slater were

1. The strength of chemical bond is proportional to the extent of overlapping between the atomic orbital.
2. Overlapping will take place only between those atomic orbitals, electrons of which take part in chemical bonding.
3. Between two orbital of the same stability, the one with more directionally concentrated cloud would form a stronger bond, *e.g., p*-orbital will form stronger bonds than *s*-orbital.
4. A spherically symmertical orbital, *e.g., s*-orbital, will not show any preference in direction whereas, non-spherical orbital, *e.g., p*-or *d*-orbital will tend to form a bond in their direction of maximum electron density.

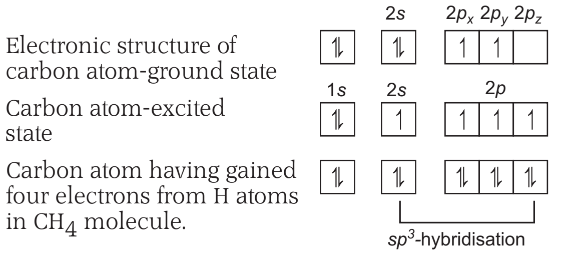
For example

(i) In HF, H has a singly occupied *s*-orbital that overlaps with a singly filled 2*p* orbital for F.

(ii) In H_2O, the O atom has two singly filled 2*p* orbitals, each of which overlaps with a single occupied *s*-orbital from two H atoms.

(iii) In NH_3, there are three singly occupied *p* orbitals on N which overlap with *s* orbitals from three H atoms.

(iv) In CH_4, the C atom in its ground state has the electronic configuration $1s^2, 2s^2, 2p_x^1, 2p_y^1$ and only has two unpaired electrons and so can form only two bonds. If the C atom is excited, then the 2*s* electrons may be unpaired, giving $1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$ configuration. There are now four unpaired electrons which overlap with singly occupied *s* orbitals on four H atoms.



CH_4 molecule uses its three *p*-orbitals p_x, p_y and p_z, which are mutually at right angles to each other, and the *s* orbital is spherically symmetrical. Hence, they form tetrahedral structure.

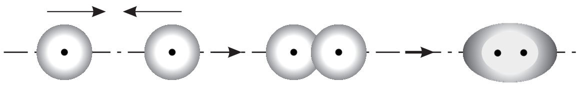
CH_4 $\quad$ H—C—H = 109°28′

Overlapping of Orbitals

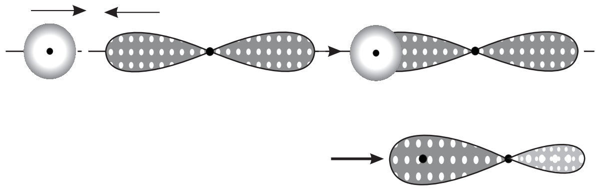
The overlapping of orbitals may be of two types

1. **End to end overlapping or axial overlapping or head on overlapping resulting** to σ-bond (sigma bond). Here, the electron density is concentrated in between the two atoms. The main examples of σ-bond include

(a) ***s-s* overlapping**



(b) ***s-p* overlapping**



(c) ***p-p* overlapping**

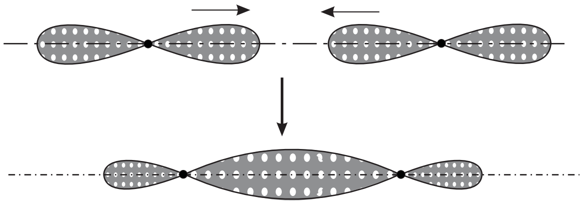


Fig 4.4 Different cases tend to end or axial overlapping

2. **Sidewise overlapping or parallel overlapping** which is seen normally after atleast one axial overlapping between orbitals of same atom and results to a π-bond (pi bond). Here, also the electron density concentrates between the atoms but on either side of line of joining nuclei as

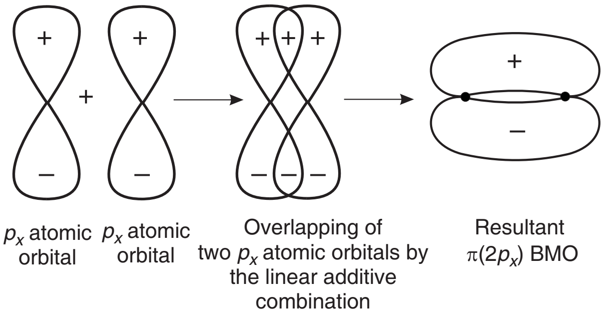


Fig 4.5 Sidewise overlapping Overlapping of two p_x atomic orbitals by linear additive combination to give $\pi 2p_x$ bonding molecular orbitals (BMO).

From the above, *it is concluded, single bond* (—) *contains only one* σ*-bond and no* π*-bond, double bond* (=) *contains one* σ *and one* π*-bond and triple bond* (≡) *contains one* σ *and two* π*-bonds.*

4.8 Hybridisation

The process of hybridisation involves the mixing of orbitals of almost similar energy belonging to same atom, to form the same number of orbitals of exactly equal energy. The new orbitals formed are called **hybrid orbitals.** The phenomenon in actual sense involves redistribution of energy.

Salient Features of the Phenomenon of Hybridisation (Rules of Hybridisation)

1. Only the valence shell atomic orbitals of an atom or ion mix together to give the hybrid orbitals.
2. *The atomic orbitals of the atom of a given molecule or ion which participate in the formation of* π*-bonds remain excluded from the hybridisation process.* For example in CO_2 molecule (O=C=O), the singly-filled $2s$ and $2p_x$-orbitals of C-atom mix together to form two *sp* hybrid orbitals while the singly-filled $2p_y$ and $2p_z$-orbitals remain excluded from the hybridisation process, since these orbitals make two (C—O) π-bonds.
3. *Atomic orbitals having lone pairs of electrons* (completely-filled orbitals) *are also involved in the hybridisation,* if the central atom of the given molecule or ion also has one or more lone pairs of electrons.
4. In a few cases, *empty atomic orbitals are also involved in hybridisation.*
5. A hybrid orbital, like an atomic orbital, can accommodate a maximum of two electrons with opposite spins.
6. The number of hybrid orbitals formed is exactly equal to the number of orbitals taking part in the process.
7. *The electronic charge in hybrid orbitals is concentrated more in one direction.* This property make the hybrid orbitals to overlap with the atomic orbitals to a greater extent and hence, give stronger bonds.
8. The hybridised orbitals have equivalent energies and identical size and shape, *i.e.,* **hybrid orbitals are degenerate.** The sum of the energies of all the hybrid orbitals is equal to the sum of the energies of orbitals which participated in the process *i.e., the process of hybridisation does not involve any loss or gain of energy.* Here, only redistribution of energy occurs.
9. Atomic orbitals can mix together effectively to give hybrid orbitals only when they are of almost same energy and same symmetry.
10. Same atom can assume different hybrid states under different situations.

11. The shapes of hybrid orbitals are different from those of the atomic orbitals which are taking part in the process of hybridisation.
12. The energy released (decrease in energy) in the formation of σ-bonds by the hybrid orbitals is more than that which is released in the formation of σ-bonds by the pure atomic orbitals. σ-bonds formed by the use of hybrid orbitals of the atom are, therefore stronger and hence, more stable than those which are formed by the use of pure atomic orbitals only.

Types of Hybridisation

The hybridisation can be of following types

(a) sp (b) sp^2 (c) sp^3 or dsp^2

(d) sp^3d (e) sp^3d^2 and (f) sp^3d^3.

Out of these the former three are described here in detail.

(a) *sp*-Hybridisation (Linear Hybridisation)

In this hybridisation, one *s* and one *p*-orbital (if axis is supposed to be the molecular *x*-axis, *p*-orbital will p_x-orbital) of the valence shell of atom combine together and give rise to the formation of a set of two equivalent hybrid orbitals, which are called *sp*-hybrid orbitals. Since, the lobes of a *p*-orbital can combine with an *s*-orbital in two different ways as shown in figure below, two *sp*-hybrid orbitals are obtained.

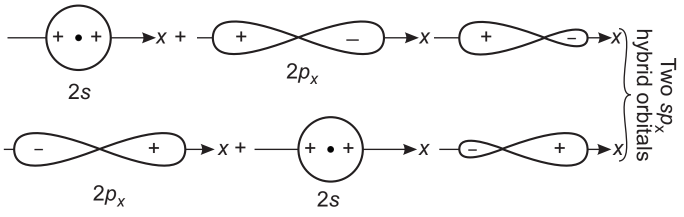


Fig 4.6 Formation of two sp_x hybrid orbitals

Characteristics of *sp*-hybrid orbitals include

1. *sp*-hybrid orbitals are equivalent and symmetrical.
2. These have same shape and same energy.
3. These are collinear, *i.e.,* they lie in one axis in a straight line and hence, the angle between them is 180° and their spatial arrangement is linear, *i.e.,* they are directed in a straight line in opposite directions.
4. *s*-orbital is spherical and *p* is pear-shaped but *sp*-hybrid orbital which results from the mixing of one *s* and one *p*-orbital is oval-shaped due to the presence of 50% *s*-character and 50% *p*-character in it.

An example of *sp*-hybridised molecule is $BeCl_2$ molecule.

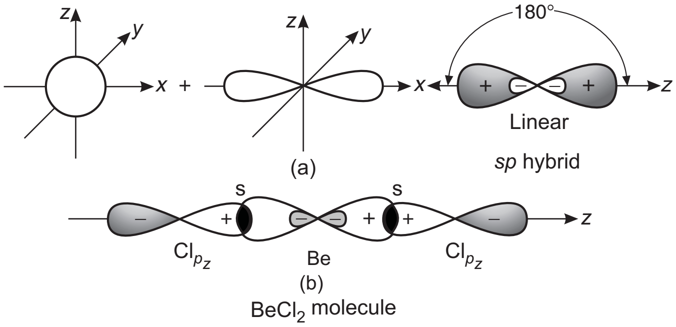


Fig 4.7 (a) Formation of *sp* hybrids formal *s* and *p* orbits; (b) Formation of the linear $BeCl_2$ molecule.

(b) sp^2-Hybridisation
(Trigonal Planar Hybridisation)

In this hybridisation, one *s* and any two *p*-orbitals of the valence shell of the atom combine together and give a set of three equivalent hybrid orbitals which are called sp^2 or trigonal hybrid orbitals.

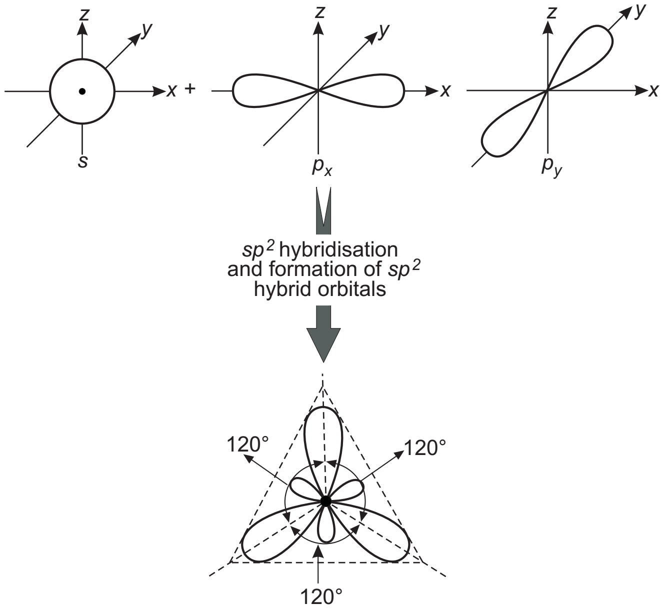


Fig. 4.8 Showing sp^2-hybridisation with angle and arrangement of orbitals

Characteristics of sp^2-hybrid orbitals include

1. They have the same shape and energy.
2. They lie in one plane.
3. They are directed towards the corners of an equilateral triangle and hence, the angle between each pair of them is 120°. Thus, in other words, we can say that the spatial arrangement of the three sp^2-hybrid orbitals is trigonal.
4. The sp^2 hybrid orbitals which result from the combination of one *s* and two *p*-orbitals are less oval than the *sp*-hybrid orbitals because the contribution of the two pear-shaped *p*-orbitals to the

formation of sp^2-hybrid orbitals is greater. The shape of sp^2-hybrid orbitals, therefore, tends more towards a pear. Here, the *s*-character is 33% and the *p*-character is 67%.

An example of sp^2-hybridised molecule is BCl_3 molecule

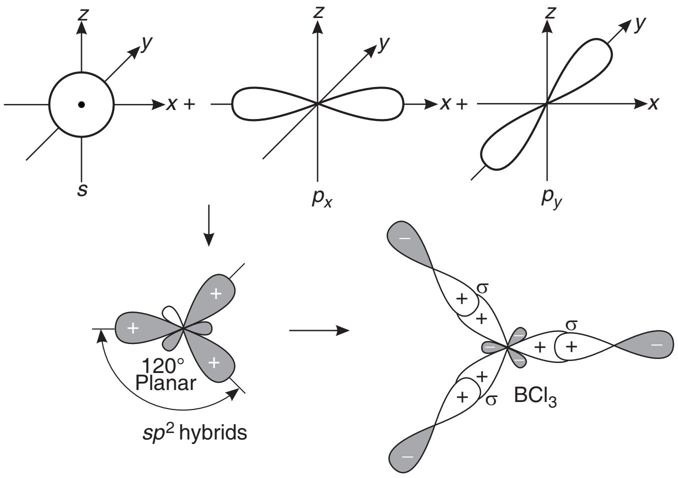
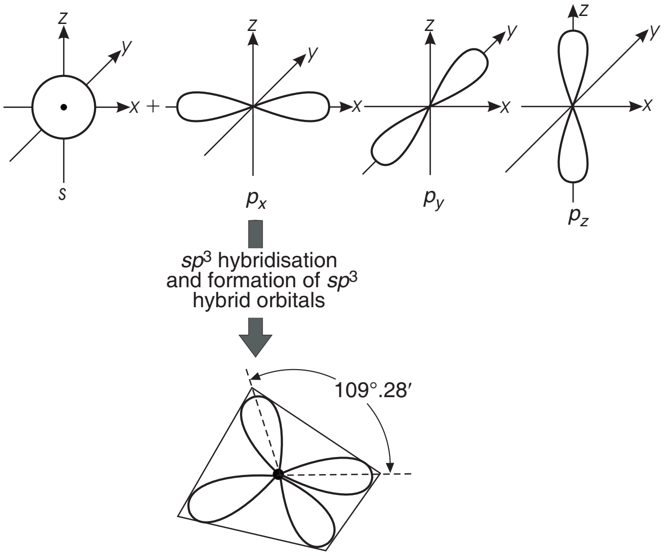


Fig. 4.9 Formation of sp^2 hybrids and the BCl_3 molecule

(c) sp^3-Hybridisation (Tetrahedral Hybridisation)

The term sp^3-hybridised means that one *s* and all the three *p*-orbitals (p_x, p_y and p_z orbitals) of the valence shell of the atom combine together and form a set of four hybrid orbitals which are called sp^3 or tetrahedral hybrid orbitals.

Four sp^3-hybrid orbitals can also be regarded as having been formed by adding one atomic *p*-orbitals to three sp^2-hybrid orbitals which, we know, lie in the same plane (co-planar) and are inclined to each other at 120°. Each pair of these sp^3-hybrids is inclined at an angle of 109°28′ approximately.



Showing sp^3 hybridisation with angle and arrangement of orbitals

Characteristics of sp^3-hybrid orbitals include

1. sp^3-hybrid orbitals are equivalent and symmetrical.
2. They are directed towards the four corners of a regular tetrahedron and the angle between each pair of them is 109.5°. This angle is called **tetrahedral angle.**
3. Each of the four sp^3-hybrid orbitals, has one fourth *s*-character and three-fourth *p*-character, *i.e.*, *s*-character = 25% and *p*-character = 75%.
4. In case of sp^3-hybrid orbitals, since the contribution of three *p*-orbitals predominates over the contribution of one *s*-orbital, the shape of sp^3-hybrid orbitals is practically the same as that of the parent *p*-orbitals except for the fact that the lobes in sp^3-hybrid orbitals are somewhat more spread and are somewhat shorter in length than the pure *p*-orbitals.

Table 4.3 **Relationship between Hybridisation, Shape and Bond Angle**

No. of atomic orbitals involved in hybridisation	Type of hybridisation	No. of hybrid orbitals	Shape of molecules	Bond angles	Examples
2	sp ($s + p$)	2	Linear	180°	$BeCl_2$, BeF_2
3	sp^2 ($s + p + p$)	3	Planar triangular	120°	BF_3, BCl_3
4	sp^3 ($s + p + p + p$)	4	Tetrahedral	109° 28′	CH_4, CCl_4
4	dsp^2 one 'd' ($d_{x^2-y^2}$) + one 's' + two 'p'	4	Square planar	90°	$[Ni(CN)_4]^{2-}$, $[PtCl_4]^{2-}$
5	dsp^3 or sp^3d one 's' + three 'p' + one d (d_{z^2})	5	Trigonal bipyramid	120° and 90°	PCl_5
6	d^2sp^3 or sp^3d^2 one 's' + three 'p' + two 'd' ($d_{x^2-y^2}$, d_{z^2})	6	Octahedral	90°	SF_6
7	d^3sp^3 or sp^3d^3 one 's' + three 'p' + two 'd' (d_{xy}, d_{yz}, d_{zx})	7	Pentagonal bipyramid	72° and 90°	IF_7

Hot Spot 2

METHOD FOR IDENTIFICATION
of Hybridisation for Molecule

Finding hybridisation of molecule is also a hot topic for JEE Main. It is a very easy topic, so scoring, if you do some practice. There are several methods that can be used to find the hybridisation of a molecules. These methods are as follows

First Method

1. Write electronic configuration for the outermost orbit or central atom using boxes.
2. Find oxidation state of central atom. Excite the electrons from orbits of higher energy in such a way that total no. of upaired electrons = oxidation state of central atom.

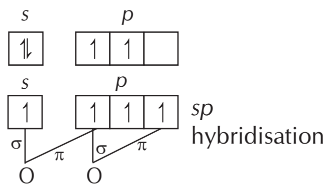
Note π-bonds are excluded from hybridisation calculation.

Sample **Problem 12** *Predict the shape of* CO_2 *molecule.*

(a) *linear*
(b) *trigonal*
(c) *planar*
(d) *tetrahedral*

Interpret (a) CO_2

Electronic configuration of C (ground state)
oxidation state of C = 4
Electronic configuration after excitation add electron to pocket

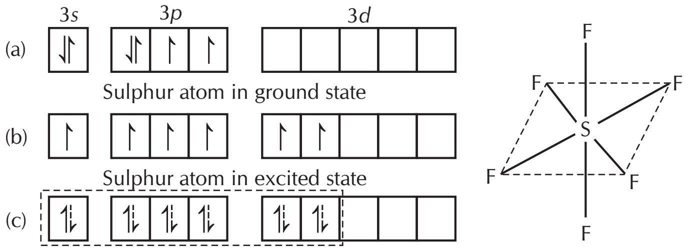


Thus, CO_2 is *sp* hybridised and hence,

Shape of the molecule is linear O═C═O

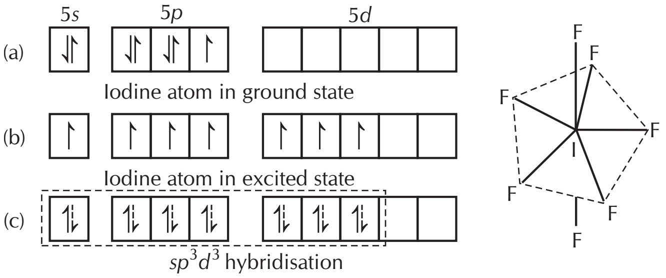
Similarly the hybridisation and shape of SF_6 and IF_7 are described.

(i) SF_6 molecule sp^3d^2 hybridisation



Octahedral geometry of SF_6 molecule resulting from sp^3d^2 hybridisation of the central S atom. Dotted arrows represent electrons supplied by fluorine atoms.

(ii) IF_7 molecule sp^3d^3 hybridisation



Pentagonal bipyramidal geometry of IF_7 molecule resulting from sp^3d^3 hybridisation of the central I atom. Dotted arrows represent electrons supplied by fluorine atoms.

Second Method

The type of hybridisation undergone by the atom/ion in a given molecule or ion depends on the sum of σ-bond pairs and lone pairs surrounding the central atom/ion, *e.g.*, if the sum of σ-*bps* and *lps* is 2 then the central atom/ion undergoes *sp*-hybridisation. Similarly for the sum equal to 3, 4, 5, 6 and 7, the central atom undergoes sp^2, sp^3, sp^3d, sp^3d^2 and sp^3d^3 hybridisation respectively.

Alongwith these, dsp^2 hybridisation is also seen in which 1*d* + 1*s* + 2*p* orbitals combine to hybridise. The shape of the molecule is **square planar** with a bond angle of 90°.

A few examples are being given below

(i) Beryllium chloride ($BeCl_2$)

No. of σ-bonds at Be atom = 2
No. of lone pair of electrons at Be atom = 0
Total = 2 + 0 = 0

Hybridisation is *sp*, *i.e.*, $BeCl_2$ is linear and bond angle is 180°.

(ii) Ammonia (NH_3)

No. of σ-bonds at N atom = 3
No. of lone pair of electrons at N atom = 1
Total = 3 + 1 = 4
Hybridisation is sp^3

Shape is trigonal pyramidal (not tetrahedral) and bond angles are not 109°28′ but 106°45′.

(iii) Water (H_2O)

No. of σ-bonds at O atom = 2

No. of lone pair of electrons at O atom = 2

Total = 2 + 2 = 4

Hybridisation is sp^3

Shape is angular or V-shape (not tetrahedral) and bond angles are not 109°28′ but 104°35′.

Third Method

An alternative way of finding hybridisation is the use of following formula

$$H = \frac{1}{2}[V + Y - C + A]$$

Here, V = valence shell electrons of the cental metal

Y = number of monovalent atom

C = total positive charge

and A = total negative charge on molecule

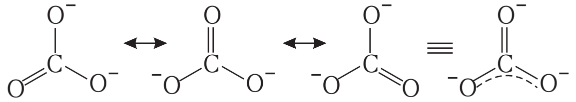
For the 2, 3, 4, 5, 6 and 7 value of H, the hybridisation is respectively sp, sp^2, sp^3, sp^3d, sp^3d^2 and sp^3d^3 *e.g.*,

PF_5	$COCl_2$	NH_4^+	ClO_4^-
$X = \frac{1}{2}[5+5]$ $= 5$	$X = \frac{1}{2}[2+4]$ $= 3$	$X = \frac{1}{2}[4+5-1]$ $= 4$	$X = \frac{1}{2}[0+7+1]$ $= 4$
Hybrid state of P is sp^3d	Hybrid state of C is sp^2	Hybrid state of N is sp^3	Hybrid state of Cl is sp^3
NO_3^-	**IF_5**	**CO_2**	**XeF_4**
$X = \frac{1}{2}[0+5+1]$ $= 3$	$X = \frac{1}{2}[5+7]$ $= 6$	$X = \frac{1}{2}[0+4]$ $= 2$	$X = \frac{1}{2}[4+8]$ $= 6$
sp^2	sp^3d^2	sp	sp^3d^2

Note From the above three method, learn and practice only one method which, you think, is easiest for you.

4.9 Resonance

In some molecules or ions, having double or triple bond, it is difficult to assign which lone pairs are used for forming these multiple bonds. If such a condition exists, all the possible structures of a molecule are called resonance structure or canonical forms and the actual molecule is considered to have a structure equivalent to an average of these structures. *e.g.*, carbonate ion is a resonance hybrid of following canonical forms



From the concept of resonance, the bond order (BO) of a molecule (or ion) is calculated as,

$$BO = \frac{\text{total number of bonds between two atoms in all the structures}}{\text{total number of canonical forms}}$$

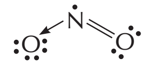
The stability of a resonance structure can be decided by considering the following points

1. A non-polar canonical form is more stable.
2. More the number of covalent bonds, more is the stability.
3. Resonance structure in which negative charge resides on electronegative atom and positive charge on electropositive atom is more stable as compared to that for which opposite is true.

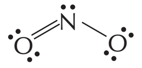
(To know more about resonance see chapter 13)

Sample **Problem 13** *Which of the following is not the correct resonating structure for* NO_2*?* **[NCERT]**

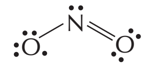
(*a*)



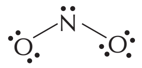
(*b*)



(*c*)



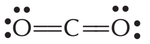
(*d*)



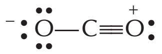
Interpret (*b*) Structure given in option (b) is not possible as in it the octet of O atom, remain incomplete.

Sample **Problem 14** *Which of the following resonating structures is not correct for* CO_2 *?*

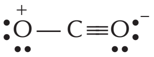
(*a*)



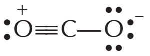
(*b*)



(*c*)



(*d*)



Interpret (*c*) Structure given in option (c) is not possible as in this structure, the O-atom, which is bonded to carbon by a triple bond, has 10 electrons in the valence shell. But this situation is impossible as *d*-orbitals are not present in O atoms. So, O cannot expand its valency beyond 8.

Check Point 2

1. σ-bonds are stronger than π bonds. Explain why?
2. Is there any change in hybridisation of atoms involved in the following reactions?
   $BF_3 + NH_3 \longrightarrow F_3B \rightarrow NH_3$
3. In PCl_5 axial Cl atoms are more reactive than equatorial Cl atoms, explain why?
4. Why does C exhibit + 4 oxidation state or forms 4 bonds although it contains only two unpaired electrons?
5. *p*-orbital will form a stronger bond as compared to *s*-orbital, why?

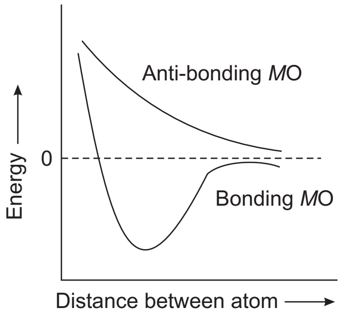
4.10 Molecular Orbital Theory (MOT)

Why He_2 molecule does not exist and why O_2 is paramagnetic? These questions cannot be explained by valence bond theory. In 1932 F. Hund, Huckel and R.S. Mulliken put forward a theory, known as Molecular Orbital Theory, to explain above questions and many others on the basis of **Schrodinger** wave interpretation of electrons.

According to this theory,

1. A molecule is supposed to have orbitals of varying energy levels in the same way as an isolated atom has. These orbitals of molecule are called **molecular orbitals** (MO) .
2. Molecular orbitals are formed by the combination of atomic orbitals of comparable energy and proportional symmerty. While an electron in atomic orbital is influenced by one nucleus, in a molecular orbital, it is influenced by two or more nuclei depending upon the number of atoms in the molecule. Thus, orbitals of atoms loose their individual identity. Hence, **an atomic orbital is monocentric while a molecular orbital is polycentric.**
3. Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution in molecule is given by molecular orbital.
4. The number of molecular orbitals formed is equal to the number of combining atomic orbitals.
5. When two atomic orbitals combine, two molecular orbitals are formed. One is known as **bonding molecular orbital** (BMO) whereas other is **anti-bonding molecular orbital** (ABMO). BMO has lower energy and hence, greater stability than the corresponding ABMO. First BMO are filled, then ABMO starts filling because BMO has lower energy than that of ABMO.
6. The shapes of molecular orbitals formed depends upon the type of combining atomic orbitals.
7. The filling of molecular orbital obey Aufbau principle, Pauli's exclusion principle and Hund's rule of maximum multiplicity.

Electron density is increased for the bonding MO's in the internuclear region but decreased for anti-bonding MO's. Shielding of the nuclei by increased electron density in bonding MO's reduces internuclear repulsions and thus stabilizes the molecule whereas lower electron density (even as compared to the individual atom in anti-bonding MO's) increases the repulsion and destabilizes the system.



Linear Combination of Atomic Orbitals (LCAO)

The Schrodinger wave equation is very difficult to apply on the system containing more than one electron because here one electron is moving in the field of several nuclei so some approximation method used in the formation of molecular orbitals can be explained on the basis of LCAO. It is very convenient method of approximation.

According to LCAO, the wave function (ψ) of individual atomic orbitals linearly combined and form molecular orbitals, *i.e.,* during the formation of AB molecule ψ of A and ψ of B will linearly combine as

$$\psi_{MO} = \psi_A + \psi_B$$

Case I When two waves are in phase (constructive interference), the waves adds up and amplitude of new wave is

$$\psi_{MO} = \psi_A + \psi_B \qquad \text{(Bonding M.O.)}$$

Case II When two waves are out of phase, the waves are subtracted from each other so that the amplitude of new wave is

$$\psi^*_{MO} = \psi_A - \psi_B \text{ (Antibonding M.O.)}$$

Knowing that probability is given by square of the amplitude, we have

$$\psi^2_{MO} = (\psi_A + \psi_B)^2$$
$$= \psi^2_A + \psi^2_B + 2\psi_A\psi_B$$

and $$(\psi^*_{MO})^2 = (\psi_A - \psi_B)^2$$
$$= \psi^2_A + \psi^2_B - 2\psi_A\psi_B$$

i.e., $$\psi^2_{MO} > \psi^2_A + \psi^2_B$$

whereas $$(\psi^*_{MO})^2 < \psi^2_A + \psi^2_B$$

Thus, by combination of two atomic orbitals, two new molecular orbitals are formed, one by constructive and other by destructive interference of atomic orbitals. These interactions are based upon the fact that when orbitals or lobes of orbitals with same wave function (ψ) combine, the result is **constructive interaction** while when orbitals or lobes of orbitals with opposite wave function (ψ) combine, the result is **destructive interaction.**

Constructive interaction of orbitals give rise to orbitals of lower energy, called **bonding orbitals** or **HOMOs** (highly occupied molecular orbitals) as electrons prefer to stay in these orbitals due to their lower energy as compared to combining atomic orbitals.

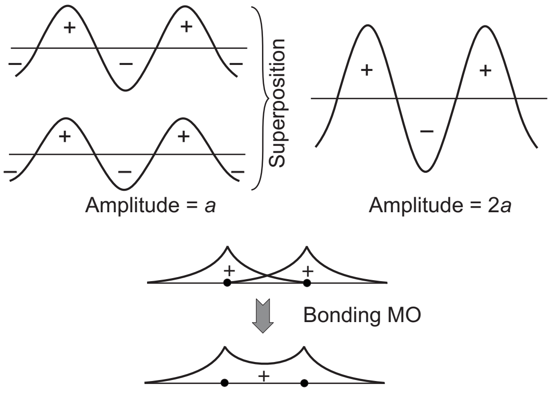


Fig 4.11 Constructive interaction

Destructive interaction, on the other hand, give rise to orbitals of higher energy, called **antibonding orbitals or LUMOs** (lowest unoccupied molecular orbitals) as electrons don't prefer them due to their higher energy as compared to combining atomic orbitals

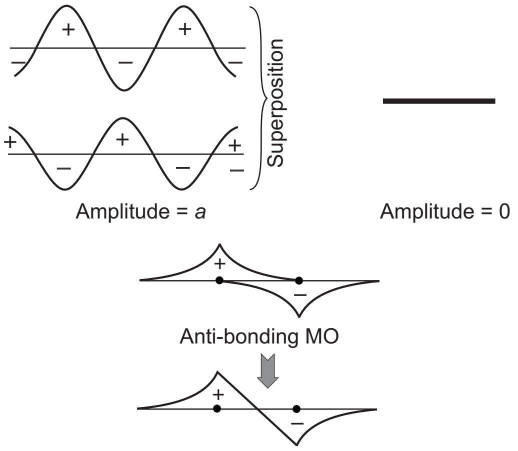


Fig 4.12 Destructive interaction

The condition of lower energy (bonding molecular orbital) is also called attractive state for electrons while condition of higher energy (antibonding molecular orbital) is also called repulsive state for electrons.

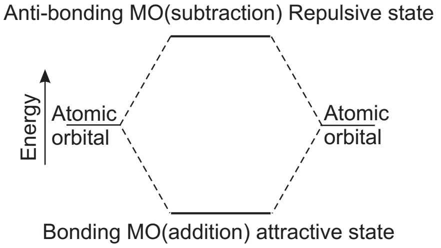


Fig 4.13 Energy level diagram of molecular orbitals

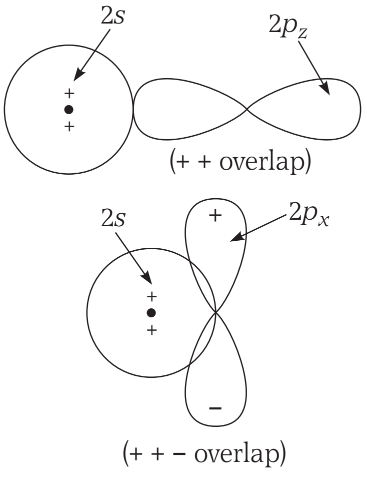
The bonding molecular orbitals are shown as σ or π*ns* or *np* while antibonding molecular orbitals are shown as σ* or π**ns* or *np* accordingly.

The total energy of two molecular orbitals, however, remains the same as that of two original atomic orbitals.

Conditions for Combination of Atomic Orbitals

The combination of the atomic orbitals is based on the following conditions.

1. *The combining atomic orbitals must have comparable energies*. It may be noted that in the homonuclear diatomic molecules of the type A_2 (*e.g.,* H_2, O_2, N_2, F_2 etc.), the participating atomic orbitals must have comparable energies. This means that 1*s* atomic orbital of one atom can combine with 1*s* atomic orbital of the other atom and not with its 2s orbital. However, in heteronuclear molecules *AB* (*e.g.,* HF, HCl etc.) such a combination is permissible.
2. *The extent of overlapping must be large*. The overlapping of the atomic orbitals results in decrease in energy and increase in stability. Thus, greater the extent of the overlapping, more will be the stability of the molecular orbital formed.
3. *The combining atomic orbitals must have same symmetry about internuclear axis*. The atomic orbitals taking part in the overlap must have same orientation or same sign of symmetry.

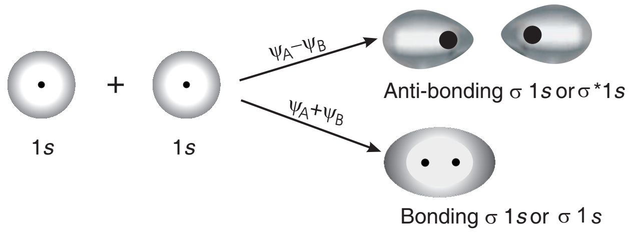


Types of Molecular Orbitals

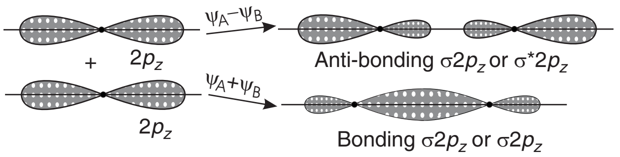
Molecular orbitals of diatomic molecule are designated as σ (sigma means head on overlap), π (pi represent side ways overlap) etc. Sigma (σ) molecular orbitals are symmetrical around the bond axis while pi (π) molecular orbitals are not symmetrical.

Formation of σ and π HOMOs and LUMOs

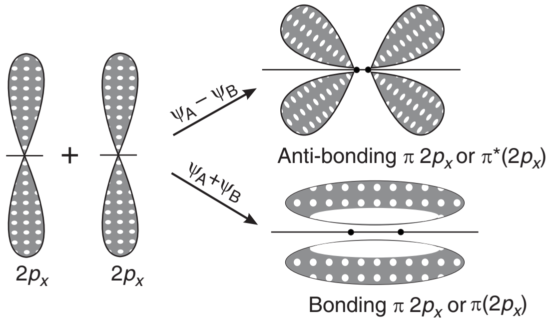
(a) **Combination of *s*-orbitals**



(b) **Head on combination of two *p*-orbitals**



(c) **Sidewise combination of two *p*-orbitals**



[Here *z* axis is considered as internuclear axis]

Hot Spot 3

MOLECULAR ORBITAL
Electronic Configuration

Molecular orbital electronic configuration is an important topic as it is related to the bond order, bond length, bond strength and magnetic nature and questions based on these topics are frequently asked. So do practice to write electronic configuration and finding its relation with these topics.

The energy levels of molecular orbitals have been determined experimentally from spectroscopic data, for homonuclear diatomic molecules of the 2nd row elements of Periodic Table. The increasing order of energies of molecular orbitals for O_2 and F_2 molecules is given as

$$\sigma 1s < \overset{*}{\sigma} 1s < \sigma 2s < \overset{*}{\sigma} 2s < \sigma 2p_z < \pi 2p_x \approx \pi 2p_y < \overset{*}{\pi} 2p_x \approx \overset{*}{\pi} 2p_y < \overset{*}{\sigma} 2p_z$$

However, for remaining molecules *i.e.*, $Li_2, Be_2, B_2, C_2, N_2$ the order is

$$\sigma 1s < \overset{*}{\sigma} 1s < \sigma 2s < \overset{*}{\sigma} 2s < \pi 2p_x \approx \pi 2p_y < \sigma 2p_z < \overset{*}{\sigma} 2p_x \approx \overset{*}{\pi} 2p_y < \overset{*}{\sigma} 2p_z$$

i.e., here the energy of $\pi 2p_x \approx \pi 2p_y$ is less than the energy of $\sigma 2p_z$ molecular orbital.

The molecular orbital energy level diagrams are different because the energy difference between 2*s* and 2*p* atomic energy level is small (except O_2 and F_2) as a result both come together and hence, repulsive forces arises which raise the energy σ2*p* above that of π2*p* molecular orbitals.

Bond Order

The one-half of the difference between the number of electrons present in bonding orbitals and number of electrons present in anti-bonding orbitals is called **bond order** of that molecule, *i.e.*,

$$\text{Bond order} = \frac{N_b - N_a}{2}$$

Here, N_b = Number of electrons in bonding orbitals

N_a = Number of electrons in anti-bonding orbitals

The **stability** of a molecule can be determined by its bond order as

1. A positive bond order means a stable molecule,
2. A negative or zero bond order means an unstable molecule,
3. Bond order values 1, 2 and 3 corresponds to single, double and triple bond respectively.

Bond length varies inversely with bond order *i.e.*, decreases as the bond order increases.

$$\text{Bond order} \propto \frac{1}{\text{Bond length}}$$

Magnetic nature of molecule can also be determined by molecular orbitals as

1. If all orbitals are fully occupied, *substance is diamagnetic.*
2. If one or more molecular orbitals are singly occupied, *substance is paramagnetic.*

Bonding in Some Homonuclear Diatomic Molecules

(i) **H_2 molecule**

Electronic configuration : $\sigma 1s^2$

$$\text{Bond order} = \frac{2-0}{2} = 1$$

Conclusion Stable molecule, with single bond between 2H atoms, diamagnetic.

(ii) **He_2 molecule**

Electronic configuration : $\sigma 1s^2, \overset{*}{\sigma} 1s^2$

$$\text{Bond order} = \frac{2-2}{2} = 0$$

Conclusion Unstable molecule, does not exist.

Similarly, Be_2 molecule with electronic configuration $\sigma 1s^2 \overset{*}{\sigma} 1s^2 \sigma 2s^2 \overset{*}{\sigma} 2s^2$ does not exist.

(iii) **Li_2 molecule**

Electronic configuration : $\sigma 1s^2, \sigma * 1s^2, \sigma 2s^2$

$$\text{Bond order} = \frac{4-2}{2} = 1$$

Conclusion Stable (known in vapour phase) with single bond between 2 Li atoms, **diamagnetic.**

(iv) **C_2 molecule**

Electronic configuration

$$\sigma 1s^2, \sigma * 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \pi 2p_x^2 \approx \pi 2p_y^2$$

$$\text{Bond order} = \frac{8-4}{2} = 2$$

Conclusion Stable (detected in vapour phase), with 2π-bonds between two C-atoms instead of 1σ and 1π, diamagnetic.

(v) **O_2 molecule**

Electronic configuration

$$\sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \overset{*}{\pi} 2p_x^1 \approx \overset{*}{\pi} 2p_y^1$$

$$\text{Bond order} = \frac{10-6}{2} = 2$$

Conclusion Stable, with double bond between two oxygen atoms, paramagnetic.

(vi) **F_2 molecule**

Electronic configuration : $\sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2$

$$\sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \overset{*}{\pi} 2p_x^2 \approx \overset{*}{\pi} 2p_y^2$$

$$\text{Bond order} = \frac{10-8}{2} = 1$$

Conclusion Stable, with one σ bond between two F atoms, diamagnetic.

Note $\pi 2p_x$ and $\pi 2p_y$ have one nodal plane while $\overset{*}{\pi} 2p_x$ and $\overset{*}{\pi} 2p_y$ have two nodal planes.

Sample Problem 15 *Which of the following options represents the correct bond order ?* **[NCERT Exemplar]**

(a) $O_2^- > O_2 > O_2^+$
(b) $O_2^- < O_2 < O_2^+$
(c) $O_2^- > O_2 < O_2^+$
(d) $O_2^- < O_2 > O_2^+$

Interpret (*b*) E.C. of O_2 (16 electrons)

$$= \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \overset{*}{\pi} 2p_x^1 \approx \overset{*}{\pi} 2p_y^1$$

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10-6) = 2$$

E.C. of O_2^+ (15 electrons)

$$= \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \overset{*}{\pi} 2p_x^1 \approx \overset{*}{\pi} 2p_y$$

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10-5) = 2.5$$

E.C. of O_2^- (17 electrons)

$$= \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \overset{*}{\pi} 2p_x^2 \approx \overset{*}{\pi} 2p_y^1$$

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10-7) = 1.5$$

Thus, the order of bond order is $O_2^- < O_2 < O_2^+$

Sample Problem 16 *The relative stabilities of* H_2, H_2^+ *and* H_2^- *are in the order of*

(a) $H_2^+ > H_2^- < H_2$
(b) $H_2^- < H_2^+ < H_2$
(c) $H_2^+ < H_2 < H_2^-$
(d) $H_2 < H_2^- < H_2^+$

Interpret (*b*) Stability ∝ Bond order

$H_2 = \sigma 1s^2$, $\quad \text{BO} = \frac{2-0}{2} = 1$

$H_2^+ = \sigma 1s^1$ $\quad \text{BO} = \frac{1-0}{2} = \frac{1}{2}$

$H_2^- = \sigma 1s^2, \overset{*}{\sigma} 1s^1$ $\quad \text{BO} = \frac{2-1}{2} = \frac{1}{2}$

Antibonding orbitals destabilises the molecule, then, correct stability order is $H_2^- < H_2^+ < H_2$

Sample Problem 17 *Which of the following molecule is paramagnetic?*

(a) *Fluorine* (b) *Oxygen* (c) *Nitrogen* (d) *Hydrogen*

Interpret (*b*)

(a) $F_2 (9 + 9 = 18) = \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \overset{*}{\pi} 2p_x^2 \approx \overset{*}{\pi} 2p_y^2.$

All the electrons are paired, so F_2 is diamagnetic.

(b) $O_2 (8 + 8 = 16) = \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \overset{*}{\pi} 2p_x^1 \approx \overset{*}{\pi} 2p_y^1$

Due to the presence of two unpaired electrons, O_2 is paramagnetic.

(c) $N_2 (7 + 7 = 14) = \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \pi 2p_x^2 \approx \pi 2p_y^2, \sigma 2p_z^2.$

Since all the electrons are paired, N_2 is diamagnetic.

(d) $H_2 (1 + 1 = 2) = \sigma 1s^2$

Since, all the electrons are paired, H_2 is also diamagnetic.

4.11 Metallic Bonding

The peculiar type of bonding which holds the metal atoms together in a metal crystal is called **metallic bonding.** Different models have been proposed to explain the nature of metallic bonding, the two important of them are as

Electron Sea Model

According to this model, a metal is regarded as a group of positive metal ions packed together as closely as possible in a regular geometric pattern and immersed in a sea of electron which move about freely in the vacant valence orbitals.

The attractive force that binds the metal ions to the mobile electrons is called **metallic bond.** The positive metal ions, here are called **positive cores** or **kernels** and mobile electrons are **electron pool** or **electron gas.**

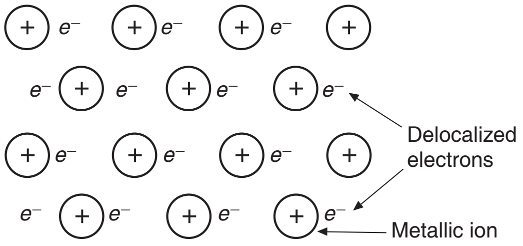
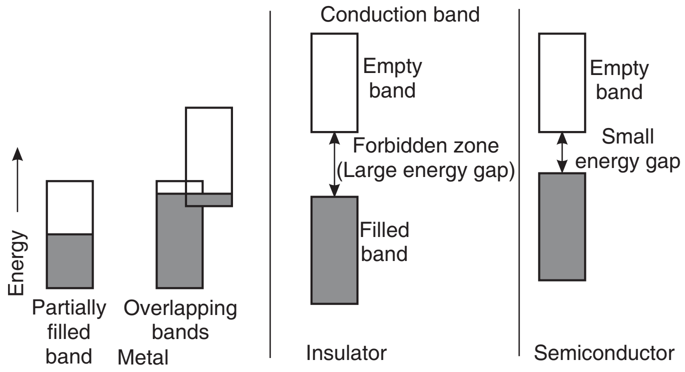


Fig 4.14 Electron sea model

Band Model

This model is based upon molecular orbital theory. According to this theory, a metal lattice has an extremely large number of atoms. The atomic orbitals of these atoms overlap together due to similar symmetry and similar energy resulting to the formation of energy bands. The arrangement of electrons in the different energy bands determines the characteristic of a metal.



(In each case, an unshaded area represents a conduction band)

Fig 4.15 Distinction among metals, insulators and semiconductors.

The highest occupied energy band is called the **valence band** while the lowest unoccupied energy band is called **conduction band.** The properties of various elemental solids can be explained by the gap present between the top of valence band and the bottom of conduction band, called **energy gap** (E_g). In the case of metals, semimetals and non-metals the valence and conduction bands can be seen as

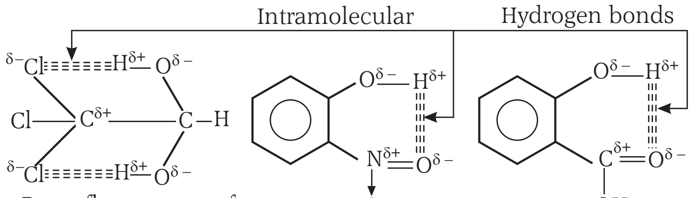
4.12 Hydrogen Bonding

The attractive electrostatic force between a hydrogen atom (which is already covalently attached to a strong electronegative atom *i.e.,* any of F, O and N) and an electronegative atom (any out of F, O and N) is known as hydrogen bond.

Hydrogen bonding is of two types

1. Intramolecular H-bonding

It is seen in a single molecule and when this type of H-bonding leads to linking of two groups in such a way that a ring like structure is formed, the effect is also called **chelation,** *e.g.,*



Butterfly structure of chloral hydrate ($CCl_3CH(OH_2)$) in which 2–OH groups are attached in stable

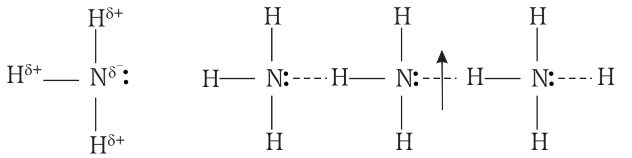
o-nitrophenol

Salicylic acid (*ortho*-hydroxy benzoic acid)

Molecules with intramolecular H-bonding are known to have lower boiling point and melting point.

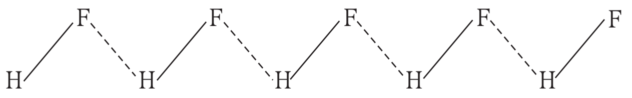
2. Intermolecular H-bonding

It occurs between two or more molecules of similar or different compounds, *e.g.,*



Ammonia molecule

Intermolecular H-bonding in NH_3



Hydrogen fluoride molecule showing intermolecular H-bonding

The intermolecular H-bonding is found to be responsible for high mp and bp of compounds in which it is seen.

Certain organic compounds like alcohols show miscibility with polar solvents like water. It is also attributed to intermolecular H-bonding between alcohol and water molecules.

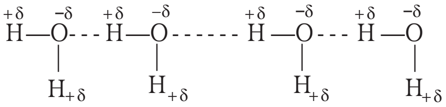
Nature and Importance of H-bonding

1. H-bond is simply dipole-dipole attraction within oppositely partially charged ends.
2. H-bond never involves more than two atoms.
3. Bond energy of H-bond is of the order of 3–10 kcal mol^{-1}, *i.e.,* about 1/10 of covalent bond.
4. As the electronegativity difference of H and other atom to which it is covalently bonded increases, the strength of H-bond increases.
   $H-$ bond order : $H-F > H-O > H > N-H > Cl$
5. All the three atoms X–H---X lie in one plane.

Effects of H-Bonding

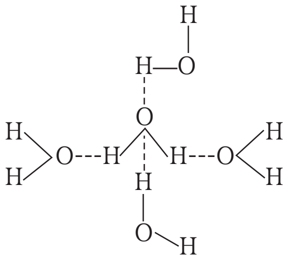
(a) High Boiling Point of Water

Due to polar nature of H_2O, there is association of water molecules giving a liquid state of abnormally high boiling point.



$\overset{+\delta}{H}-\underset{\underset{H_{+\delta}}{|}}{\overset{-\delta}{O}}\cdots\overset{+\delta}{H}-\underset{\underset{H_{+\delta}}{|}}{\overset{-\delta}{O}}\cdots\cdots\overset{+\delta}{H}-\underset{\underset{H_{+\delta}}{|}}{\overset{-\delta}{O}}\cdots\overset{+\delta}{H}-\underset{\underset{H_{+\delta}}{|}}{\overset{-\delta}{O}}$

Actually, in water, one water molecule is joined to four water molecules (two with H-atom and other two with O-atoms.) *Thus, coordination number of water molecule in water is four.*

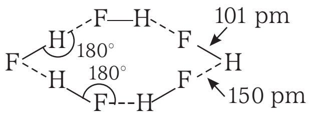


(b) Low Density of Ice as Compared to Water

When ice is formed from liquid water, some air gap is formed (in tetrahedral packing of water molecules). Due to this, volume of ice is greater than liquid water and thus, ice is lighter than water. In another word, we can say that density decreases when ice is formed. Reversely when ice melts, density increases but only upto 4°C, after this intermolecular H-bonding between water molecules breaks, hence volume increases and hence, density decreases. *Thus, water has maximum density at* 4°*C.*

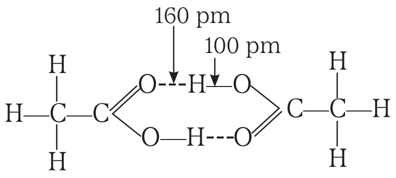
(c) Pentagonal Arrangement of HF

In the gaseous state, several polymeric forms of HF molecules exist in which the monomers are held together through H-bonding. A pentagonal arrangement of H–F molecules is shown below



(d) Dimerisation of Carboxylic Acids

Carboxylic acid dimerises in gaseous state due to H-bonding.



Check Point 3

1. The bonding σ 2*s* orbital has a higher energy than the antibonding $\overset{*}{\sigma}$ 1*s* orbital. Why is the former a bonding orbital while the latter is antibonding?
2. Explain, why N_2 has a greater dissociation energy than N_2^+, whereas O_2 has a lower dissociation energy than O_2^+.
3. Though the electronegativity of N and Cl both are same, NH_3 exists as liquid whereas, HCl as gas, Explain why?
4. Usually solids have high density as compared to liquid but density of ice is less than that of water, Explain.
5. Is hydrogen bond weaker or stronger than the van der Waals' forces?

WORKED OUT
Examples

Example 1 *Which of the following substances has the highest melting point?*

(a) BaO (b) MgO (c) KCl (d) NaCl

Solution (*b*) Melting point depends upon lattice energy. NaCl and KCl have unit charge on their ions while MgO and BaO have two units of charge, therefore, lattice energies of MgO and BaO are expected to be larger than those of NaCl and KCl.

Since, Mg^{2+} is smaller than Ba^{2+}, therefore, MgO has the highest lattice energy and hence, has the highest melting point.

Example 2 *Consider two elements with atomic no. 37 and 53, the bond between their atoms would be*

(a) *covalent* (b) *Ionic*
(c) *coordinate* (d) *metallic*

Solution (*b*) $37 = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^1$

Thus, the element belongs to IA group and has valency +1.
$53 = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^5$

Since, there are 7 electrons in the valence shell, thus this element requires one electron to complete its octet, *i.e.,* has valency –1.

Hence, element with atomic number 37 transfers its electron to the element having atomic number 53 and results in the formation of an ionic bond.

Example 3 *The molecule ML_x is planar with six pairs of electrons around M in the valence shell. The value of x is*

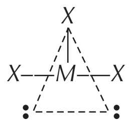
(a) 6 (b) 2 (c) 4 (d) 3

Solution (*c*) Since, the molecule has six pairs, it should have octahedral geometry. But the structure is planar, therefore it should have two lone pairs and four bond pairs. Therefore, value of *x* in ML_x is 4.

Example 4 *A σ bonded molecule MX_3 is T-shaped. The number of non-bonding pairs of electron is*

(a) 0
(b) 2
(c) 1
(d) *can be predicted only if atomic number of M is known*

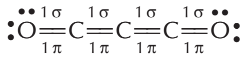
Solution (*b*) The formula of MX_3 shows the presence of 3σ bonds. Since, it has *T*-shape geometry, it must contain 2 lone pair as



Example 5 *Each carbon in carbon suboxide is*

(a) *sp^2-hybridised*
(b) *sp^3-hybridised*
(c) *sp-hybridised*
(d) *sp^2-hybridised but linked with one coordinate bond.*

Solution (c) The structure of carbon suboxide is



$$:\ddot{\mathrm{O}}\underset{1\pi}{\overset{1\sigma}{=}}\mathrm{C}\underset{1\pi}{\overset{1\sigma}{=}}\mathrm{C}\underset{1\pi}{\overset{1\sigma}{=}}\mathrm{C}\underset{1\pi}{\overset{1\sigma}{=}}\ddot{\mathrm{O}}:$$

Number of hybrid orbitals of carbon = no. of bonds + no. of *lps*
= 2 + 0 = 2

Thus, each carbon is *sp*-hybridised.

Example 6 *Which of the following has least covalent* P—H *bond?*

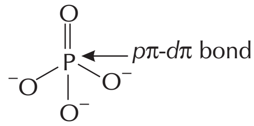
(a) PH_3 (b) P_2H_6 (c) P_2H_5 (d) PH_6^+

Solution (*d*) Due to the presence of positive charge on P, it attracts the electrons of the P—H bond towards itself. Consequently, the bond has some ionic character. In other words, the P—H bond in PH_6^+ is least covalent.

Example 7 *Among the following ions, the pπ - dπ overlapping could be present in*

(a) PO_4^{3-} (b) NO_2^- (c) NO_3^- (d) CO_3^{2-}

Solution (*a*) In PO_4^{3-}, P is sp^3 hybridised, it forms four P—O σ bonds by overlap of sp^3-orbitals of P with *p*-orbitals of O. The bond is, however, formed by overlap of *p*-orbitals of O and *d*-orbitals of P.



N and C, on the other hand, can't form pπ - dπ bond, since they do not have *d*-orbitals.

Example 8 *Which of the following liquids is not deflected by a non-uniform electrostatic field?*

(a) H_2O (b) $CHCl_3$ (c) C_6H_{14} (d) $C_6H_5NO_2$

Solution (c) C_6H_{14} has symmetrical geometry, thus its dipole moment is zero and it is not deflected by a non-uniform electrostatic field.

Example 9 *Which of the following species has the lowest ionization potential?*

(a) O (b) O_2 (c) O_2^+ (d) O_2^-

Solution (*d*) O_2^- has three electrons in the anti-bonding orbitals and hence, has the highest energy of least ionization potential.

Start **Practice** *for* JEE Main

Round I (Topically Divided Problems)

Octet Rule and Ionic Bonding

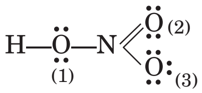
1. Which of the following compounds does not follow the octet rule for electron distribution?
(a) H_2O (b) PH_3
(c) PCl_3 (d) PCl_5

2. Which of the following has an electrovalent linkage?
(a) CH_4 (b) $SiCl_4$
(c) $MgCl_2$ (d) BF_3

3. As compared to covalent compounds, electrovalent compounds generally have
(a) low melting points and low boiling points
(b) high melting points and high boiling points
(c) low melting points and high boiling points
(d) high melting points and low boiling points

4. Arrange the bonds in order of increasing ionic character in the molecules; LiF, K_2O, N_2, SO_2 and ClF_3. **[NCERT]**
(a) $N_2 < ClF_3 < SO_2 < LiF < K_2O$
(b) $N_2 < SO_2 < ClF_3 < K_2O < LiF$
(c) $N_2 < ClF_3 < SO_2 < K_2O < LiF$
(d) $N_2 < SO_2 < ClF_3 < Lif < K_2O$

5. In the following Lewis structure of HNO_3, the formal charge on O_3 atom is **[NCERT]**



(a) 0 (b) −1
(c) −2 (d) +1

6. Arrange the following bonds in order of increasing ionic character N—H, F—H, C—H and O—H **[NCERT]**
(a) F—H < O—H < C—H < N—H
(b) N—H < O—H < C—H < F—H
(c) C—H < N—H < O—H < F—H
(d) F—H < C—H < O—H < N—H

7. X, Y and Z elements have 4, 5 and 7 valence electrons. Among the given the correct formula is **[NCERT]**
(a) XH_3 (b) YH_4
(c) HZ (d) YH_5

8. If the electronegativity difference between two atoms A and B is 2.0, then the percentage of covalent character in the molecule is
(a) 54% (b) 46%
(c) 23% (d) 72%

9. Among the following isostructural compounds, identify the compound which has the highest lattice energy.
(a) LiF (b) LiCl
(c) NaCl (d) MgO

10. A pair of compounds which have odd electrons in the group NO, CO, ClO_2, N_2O_5, SO_2 and O_3 are
(a) NO and ClO_2 (b) CO and SO_2
(c) ClO_2 and CO (d) SO_2 and O_3

11. CaO and NaCl have the same crystal structure and approximately the same ionic radii. If U is the lattice energy of NaCl, the approximate lattice energy of CaO is
(a) $\frac{U}{2}$ (b) U
(c) $2U$ (d) $4U$

12. An atom X has three valence electrons and atom Y has six valence electrons. The compound formed between them will have the formula
(a) X_2Y_6 (b) XY_2
(c) X_2Y_3 (d) X_3Y_2

Covalent Bonding and Coordinate Bonding

13. The order of resultant dipole moment in CO_2, NF_3 and $CHCl_3$ is **[NCERT]**

(a) $NF_3 < CO_2 < CHCl_3$
(b) $CHCl_3 < CO_2 < NF_3$
(c) $CO_2 < NF_3 < CHCl_3$
(d) $CO_2 < CHCl_3 < NF_3$

14. Which of the following does not have a coordinate bond?

(a) SO_2 (b) H_2SO_3
(c) HNO_2 (d) HNO_3

15. Which is the most covalent?

(a) C—F (b) C—O
(c) C—S (d) C—Br

16. The number of electrons involved in the bond formation of N_2 molecule is

(a) 2 (b) 4
(c) 6 (d) 10

17. Which has maximum covalent character?

(a) $SiCl_4$ (b) $MgCl_2$
(c) NaCl (d) $AlCl_3$

18. Why BeH_2 molecule has a zero dipole moment although the Be—H bonds are polar? **[NCERT]**

(a) Because of its linear geometry
(b) Because of two opposite and equal dipoles
(c) Both (a) and (b)
(d) None of the above

19. Although both CO_2 and H_2O are triatomic molecules, the shape of the H_2O molecule is bent while that of CO_2 is linear. This is because **[NCERT]**

(a) C is less electronegative than H
(b) C is more electronegative than H
(c) lone pairs are present on O atom of H_2O but not in O atom of CO_2
(d) lone pairs carrying O is the central atom in H_2O but not in CO_2

20. The types of bonds present in $CuSO_4 \cdot 5H_2O$ are only

(a) electrovalent and covalent
(b) electrovalent and coordinate
(c) electrovalent, covalent and coordinate covalent
(d) covalent and coordinate covalent.

21. Isostructural species are those which have the same shape and hybridisation. Among the given species identify the isostructural pairs. **[NCERT Exemplar]**

(a) NF_3 and BF_3 (b) BF_4^- and NH_4^+
(c) BCl_3 and $BrCl_3$ (d) NH_3 and NO_3^-

22. N_2 is less reactive than CN^- due to

(a) difference in spin quantum number
(b) presence of more electrons in orbitals
(c) absence of dipole moment
(d) None of the above

23. Which of the following has a bond order of 1.75?

(a) ClO_3^- (b) ClO_4^-
(c) NO_3^- (d) CO_3^{2-}

24. Amongst LiCl, RbCl, $BeCl_2$ and $MgCl_2$, the compounds with the greatest and the least ionic character, respectively are

(a) LiCl and RbCl (b) RbCl and $MgCl_2$
(c) RbCl and $BeCl_2$ (d) $MgCl_2$ and $BeCl_2$

25. The correct order of decreasing polarity is

(a) $HF > SO_2 > H_2O > NH_3$
(b) $HF > H_2O > SO_2 > NH_3$
(c) $HF > NH_3 > SO_2 > H_2O$
(d) $H_2O > NH_3 > SO_2 > HF$

26. Which one of the following compounds has bond angle as nearly 90°?

(a) NH_3 (b) H_2S
(c) H_2O (d) CH_4

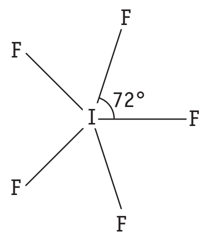
27. The bond angles of NH_3, NH_4^+ and NH_2^- are in the order

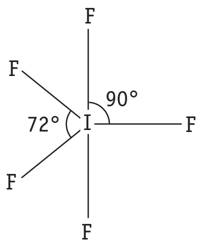
(a) $NH_2^- > NH_3 > NH_4^+$ (b) $NH_4^+ > NH_3 > NH_2^-$
(c) $NH_3 > NH_2^- > NH_4^+$ (d) $NH > NH_4^+ > NH_2^-$

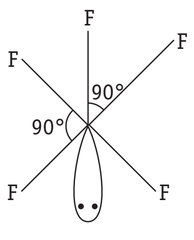
28. In the electronic structure of H_2SO_4, the total number of unshared electrons is

(a) 20 (b) 16
(c) 12 (d) 8

29. The structure of IF_5 can be best described as

(a)


(b)


(c)


(d) None of these

30. The correct order in which the O—O bond length increases in the following is

(a) $O_2 < O_3 < H_2O_2$ (b) $H_2O_2 < O_3 < O_2$
(c) $O_3 < O_2 < H_2O_2$ (d) $O_2 < H_2O_2 < O_3$

31. Although geometries of NH_3 and H_2O molecules are distorted tetrahedral, bond angle in water is less than that of ammonia. This is due to **[NCERT]**

(a) *lp-lp* repulsion in NH_3 and *lp bp* repulsion in H_2O
(b) *lp-lp* repulsion in H_2O and *lp-bp* repulsion in NH_3
(c) *bp-bp* repulsion in NH_3 and *lp-bp* repulsion in H_2O
(d) None of the above

32. In which of the following molecule/ion all the bonds are not equal? **[NCERT Exemplar]**

(a) XeF_4 (b) BF_4^- (c) C_2H_4 (d) SiF_4

33. Apart from tetrahedral geometry, another possible geometry for CH_4 is square planar with the four H-atoms at the corners of the square and the C atom at its centre. But CH_4 does not have square planar geometry because of **[NCERT]**

(a) the absence of *d* orbital
(b) the smaller size of C atom
(c) the smaller size of H atom
(d) All of the above

34. Which of the following species has tetrahedral geometry? **[NCERT Exemplar]**

(a) BH_4^- (b) NH_2^-
(c) CO_3^{2-} (d) H_3O^+

35. The correct order towards bond angle is

(a) $sp^3 < sp^2 < sp$ (b) $sp < sp^2 < sp^3$
(c) $sp < sp^3 < sp^2$ (d) $sp^2 < sp^3 < sp$

36. Which molecule is linear ?

(a) H_2S (b) NO_2 (c) ClO_2 (d) CO_2

37. Which of the following pair has same structure?

(a) PCl_5 and SF_6 (b) SO_2 and NH_3
(c) PH_3 and BCl_3 (d) NH_4^+ and SO_4^{2-}

38. In a polar molecule, the ionic charge is 4.8×10^{-10} esu. If the interionic distance is 1 Å unit, then the dipole moment is

(a) 0.48 debye (b) 4.18 debye
(c) 4.8 debye (d) 41.8 debye

VBT, Resonance, Hybridisation

39. The *d*-orbital involved in sp^3d hybridisation is

(a) $d_{x^2-y^2}$ (b) d_{xy}
(c) d_{z^2} (d) d_{zx}

40. In which molecule are all atoms coplanar?

(a) PF_3 (b) NH_3
(c) BF_3 (d) CH_4

41. Resonance structures can be written for

(a) O_3 (b) NH_3
(c) CH_4 (d) H_2O

42. Which of the following statements is not correct?

(a) Hybridisation is the mixing of atomic orbitals prior to their combining into molecular orbitals
(b) sp^2 hybrid orbitals are formed from two *p*-atomic orbitals and one *s*-orbital
(c) d^2sp^3 hybrid orbitals are directed towards the corners of a regular octahedron
(d) dsp^3 hybrid orbitals are all at 90° to one another

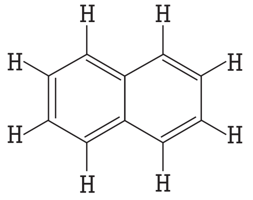
43. The bond in the formation of fluorine molecule will be

(a) due to *s-s* overlapping
(b) due to *s-p* overlapping
(c) due to *p-p* overlapping
(d) due to hybridisation

44. Which of the following angle corresponds to sp^2 hybridisation? **[NCERT Exemplar]**

(a) 90° (b) 120°
(c) 180° (d) 109°

45. Number of π bonds and σ bonds in the following structure is



(a) 6, 19 (b) 4, 20
(c) 5, 19 (d) 5, 20

46. Which orbital is used by oxygen atom to form a sigma bond with other oxygen atom in O_2 molecule?

(a) pure *p*-orbital
(b) sp^2-hybrid orbital
(c) sp^3-hybrid orbital
(d) *sp*-hybrid orbital

47. Two hybrid orbitals have a bond angle of 120°. The percentage of *s* character in the hybrid orbital is nearly

(a) 25% (b) 33%
(c) 50% (d) 66%

48. The hybrid state of S in SO_3 is similar to that of

(a) C in C_2H_2 (b) C in C_2H_4
(c) C in CH_4 (d) C in CO_2

49. Which of the following will provide the most efficient overlap?

(a) s-s
(b) s-p
(c) sp^2-sp^2
(d) sp-sp

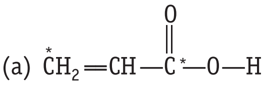
50. Considering x-axis as the internuclear axis, which out of the following will not form a sigma bond ? **[NCERT]**

(a) $1s$ and $1s$
(b) $1s$ and $2p_x$
(c) $2p_y$ and $2p_y$
(d) $1s$ and $2s$

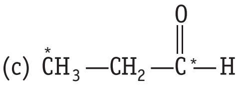
51. The types of hybrid orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ respectively are expected to be **[NCERT Exemplar, AIEEE 2011]**

(a) sp, sp^3 and sp^2
(b) sp, sp^2 and sp^3
(c) sp^2, sp and sp^3
(d) sp^2, sp^3 and sp

52. In which of the following the carbon atoms marked with star is sp hybridised?

(a) 
$\overset{*}{C}H_2{=}CH{-}\overset{\overset{O}{\|}}{C^*}{-}O{-}H$

(b) $CH_3{-}\overset{*}{C}H_2{-}OH$

(c) 
$\overset{*}{C}H_3{-}CH_2{-}\overset{\overset{O}{\|}}{C^*}{-}H$

(d) $CH_3{-}\overset{*}{C}{\equiv}CH$

53. The possible number of resonance structures for NO_3^- is. **[NCERT]**

(a) 2
(b) 3
(c) 4
(d) 5

Molecular Orbital Theory (MOT)

54. Molecular orbital theory was developed mainly by

(a) Pauling
(b) Mulliken
(c) Thomson
(d) Pauling and Slater

55. Which one is paramagnetic and has the bond order half (0.5)?

(a) F_2
(b) N_2
(c) O_2
(d) H_2^+

56. Which of the following molecular orbitals has two nodal planes?

(a) $\sigma 2p_x$
(b) $\pi 2p_y$
(c) $\pi^* 2p_y$
(d) $\sigma^* 2p_x$

57. In which of the following diatomic molecules/ions is the bond order of each molecule/ion = 2.5?

(a) O_2^+, NO, CN^-
(b) CN^-, N_2^+, N_2
(c) N_2^+, NO, O_2^+
(d) O_2^+, CN^-, N_2^+

58. Bond energies in NO, NO^+ and NO^- are such as

(a) $NO^- > NO > NO^+$
(b) $NO^+ > NO^- > NO$
(c) $NO > NO^- > NO^+$
(d) $NO^+ > NO > NO^-$

59. The bond length of species O_2, O_2^+ and O_2^- are in the order of

(a) $O_2^+ > O_2 > O_2^-$
(b) $O_2^- > O_2 > O_2^+$
(c) $O_2 > O_2^+ > O_2^-$
(d) $O_2 > O_2^- > O_2^+$

60. In which of the following pairs molecules have bond order three and are isoelectronic?

(a) CN^-, CO
(b) CO, O_2^+
(c) NO^+, CO^+
(d) CN^-, O_2^+

61. In the formation of NO^+ from NO, the electron is removed from

(a) a σ orbital
(b) a π orbital
(c) a σ^* orbital
(d) a π^* orbital

62. Which among the following molecules/ions is diamagnetic?

(a) Super oxide ion
(b) Oxygen
(c) Carbon molecule
(d) Unipositive ion of N_2 molecule

63. If Z-axis is the molecular axis, then π-molecular orbitals are formed by the overlap of

(a) $s + p_z$
(b) $p_x + p_y$
(c) $p_z + p_z$
(d) $p_x + p_x$

64. N_2 and O_2 are converted into monocations, N_2^+ and O_2^+ respectively. Which of the following is wrong?

(a) In N_2^+, N—N bond weakens
(b) In O_2^+, the O—O bond order increases
(c) In O_2^+, paramagnetism decreases
(d) N_2^+ becomes diamagentic

65. Which of the following diatomic molecules would be stabilized by the removal of an electron?

(a) C_2
(b) CN
(c) N_2
(d) O_2

Metallic and Hydrogen Bonding

66. In the following, which bond will be responsible for maximum value of hydrogen bond?

(a) N—H
(b) O—H
(c) F—H
(d) S—H

67. Two ice cubes are pressed over each other until they unite to form one block. Which one of the following forces dominates for holding them together?

(a) Dipole-dipole interaction
(b) van der Waals' forces
(c) Hydrogen bond formation
(d) Covalent attraction

68. Which of the following does not apply to metallic bond?
(a) Overlapping valence orbitals
(b) Mobile valence electrons
(c) Delocalized electrons
(d) Highly directed bonds

69. The maximum possible number of hydrogen bonds in a H_2O molecule that can participate is
(a) 1 (b) 2 (c) 3 (d) 4

70. Hydrogen bonds are formed in many compounds *e.g.*, H_2O, HF, NH_3. The boiling point of such compounds depends to a large extent on the strength of hydrogen bond and the number of hydrogen bonds. The correct decreasing order of the boiling points of above compounds is **[NCERT Exemplar]**
(a) $HF > H_2O > NH_3$ (b) $H_2O > HF > NH_3$
(c) $NH_3 > HF > H_2O$ (d) $NH_3 > H_2O > HF$

Round II (Mixed Bag)

Only One Correct Option

1. The electronic configuration of four elements *L*, *P*, *Q* and *R* are given in brackets $L(1s^2, 2s^2, 2p^4)$, $P(1s^2, 2s^2, 2p^6, 3s^1)$, $Q(1s^2, 2s^2, 2p^6, 3s^2, 3p^5)$, $R(1s^2, 2s^2, 2p^6, 3s^2)$. The formula of ionic compounds that can be formed between these elements are
(a) L_2P, RL, PQ and R_2Q (b) LP, RL, PQ and RQ
(c) P_2L, RL, PQ and RQ_2 (d) LP, R_2L, P_2Q, and RQ

2. With which of the given pairs CO_2 resembles?
(a) $HgCl_2, C_2H_2$ (b) C_2H_2, NO_2
(c) $HgCl_2, SnCl_4$ (d) N_2O, NO_2

3. Which of the following has maximum dipole moment?
(a) NCl_3 (b) NBr_3
(c) NH_3 (d) NI_3

4. Carbon suboxide (C_3O_2) has recently been shown as a component of the atmosphere of Venus. Which of the following formulation represents the correct ground state Lewis structure for carbon suboxide?
(a) :O: C::C :C: O:
(b) : O ::C::C: C ::O:
(c) $:\ddot{\text{O}}::\text{C}::\text{C}::\text{C}::\ddot{\text{O}}:$
(d) : O: C: C: C: O:

5. Among the species: $CO_2, CH_3COO^-, CO, CO_3^{2-}$, HCHO which has the weakest C—O bond?
(a) CO (b) CO_2
(c) CO_3^{2-} (d) CH_3COO^-

6. In which one of the following cases breaking of covalent bond takes place?
(a) Boiling of H_2O (b) Melting of KCN
(c) Boiling of CF_4 (d) Melting of SiO_2

7. Which of the following does not contain coordinate bond?
(a) BH_4^- (b) NH_4^+ (c) CO_3^{2-} (d) H_3O^+

8. The species C_2
(a) has one σ bond and one π bond
(b) has both π bonds
(c) has both σ bonds
(d) does not exist

9. The AsF_5 molecule is trigonal bipyramidal. The hybrid orbitals used by the As atoms for bonding are
(a) $d_{x^2-y^2}, d_{z^2}, s, p_x, p_y$ (b) d_{xy}, s, p_x, p_y, p_z
(c) $s, p_x, p_y, p_z, d_{z^2}$ (d) $d_{x^2-y^2}, s, p_x, p_y$

10. The bond angle between two hybrid orbitals is 105°. The percentage of *s*-character of hybrid orbital is between
(a) 50–55% (b) 9–12%
(c) 22–23% (d) 11–12%

11. The true statements from the following are
1. PH_5 and $BiCl_5$ do not exist
2. $p\pi$-$d\pi$ bond is present in SO_2
3. Electrons travel at the speed of light
4. SeF_4 and CH_4 have same shape
5. I_3^+ has bent geometry

(a) 1, 3 (b) 1, 2, 5
(c) 1, 3, 5 (d) 1, 2, 4

12. The HOMO in CO is
(a) π-bonding (b) π-antibonding
(c) σ-antibonding (d) σ-bonding

13. Which of the following hydrogen bonds are strongest in vapour phase?
(a) HF---HF (b) HF---HCl
(c) HCl---HCl (d) HF---HI

14. Which combination is best explained by the coordinate covalent bond?
(a) $H^+ + H_2O$ (b) Cl + Cl
(c) $Mg + \frac{1}{2} O_2$ (d) $H_2 + I_2$

15. The species having pyramidal shape is

(a) SO_3 (b) BrF_3

(c) SiO_3^{2-} (d) OSF_2

16. Assuming that Hund's rule is violated, the bond order and magnetic nature of the diatomic molecule B_2 is

(a) 1 and diamagnetic

(b) 0 and diamagnetic

(c) 1 and paramagnetic

(d) 0 and paramagnetic

17. Peroxide ion

(i) has five completely filled antibonding molecular orbitals

(ii) is diamagnetic

(iii) has bond order one

(iv) is isoelectronic with neon

Which of these are correct?

(a) (ii) and (iii) (b) (i), (ii) and (iv)

(c) (i), (iii) and (iii) (d) (i) and (iv)

18. Which one of the following conversions involve change in both hybridisation and shape?

(a) $CH_4 \longrightarrow C_2H_6$ (b) $NH_3 \longrightarrow NH_4^+$

(c) $BF_3 \longrightarrow BF_4^-$ (d) $H_2O \longrightarrow H_3O^+$

19. Which is the correct statement about σ and π molecular orbitals? Statements are

(i) π-bonding orbitals are ungerade

(ii) π-antibonding orbitals are ungerade

(iii) σ-antibonding orbitals are gerade

(a) (i) only (b) (ii) and (iii) only

(c) (iii) only (d) (ii) only

20. Two types of F*X* F angles are present in which of the following molecules? ($X =$ S, Xe, C)

(a) SF_4 (b) XeF_4

(c) SF_6 (d) CF_4

21. Which of the following statements is not correct from the view point of molecular orbital therory? **[NCERT Exemplar]**

(a) Be_2 is not a stable molecule

(b) He_2 is not stable but He_2^+ is expected to exist

(c) Bond strength of N_2 is maximum amongst the homonuclear diatomic molecules belonging to the second period

(d) The order of energies of molecular orbitals in N_2 molecule is

$$\sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x \approx \pi 2p_y) < (\pi^* 2p_x \approx \pi^* 2p_y) < \sigma^* 2p_z$$

22. Match the species in Column I with the geometry/shape in Column II. **[NCERT Exemplar]**

Column I		Column II	
A.	H_3O^+	1.	Linear
B.	$HC \equiv CH$	2.	Angular
C.	ClO_2^-	3.	Tetrahedral
D.	NH_4^+	4.	Trigonal bipyramidal
		5.	Pyramidal

Codes

	A	B	C	D
(a)	1	2	3	4
(b)	5	1	2	3
(c)	1	2	5	3
(d)	3	2	4	1

23. Match the species in Column I with the bond order in Column II. **[NCERT Exemplar]**

Column I		Column II	
A.	NO	1.	1.5
B.	CO	2.	2.0
C.	O_2^-	3.	2.5
D.	O_2	4.	3.0

Codes

	A	B	C	D
(a)	3	4	1	2
(b)	1	2	3	4
(c)	2	4	3	1
(d)	3	1	2	4

More than One Correct Option

24. Which of the following have identical bond order? **[NCERT Exemplar]**

(a) CN^- (b) NO^+

(c) O_2^- (d) O_2^{2-}

25. Which of the following attain the linear structure? **[NCERT Exemplar]**

(a) $BeCl_2$ (b) NCO^+

(c) NO_2 (d) CS_2

26. Which of the following statements are correct about CO_3^{2-}? **[NCERT Exemplar]**

(a) The hybridisation of central atom is sp^3

(b) Its resonance structure has one C—O single bond and two C ═O double bonds

(c) The average formal charge on each oxygen atom is 0.67 units

(d) All C—O bond lengths are equal

27. Which of the following statements are not correct? **[NCERT Exemplar]**

(a) NaCl being an ionic compound is a good conductor of electricity in the solid state

(b) In canonical structures there is a difference in the arrangement of atoms

(c) Hybrid orbitals form stronger bonds than pure orbitals

(d) VSEPR theory can explain the square planar geometry of XeF_4

28. Which of the following pairs contain same number of electrons but their shapes are different?

(a) BF_3, BCl_3 (b) CH_4, NH_3

(c) NH_3, H_2O (d) $BeCl_2, BeF_2$

Assertion and Reason

Directions (Q. Nos. 29 to 32) *Each of these questions contains two statements : Statement* I (*Assertion*) *and Statement* II (*Reason*). *Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes* (*a*), (*b*), (*c*), (*d*) *given below*

(a) Statement I is true; Statement II is true; Statement II is a correct explanation for Statement I.

(b) Statement I is true; Statement II is true; Statement II is not a correct explanation for Statement I.

(c) Statement I is true; Statement II is false.

(d) Statement I is false; Statement II is true.

29. **Statement I** F—F bond has low bond dissociation energy.

Statement II The fluorine has low reactivity.

30. **Statement I** CO_2 molecules are linear.

Statement II The value of dipole moment of CO_2 is zero.

31. **Statement I** Sodium chloride formed by the action of chlorine gas on sodium metal is a stable compound.

Statement II This is because sodium and chloride ions acquire octet in sodium chloride formation. **[NCERT Exemplar]**

32. **Statement I** Though the central atom of both NH_3 and H_2O molecules are sp^3 hybridised, yet H—N—H bond angle is greater than that of H—O—H.

Statement II This is because nitrogen atom has one lone pair and oxygen atom has two lone pairs. **[NCERT Exemplar]**

33. **Statement I** Among the two O—H bonds in H_2O molecule, the energy required to break the first O—H bond and the other O—H bond is the same.

Statement II This is because the electronic environment around oxygen is the same even after breakage of one O—H bond. **[NCERT Exemplar]**

Comprehension Based Questions

Directions (Q. Nos. 34 to 36) The electronic configurations of three elements, A, B and C are given below.
Answer the questions 34 to 36 on the basis of these configurations. **[NCERT Exemplar]**

A	$1s^2$	$2s^2$	$2p^6$		
B	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^3$
C	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^5$

34. Stable form of A may be represented by the formula

(a) A (b) A_2

(c) A_3 (d) A_4

35. The molecular formula of the compound formed from B and C will be

(a) BC (b) B_2C

(c) BC_2 (d) BC_3

36. The bond between B and C will be

(a) ionic (b) covalent

(c) hydrogen (d) coordinate

Directions (Q. Nos. 37 to 39) According to the concept of resonance, whenever a single Lewis structure can't describe a molecule accurately, then a number of structures called resonating structures, with similar energy, same relative position of all nuclei and with same number of paired and unpaired electrons are drawn.
The molecule as such has a single definite structure which is the resonance hybrid of the resonating structures and can't as such be depicted by a single Lewis structure. As a result of resonance, the bond order may change in many molecules or ions and is given by formula.

$$\text{Bond order} = \frac{\text{Total number of bonds between two atom in all the structures}}{\text{Total number of resonating structures}}$$

37. Which of the following molecule contains one pair of non-bonding electrons?

(a) H_2O

(b) HF

(c) NH_3

(d) CH_4

38. What is the bond order of benzene?

(a) 2 (b) 1.5

(c) 2.5 (d) 3.0

39. Bond order of N—O bonds in nitrate ion is

(a) 1.25

(b) 2.00

(c) 1.45

(d) 1.33

Previous Years' Questions

40. In which of the following pairs, the two species are not isostructural? [AIEEE 2012]

(a) CO_3^{2-} and NO_3^- (b) PCl_4^+ and $SiCl_4$

(c) PF_5 and BrF_5 (d) AlF_6^{3-} and SF_6

41. Among the following the maximum covalent character is shown by the compound [AIEEE 2011]

(a) $FeCl_2$ (b) $SnCl_2$

(c) $AlCl_3$ (d) $MgCl_2$

42. The structure of IF_7 is [AIEEE 2011]

(a) square pyramid (b) trigonal bipyramid

(c) octahedral (d) pentagonal bipyramid

43. Which of the following has maximum number of lone pairs associated with Xe? [AIEEE 2011]

(a) XeO_3 (b) XeF_4

(c) XeF_6 (d) XeF_2

44. The number and types of bonds between two carbon atoms in calcium carbide is [AIEEE 2011, 2005]

(a) one sigma, two pi (b) one sigma, one pi

(c) two sigma, one pi (d) two sigma, two pi

45. Using MO theory predict which of following species has the shortest bond length? [AIEEE 2009]

(a) O_2^+ (b) O_2^{2+}

(c) O_2^- (d) O_2^{2-}

46. Which one of the following constitutes a group of the isoelectronic species? [AIEEE 2008]

(a) C_2^{2-}, O_2^-, CO, NO (b) $NO^+, C_2^{2-}, CN^-, N_2$

(c) $CN^-, N_2, O_2^{2-}, CO_2^{2-}$ (d) N_2, O_2^-, NO^+, CO

47. Which of the following molecules/ions does not contain unpaired electrons? [AIEEE 2006]

(a) O_2^{2-} (b) B_2 (c) N_2^+ (d) O_2

48. In which of the following molecules/ions all the bonds are not equal? [AIEEE 2006]

(a) SF_4 (b) SiF_4 (c) XeF_4 (d) BF_4

49. Of the following sets which one does not contain isoelectric species? [AIEEE 2005]

(a) $BO_3^{3-}, CO_3^{2-}, NO_3^-$ (b) $SO_3^{2-}, CO_3^{2-}, NO_3^-$

(c) CN^-, N_2, C_2^{2-} (d) $PO_4^{3-}, SO_4^{2-}, ClO_4^-$

50. The molecular shapes of SF_4, CF_4 and XeF_4 are [AIEEE 2005]

(a) different with 1, 0 and 2 lone pairs of electrons on the central atom, respectively

(b) different with 0, 1 and 2 lone pairs of electrons on the central atom, respectively

(c) the same with 1, 1 and 1 lone pair of electrons on the central atoms, respectively

(d) the same with 2, 0 and 1 lone pairs of electrons on the central atom, respectively

Answers

Round I

1. (d) **2.** (c) **3.** (b) **4.** (b) **5.** (b) **6.** (c) **7.** (d) **8.** (a) **9.** (d) **10.** (a)
11. (d) **12.** (c) **13.** (c) **14.** (c) **15.** (c) **16.** (c) **17.** (a) **18.** (b) **19.** (d) **20.** (c)
21. (b) **22.** (c) **23.** (b) **24.** (c) **25.** (b) **26.** (b) **27.** (b) **28.** (b) **29.** (c) **30.** (a)
31. (b) **32.** (c) **33.** (a) **34.** (a) **35.** (a) **36.** (d) **37.** (d) **38.** (c) **39.** (c) **40.** (c)
41. (a) **42.** (d) **43.** (c) **44.** (b) **45.** (c) **46.** (a) **47.** (b) **48.** (b) **49.** (a) **50.** (c)
51. (b) **52.** (d) **53.** (b) **54.** (b) **55.** (d) **56.** (c) **57.** (c) **58.** (d) **59.** (b) **60.** (a)
61. (d) **62.** (c) **63.** (d) **64.** (d) **65.** (d) **66.** (c) **67.** (c) **68.** (d) **69.** (d) **70.** (b)

Round II

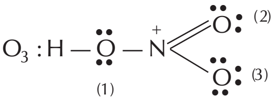
1. (c) **2.** (a) **3.** (c) **4.** (c) **5.** (c) **6.** (d) **7.** (c) **8.** (b) **9.** (c) **10.** (c)
11. (b) **12.** (d) **13.** (a) **14.** (a) **15.** (d) **16.** (a) **17.** (a) **18.** (c) **19.** (a) **20.** (a)
21. (d) **22.** (b) **23.** (a) **24.** (a,b) **25.** (a,d) **26.** (c,d) **27.** (a,b) **28.** (b,c) **29.** (c) **30.** (a)
31. (a) **32.** (a) **33.** (c) **34.** (a) **35.** (d) **36.** (b) **37.** (c) **38.** (b) **39.** (d) **40.** (c)
41. (c) **42.** (d) **43.** (d) **44.** (a) **45.** (b) **46.** (b) **47.** (a) **48.** (a) **49.** (b) **50.** (a)

the Guidance

Round I

4. $N_2 < SO_2 < ClF_3 < K_2O < LiF$

5. HNO_3 :



Formal charge on an atom in a Lewis structure

$$= [\text{total number of valence electrons in free atom}] - [\text{total number of non-bonding (lone pairs) electrons}] - \frac{1}{2}[\text{total number of bonding or shared electrons}]$$

Formal charge on $H = 1 - 0 - \frac{1}{2} \times 2 = 0$

Formal charge on $N = 5 - 0 - \frac{1}{2} \times 8 = 1$

Formal charge on $O(1) = 6 - 4 - \frac{1}{2} \times 4 = 0$

Formal charge on $O(2) = 6 - 4 - \frac{1}{2} \times 4 = 0$

Formal charge on $O(3) = 6 - 6 - \frac{1}{2} \times 2 = -1$

6. Greater is the electronegativity difference between the two bonded atoms, greater is the ionic character.

	N—H	F—H	C—H and	O—H
Electronegativity	(3.0 − 2.1) =	(4.0 − 2.1) =	(2.5 − 2.1) =	(3.5 − 2.1)
difference	0.9	1.9	0.4	= 1.4

Therefore, increasing order of ionic character of the given bonds is as follow

$$C—H < N—H < O—H < F—H$$

7. In order to complete their octet *X* requires 4, *Y* requires 3 and *Z* requires only one electron.

Thus, valency of X, Y and Z are respectively 4,3,1.

Thus, the formulae of their hydrides are XH_4, YH_3 and YH_5, $Z—H$.

Thus, YH_5 is the correct formula.

8. % ionic character $= 16(x_A - x_B) + 3.5(x_A - x_B)^2$

$$= 16 \times 2 + 3.5 \times (2^2)$$

$$= 46\ \%$$

$\therefore$ The % covalent character $= 100 - 46 = 54\ \%$

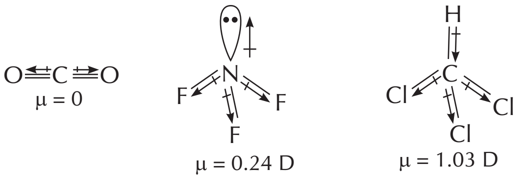
9. Lattice energy $\propto$ charge of ions $\propto \frac{1}{\text{size of ions}}$

11. Lattice energy, $U = \frac{q_1 q_2}{r^2}$

Since, interionic distances in CaO and NaCl are similar, (larger cation has smaller anion and *vice -versa*) *r* is almost the same. Therefore, lattice energy depends only on charge.

Since, the magnitude of charge on Na^+ and Cl^- ions is same *i.e.*, unity and that on Ca^{2+} and O^{2-} ions is 2 each, therefore, the lattice energy of CaO is four times the lattice energy of NaCl, *i.e.*, 4U.

13.

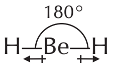


Order of dipole moment

$$CO_2 < NF_3 < CHCl_3$$

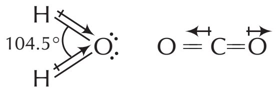
17. $SiCl_4$ because covalent character α charge of cation.

18. BeH_2 molecule is linear. The two equal bond dipoles point in opposite directions and cancel the effect of each other. That's why its dipole moment is zero.



BeH_2 molecule, $\mu = 0$

19. The net dipole moment of CO_2 is zero. This is because the two equal bond dipoles ($\overset{\delta^+}{C}—\overset{\delta^-}{O}$) point in opposite directions and cancel the effect of each other. Hence, CO_2 is linear. On the other hand, H_2O molecule is found to have a net dipole moment (1.84 D) which suggests that the two O—H dipoles are not in a straight line opposing each other, *i.e.*, H_2O does not have linear structure, but they (O—H) must be inclined to each other at certain angle. Thus, H_2O molecule has a bent structure in which the two O—H bonds are oriented at an angle of 104.5°.



21. (a) $NF_3 \Rightarrow 3\,bp + 1\,lp \Rightarrow$ pyramidal

$BF_3 \Rightarrow 3\,bp + 0\,lp \Rightarrow$ trigonal planar

(b) $BF^- \Rightarrow 4\,bp + 0\,lp \Rightarrow$ tetrahedral

$NH_4^+ \Rightarrow 4\,bp + 0\,lp \Rightarrow$ tetrahedral

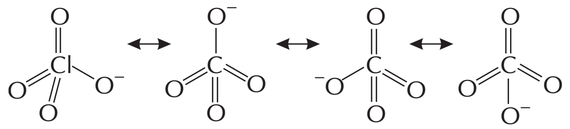
(c) $BCl_3 \Rightarrow 3\,bp + 0\,lp \Rightarrow$ trigonal planar

$BrCl_3 \Rightarrow 3\,bp + 2\,lp \Rightarrow$ T-shape

(d) $NH_3 \Rightarrow 3bp + 1\,lp \Rightarrow$ pyramidal

$NO_3^- \Rightarrow 3\,bp + 0\,lp \Rightarrow$ trigonal planar

23. The resonating structures of ClO_4^- are as



$$\text{Bond order} = \frac{\text{Total number of bonds between Cl and O}}{\text{Total number of resonating structures}}$$

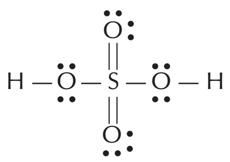
$$= \frac{7}{4} = 1.75$$

24. According to Fajan's rule, largest cation and smallest anion form ionic bond.

27. As the number of lone pairs of electrons increases, bond angle decreases. Thus, the order of bond angle is

$$\underset{(\text{no } lp)}{NH_4^+} > \underset{(1\,lp)}{NH_3} > \underset{(2\,lp)}{NH_2^-}$$

28.

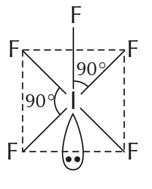


Total number of unshared electrons $= 4 \times 4 = 16$.

29. Number of hybrid orbitals = no. of bp + no. of lp

$$= 5 + 1 = 6$$

Thus, hybridisation is sp^3d^2 but geometry, due to the presence of one lone pair, is square pyramidal, *i.e.,*

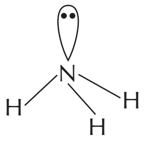


30. H—O—O—H, O ← O═O, O═O

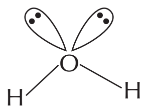
Due to resonance, in O_3, the O—O bond length will be in between O═O and O—O.

O—O being a single bond is larger than the O═O.

31.



NH_3
$bp = 3$
$lp = 1$

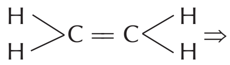


H_2O
$bp = 2$
$lp = 2$

In H_2O molecule, there is lone pair-lone pair repulsion due to the presence of two lone pairs of electrons while in NH_3 molecule there found only lone pair-bond pair repulsion. According to VSEPR theory, the former one is more stronger and hence, the bond angle in water is less than that of ammonia (NH_3).

32. $XeF_4 \Rightarrow 4bp + 2\,lp \Rightarrow$ square planar $\Rightarrow$ all bonds equal

$BF_4^- \Rightarrow 4bp + 0\,lp \Rightarrow$ tetrahedral (all bonds equal)

$C_2H_4 \Rightarrow$  $\Rightarrow$ C ═ C bond is not equal to C—H bond

$SiF_4 \Rightarrow 4\,bp + 0\,lp \Rightarrow$ tetrahedral (all bonds equal)

Thus, in C_2H_4 all the bonds are not equal.

33. Electronic configuration of carbon

In ground state : ${}_6C — 1s^2, 2s^2, 2p_x^1, 2p_y^1$

In excited state : $1s^2, \underbrace{2s^1, 2p_x^1, 2p_y^1, 2p_z^1}_{sp^3 \text{ hybridised}}$

In CH_4 molecule, carbon is sp^3 hybridised, so it is tetrahedral in shape. For square planar, dsp^2 hybridisation is required which is not possible in carbon due to absence of d-orbitals. Furthermore according to VSEPR theory, the four bonded electron pairs around carbon atom arranged themselves in a regular tetrahedron geometry. For tetrahedral structure, the bond angle is 109°28′ while in square planar structure, the bond angle is 90°.Therefore, in tetrahedral structure repulsions between bonded electron pairs is less than that of the square planar.

34. $BH_4^- \Rightarrow 4\,bd + 0\,lp \Rightarrow sp^3$ hybridised = tetrahedral geomety

38. Given, ionic charge $= 4.8 \times 10^{-10}$ esu

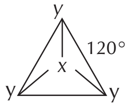
and, ionic distance $= 1$ Å $= 10^{-8}$ cm

We know that

Dipole moment = ionic charge × ionic distance

$$= 4.8 \times 10^{-10} \times 10^{-8}$$
$$= 4.8 \times 10^{-18} \text{ esu cm}^{-1}$$
$$= 4.8 \text{ debye}$$

44. For sp^2 hybridisation, the geometry is generally triangular planar.



Thus, bond angle is 120°.

45. A single bond $= 1\sigma$ bond

Double bond $= 1\sigma$ and 1π bonds

Triple bond $= 1\sigma$ and 2π bonds

Thus, the given molecule contains 19σ and 5π bonds.

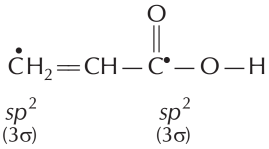
47. Since bond angle is 120°, orbital is sp^2 hybridised. In sp^2 hybridised orbital, % of s-character $= \frac{1}{1+2} \times 100 = 33\%$

50. Only (c) will not form a σ-bond. Because on taking x-axis as the internuclear axis, $2p_y$ and $2p_y$ orbitals overlap sideway (lateral overlapping) resulting in the formation of a π-bond.

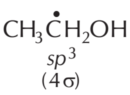
51. $NO_2^+ = 2bp + 0lp$ = linear = sp hybridised

$NO_3^- = 3\ bp + 0\ lp \Rightarrow sp^2$ hybridised

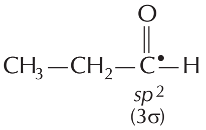
$NH_4^+ \Rightarrow 4\ bp + 0\ lp \Rightarrow sp^3$ hybridised

52. (a) 

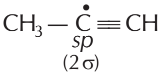
$\underset{\substack{sp^2\\(3\sigma)}}{\dot{C}H_2}=CH-\underset{\substack{sp^2\\(3\sigma)}}{\overset{\overset{\displaystyle O}{\|}}{C^{\bullet}}}-O-H$

(b) 

$CH_3\underset{\substack{sp^3\\(4\sigma)}}{\dot{C}}H_2OH$

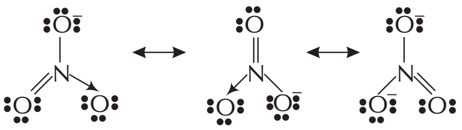
(c) 

$CH_3-CH_2-\underset{\substack{sp^2\\(3\sigma)}}{\overset{\overset{\displaystyle O}{\|}}{C^{\bullet}}}-H$

(d) 

$CH_3-\underset{\substack{sp\\(2\sigma)}}{\dot{C}}\equiv CH$

53. Nitrate ion, NO_3^-



55. $H_2^+ (1+1-1=1) = \sigma 1s^1$

$$BO = \frac{1-0}{2} = 0.5$$

Since one unpaired electron is peresent, it is a paramagnetic species.

58. $NO^+ (7+8-1=14)$

$= \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \pi 2p_x^2 \approx 2p_y^2, \sigma 2p_z^2, \overset{*}{\pi} 2p_x^0 \approx \overset{*}{\pi} 2p_y^0$

$$BO = \frac{10-4}{2} = 3$$

$NO (7+8=15)$ $\quad BO = \frac{10-5}{2} = 2.5$

$NO^- (7+8+1=16)$

$$BO = \frac{10-6}{2} = 2$$

Since, bond length $\propto \frac{1}{BO}$

So, the order of bond length is

$$NO^- < NO < NO^+$$

59. Find BO for each species from MO configuration (BO of $O_2^+ = 2.5, O_2 = 2\ O_2^- = 1.5$). So, the order of bond length is $O_2^- > O_2 > O_2^+$.

60. For BO 3, there should be 14 electrons which are present in CN^- and CO.

61. $NO (7+8=15) = \sigma 1s^2 \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^2, \pi 2p_x^2$

$$\approx \pi 2p_y^2, \overset{*}{\pi} 2p_x^1$$

$NO^+ (7+8-1=14) = \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^2, \pi 2p_x^2$

$$\approx \pi 2p_y^2$$

Thus, electron is removed from $\overset{*}{\pi}$ orbital.

62. $C_2 (6+6=12)\ \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \pi 2p_x^2 \approx \pi 2p_y^2$

64. $N_2 (7+7=14) = \sigma 1s^2 \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \pi 2p_x^2 \approx \pi 2p_y^2, \sigma 2p_z^2$

$$BO = \frac{10-4}{2} = 3$$

$N_2^+ (7+7-1=13) = \sigma 1s^2 \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \pi 2p_x^2 \approx \pi 2p_y^2, \sigma 2p_z^1$ (paramagnetic)

$$BO = \frac{9-4}{2} = 2.5$$

$O_2 (8+8=16) = \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^2,$

$$\pi 2p_z^2 \approx \pi 2p_y^2, \overset{*}{\pi} 2p_x^1 \approx \overset{*}{\pi} 2p_y^1$$

$$BO = \frac{10-6}{2} = 2$$

$O_2^+ (8+8-1=15)$

$$BO = \frac{10-5}{2} = 2.5$$

Thus, $N_2 > N_2^+$ and $O_2^+ > O_2$ (stability order)

N_2^+ is paramagnetic.

65. In O_2, there are two electrons in antibonding orbitals. Removal of one electron from the O_2 molecule gives O_2^+ in which the number of antibonding electrons is one less and hence, BO increases. Thus, removal of one electron from O_2 stabilizes the molecule.

66. Hydrogen bonding $\propto$ electronegativity.

69. In case of water, five water molecules are attached together through four hydrogen bonding.

70. Although F forms stronger H bonding, but H_2O has higher boiling point due to more number of H_2O molecules that bonded together by H bonds.

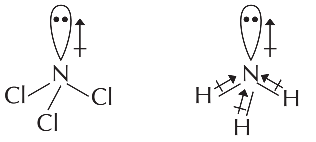
Round II

1. Valencies of *L, Q, P* and *R* is –2, –1, +1, and +2 respectively. So, they will form P_2L, *RL PQ*, and RQ_2.

2. All have linear structure.

$$O{=}C{=}O,\ Cl{-}Hg{-}Cl,\ H{-}C{\equiv}C{-}H$$

3. Electronegativity difference between N (3.0) and Cl (3.0) is zero and hence, N—Cl bonds are non-polar. As a result, the overall dipole moment of NCl_3 molecule and its direction is just the dipole moment of the lone pair of electrons.



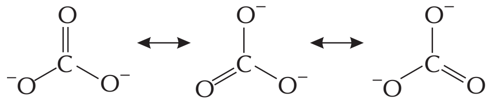
On the other hand, N—Br, (3.0 – 2.8), N—I (3.0 – 2.5) and N—H (3.0 – 2.1) bonds are polar and hence, contribute towards the overall dipole moment of the respective molecules. Since, the EN difference is higher in case of N—H bonds, therefore, NH_3 has the higher dipole moment.

4. In structure (c), all the atoms have complete octet. Thus, it is the correct representation of carbon suboxide.

5. Among the given species, the bond dissociation energy of C—O bond is minimum in case of CO_3^{2-} by which C—O bond become more weaker in CO_3^{2-} or the bond order of CO_3^{2-}(1.33) is minimum so, the bond become weaker.

6. During melting of SiO_2, the giant network structure held by covalent bonds breaks to give individual molecules of SiO_2. In contrast, during boiling of H_2O only change of state occurs from liquid to gaseous; during melting of KCN, electrostatic attraction between K^+ and CN^- ions is overcome; during boiling of CF_4, van der Waals' forces of attraction breaks.

7. CO_3^{2-} has the following structure



It contains only covalent bonds.

8. In C_2 only 2π bonds are present.

9. AsF_5 has sp^3d hybridisation. In sp^3d hybridisation, it is d_{z^2} orbitals which takes part.

10. *s*-character ∝ bond angle

For 25% *s* character (as in sp^3 hybrid orbital), bond angle is 109.5°, for 33.3% *s* character (as in sp^2 hybrid orbital), bond angle is 120° and for 50% *s* character (as in *sp* hybrid orbital), bond angle is 180°.

Similarly, when the bond angle decreases below 109.5°, the *s*-character will decrease accordingly.

$$\text{Decrease in bond angle} = 120° - 109.5° = 10.5°$$

$$\therefore\ \text{Decrease in } s\text{-character} = 33.3 - 25 = 8.3$$

$$\text{Actual decrease in bond angle} = 109.5° - 105° = 4.5°$$

$$\therefore\ \text{Expected decrease in } s\text{-character} = \frac{8.3}{10.5} \times 4.5 = 3.56\%$$

Thus, the *s*-character should decrease by about 3.56%, *i.e.*, *s*-character = 25 – 3.56 = 21.44%

11. SeF_4 has distorted tetrahedral geometry while, CH_4 has tetrahedral geometry.

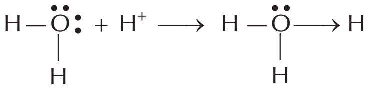
Speed of electron ≠ speed of light

12. HOMO, means highest occupied molecular orbital and in CO (14 electron ion), σ bonding molecular orbital is HOMO.

$$CO = \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \pi 2p_x^2 \approx \pi 2p_y^2, \sigma 2p_z^2$$

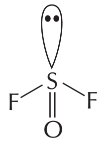
13. A compound having maximum electronegative element will form strong hydrogen bond.

14.



$$H{-}\ddot{O}{:}(H) + H^+ \longrightarrow H{-}\ddot{O}(H){\longrightarrow}H$$

15. OSF_2 has pyramidal shape.



16. B_2 : Total electrons = 10

Configuration: $\sigma 1s^2, \overset{*}{\sigma} 2s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \pi 2p_x^1 \approx \pi 2p_y^1$

If Hund's rule is violated, then

$$\sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \pi 2p_x^2 \approx \pi 2p_y^0$$

So, diamagnetic,

$$\text{Bond order} = \frac{6-4}{2} = 1$$

17. Peroxide ion is O_2^{2-}

$$O_2^{2-}(18) = \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^2$$

$$\pi 2p_x^2 \approx \pi 2p_y^2, \overset{*}{\pi} 2p_x^2 \approx \overset{*}{\pi} 2p_y^2$$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10-8}{2} = 1$$

It contains four completely filled antibonding molecular orbitals. Since, all the electrons are paired, O_2^{2-} is diamagnetic.

Peroxide ion is isoelectronic with argon, not with neon.

18. (a)

	CH_4	$\longrightarrow$	$CH_3{-}CH_3$	
	$4bp + 0\,lp$		$4bp$	$4bp$
Hybridisation	sp^3		sp^3	sp^3
Structure	Tetrahedral		Tetrahedral	

(b)

	NH_3	$\longrightarrow$	NH_4^+
	$3bp + 1\,lp$		$4bp$
Hybridisation	sp^3		sp^3
Structure	Pyramidal		Tetrahedral

(c) $\underset{3bp}{BF_3} \longrightarrow \underset{4bp}{BF_4^-}$

Hybridisation sp^2 sp^3

Structure Trigonal planar Tetrahedral

(d) $\underset{2bp\,+\,2lp}{H_2O} \longrightarrow \underset{3bp\,+\,1\,lp}{H_3O^+}$

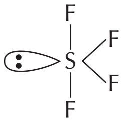
Hybridisation sp^3 sp^3

Structure angular pyramidal

Thus, conversion of BF_3 into BF_4^- involves change in both hybridisation and shape.

19. According to molecular orbital theory, π-bonding orbitals an ungerade.

20. FXF angles of two types are present in sp^3d hybrid orbitals. Since, SF_4 shows sp^3d hybridisation as follows, therefore, it exhibits two different FXF angles.



21. (a) $Be_2\ (4 + 4 = 8) = \sigma 1s^2, \overset{*}{\sigma}1s^2, \sigma 2s^2, \overset{*}{\sigma}2s^2$

$$BO = \frac{4-4}{2} = 0$$

Thus, it does not exist.

(b) $He_2\ (2 + 2 = 4) = \sigma 1s^2, \overset{*}{\sigma}1s^2, BO = \frac{2-2}{2} = 0$

Hence, it also does not exist.

$He_2^+\ (2 + 2 - 1 = 3) = \sigma 1s^2, \overset{*}{\sigma}1s^1, BO = \frac{2-1}{2} = 0.5$

Since the bond order is not zero, this molecule is expected to exist.

(c) $N_2\ (7+7=14) = \sigma 1s^2, \overset{*}{\sigma}1s^2, \sigma 2s^2, \overset{*}{\sigma}2s^2, \pi 2p_x^2 \approx \pi 2p_y^2, \sigma 2p_z^2$

$$BO = \frac{10-4}{2} = 3$$

(d) It is incorrect

22. (a) $H_3O^+ = 3bp + 1lp \Rightarrow$ pyramidal

(b) $HC \equiv CH$ = linear as sp hybridised

(c) $ClO_2^- \Rightarrow 2bp + 2lp \Rightarrow$ angular

(d) $NH_4^+ \Rightarrow 4bp + 0lp \Rightarrow$ tetrahedral

23. $NO\ (7 + 8 = 15) = \sigma 1s^2, \overset{*}{\sigma}1s^2, \sigma 2s^2, \overset{*}{\sigma}2s^2, \sigma 2p_z^2,$

$$\pi 2p_x^2 \approx \pi 2p_y^2, \overset{*}{\pi}2p_x^1$$

$$BO = \frac{10-5}{2} = 2.5$$

$CO\ (6 + 8 = 14)$

$$BO = \frac{10-4}{2} = 3$$

$O_2^-\ (8 + 8 + 1 = 17) = \sigma 1s^2, \overset{*}{\sigma}1s^2, \sigma 2s^2, \overset{*}{\sigma}2s^2, \sigma 2p_z^2,$

$$\pi 2p_x^2 \approx \pi 2p_y^2, \overset{*}{\pi}2p_x^2 \approx \overset{*}{\pi}2p_y^1$$

$$BO = \frac{10-7}{2} = 1.5$$

$O_2\ (8 + 8 = 16),\ BO = \frac{10-6}{2} = 2$

24. $CN^-\ (6 + 7 + 1 = 14)$

$NO^+\ (7 + 8 - 1 = 14)$

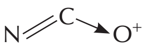
$O_2^-\ (8 + 8 + 1 = 17)$

$O_2^{2-}\ (8 + 8 + 2 = 18)$

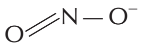
Thus, CN^- and NO^+ because of the presence of same number of electrons have same bond order.

25. Cl—Be—Cl

linear



non -linear



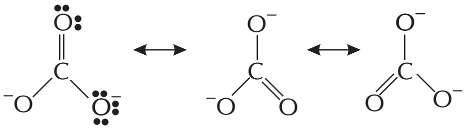
non-linear

S═C═S

linear

26. $CO_3^{2-} \Rightarrow 3bp + 0lp \Rightarrow$ trigonal planar

$\Rightarrow sp^2$ hybridised



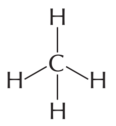
Due to resonance all C—O bond lengths are equal.

Average FC over O = 0.67

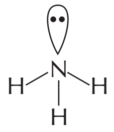
27. (a) NaCl is a bad conductor of electricity in solid state due to the absence of free ions.

(b) Canonical structures differ in the arrangement of electrons, not in the arrangement of atoms.

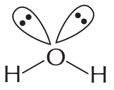
28. The central atom in each of three molecules CH_4, NH_3 and H_2O undergoes sp^3 hybridisation. In CH_4 no lone pair is present. In NH_3 one lone pair is present while in water two lone pairs are present.



tetrahedral (109°28′)



pyramidal structure (106.5°)



V-structure (104.5°)

29. Fluorine is highly reactive because F—F bond has low bond dissociation energy.

30. The values of dipole moments provide valuable information about the structure of molecules.

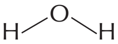
31. $\underset{(2,8,1)}{\text{Na}} + \underset{(2,8,7)}{\text{Cl}} \longrightarrow \underset{(2,8)\ (2,8,8)}{\text{NaCl}}$

Thus, statement (II) is the correct explanation for statement (I).

32.

Thus, statement (II) is the correct explanation for statement (I).

33.

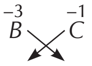


The O—H bond energy is same for both the bonds. After the cleavage of one O—H bond, the electronic environment get changed. Hence, statement II is incorrect.

34. Since the outer shell of *A* is completely filled it exists as monovalent atom, *i.e.*, as *A*.

35. Valency of $B = -3$

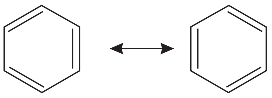
Valency of $C = -1$


or BC_3

36. Since both *B* and *C* are electronegative atom, *i.e.*, non-metals, the bond formed between them is covalent.

37. In NH_3, nitrogen has one lone pair of electrons.

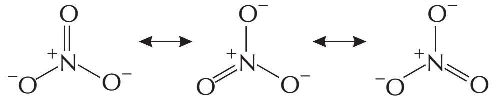
38.



$$80 = \frac{\text{Total number of bonds between two atoms in all structure}}{\text{Total number of resonating structures}}$$

$$= \frac{2+1}{2} = 1.5$$

39. Nitrate ion has the following three resonating structures.



As it evident, three O-atoms are attached to the N-atom by four bonds, therefore, bond order of N—O bond is $\frac{4}{3} = 1.33$.

40. (a) CO_3^{2-}, NO_3^-; triangular planar

(b) $PCl_4^+, SiCl_4$; tetrahedral

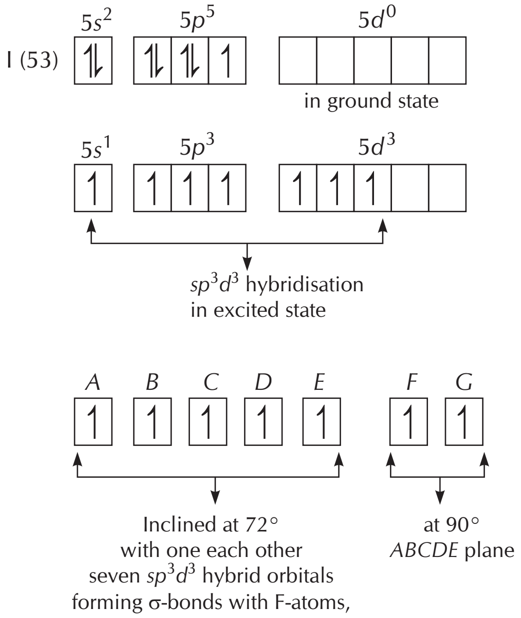
(c) PF_5; trigonal bipyramidal

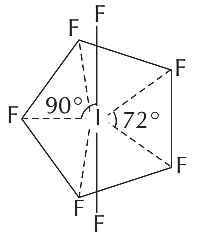
BrF_5; square pyramidal

(d) AlF_6^{3-}, SF_6; octahedral

41. In all the given compounds, anion is same (Cl^-), hence polarising power is decided by size and charge of cation. Al^{3+} with maximum charge and smallest size has maximum polarising power hence, $AlCl_3$ is maximum covalent.

42. IF_7





Pentagonal bipyramidal structure

43.

	Species	Hybridisation of Xe	Lone pair of Xe	Bonding pairs
(a)	XeO_3	sp^3	1	3
(b)	XeF_4	sp^3d^2	2	4
(c)	XeF_6	sp^3d^3	1	6
(d)	XeF_2	sp^3d	3 (Max.)	2

44. $CaC_2 \rightleftharpoons Ca^{2+} + \underset{\text{carbide ion}}{C_2^{2-}}$

In carbide ion, two carbon atoms are joined by triple bond (It is isoelectronic with N_2)

$$—C{\equiv}C—$$

with two π and one σ-bonds.

45. Higher the bond order shorter the bond length. Therefore O_2^{2+} has the shortest bond length (BO = 3)

Bond order of remaining species are

$O_2^{+}(2.5)$, $O_2^{-}(1.5)$ and $O_2^{2-}(1)$

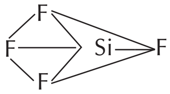
46. Isoelectronic species have same number of electrons, NO^+ C_2^{2-}, CN^- and N_2 all have 14 electrons.

47. O_2^{2-} (Total number of electrons = 18)

$$\sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \overset{*}{\pi} 2p_x^2 \approx \overset{*}{\pi} 2p_y^2$$

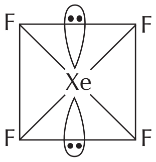
48. SF_4 has trigonal bipyramidal geometry, lone pair of electrons repels the axial bond pair and decrease the bond angle to 73°.

SiF_4



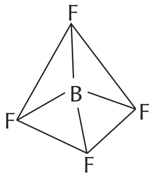
regular tetrahedral

XeF_4



square planar

BF_4^-



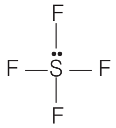
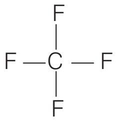
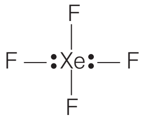
tetrahedral

49.

Species	Electron in central element	Electrons in other element	Charge gained	Total
BO_3^{3-}	5	$3 \times 8 = 24$	+3	32
CO_3^{2-}	6	$3 \times 8 = 24$	+2	32
NO_3^-	7	$3 \times 8 = 24$	+1	32
SO_3^{2-}	16	$3 \times 8 = 24$	+2	42
CN^-	6	7	1	14
N_2	7	7	0	14
C_2^{2-}	6	6	+2	14
PO_4^{3-}	15	$4 \times 8 = 32$	+3	50
SO_4^{2-}	16	$4 \times 8 = 32$	+2	50
ClO_4^-	17	$4 \times 8 = 32$	+1	50

Thus, SO_3^{2-}, CO_3^{2-}, NO_3^- are not isoelectronic.

50.

Molecule	Structure	Hybridisation of central atom	Lone pair
SF_4		sp^3d	one
CF_4		sp^3	zero
XeF_4		sp^3d^2	two

5 Chemical Thermodynamics

JEE Main MILESTONE

- Fundamentals of Thermodynamics
- Work
- Heat
- Zeroth Law of Thermodynamics
- Internal Energy
- First Law of Thermodynamics
- Heat Capacity
- Spontaneous and Non-spontaneous Processes
- Entropy
- Second and Third Laws of Thermodynamics

5.1 Fundamentals of Thermodynamics

Several terms used in thermodynamics are described below.

System, Surroundings and Boundary

A **system** is the specific portion which is under thermodynamic studies. Besides system, the rest of the universe, *i.e.*, **all other matter that can interact** with the system is called **surroundings.**

The real or imaginary surfaces or lines separating two or more systems or a system from its surroundings is called **boundary**. The boundary may be diathermic (*i.e.*, allow passage of heat) or adiabatic (*i.e.*, does not allow passage of heat).

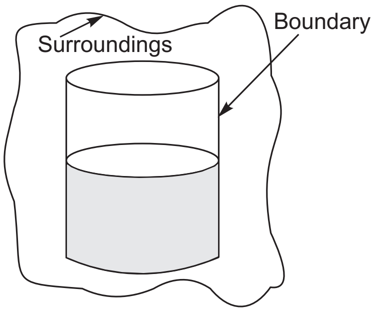


Fig. 5.1 Representation of system surrounding and boundary

The study of heat or any other form of energy into or out of a system, due to physical or chemical transformations is called **thermodynamics**. *It is concerned with energy changes only and not with the total energy of a body.*

Types of System

Depending upon the nature of boundary, the system can be of the following types :

(a) Open System

An open system can exchange matter as well as energy with its surroundings. The boundary here is not sealed and non-insulated thermally, *e. g.*, all living systems, car engines, etc. For such a system, $\Delta m \neq 0$, $\Delta E \neq 0$.

(b) Close System

A *closed system* does not exchange matter with its surroundings but can exchange energy in the form of heat, work or radiations *i.e.*, the boundary is sealed but not insulated. *e.g.,* hot water kept in a closed container. For such a system, $\Delta m = 0$, $\Delta E \neq 0$.

(c) Isolated System

An *isolated system* neither exchange matter nor energy with its surroundings *i.e.,* the boundary is sealed as well as insulated, *e.g.,* thermosflask. For such a system, $\Delta m = 0$, $\Delta E = 0$.

Besides above written types, the system may be **homogeneous** (with identical properties and chemical composition throughout *i.e.*, with one phase only) or **heterogeneous** (consisting of two or more phases).

Caution Point *A phase may be defined as the physically distinct and mechanically separable part of the system from the other parts.*

Macroscopic Properties

The physical quantities used to define the state of a system are called properties. Thermodynamics deals with matter in bulk (*i.e.*, in large excess) and the properties that arises because of bulk behaviour of matter are called **macroscopic properties** or **bulk properties of the system.**

These are further of two types

(a) Intensive Properties

The properties which do not depend upon the quantity of matter are called **intensive properties**, *e.g.*, pressure, temperature, density, concentration, surface tension, viscosity, refractive index etc.

(b) Extensive Properties

The properties which depend upon the quantity of matter are called **extensive properties,** *e.g.*, volume, number of moles, enthalpy, entropy, mass, work etc.

The above properties can be best understood by the following example : If at a certain temperature, a solution is taken in a beaker and a partition is inserted in the beaker in such a way that it divides the solution into two halves, the volume of the solution becomes half while temperature of each part remains the same. It is obvious, temperature is an intensive property while volume is an extensive property.

It may be noted that the **ratio of the two extensive properties becomes intensive in nature**. *e.g.,* mass and volume are extensive properties, but the ratio of mass and volume *i.e.,* density is intensive, it is independent of quantity of matter. Similarly, heat capacity is extensive, but molar heat capacity is intensive. In general, if x is any extensive property of n moles of system, the molar property of the system x_m is intensive because it refers to the property of 1 mole of the system and is independent of the quantity of matter $x_m = x/n$.

Intensive properties cannot be added or subtracted directly. Only extensive properties can be added or subtracted.

State Variables

A thermodynamic system is said to be in certain state when all of its properties are fixed *i.e.,* its measurable properties have a definite value. If any of such properties changes, then the state of system also changes. The measurable properties here are called **state variables,** *e.g.* temperature, pressure, volume, composition, number of moles, internal energy, entropy, enthalpy, free energy, etc.

State and Path Functions

The property of a system whose value depends only upon the state of the system (*i.e.*, initial and final state) and is independent of the path or manner by which the state is reached is called the **state function**. Thus, most of the common variables are infact state functions.

Examples of state functions are pressure, volume, temperature, internal energy, enthalpy, entropy etc.

If $z = f(x, y)$ and $\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right) = \frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)$, then z is called exact differentiable function. The above condition is also representing that z should be state function and hence, we may say that **state functions are exact differentials.**

The functions that depend upon the path followed are called **path functions** *e.g.,* work done, heat etc.

Types of Processes

The state of a variable can be changed *via* a thermodynamic process.

These processes are of the following types

(a) Adiabatic Process

In adiabatic process, the system does not exchange heat with its surroundings *i.e.,* no heat can flow in or out of the system. For an adiabatic process,

$$dq = 0$$

(b) Isothermal Process

The isothermal process is carried out at constant temperature *i.e.,* it is the process in which temperature remains fixed. For an isothermal process,

$$dT = 0 \text{ and thus, } \Delta E = 0$$

(c) Isobaric Process

In isobaric process, change of state is brought about at constant pressure *i.e.*,

$$dp = 0$$

(d) Isochoric Process

In an isochoric process, volumes of the system remains constant *i.e.,*

$$dV = 0$$

The above four basic thermodynamic processes can be represented in a graph as

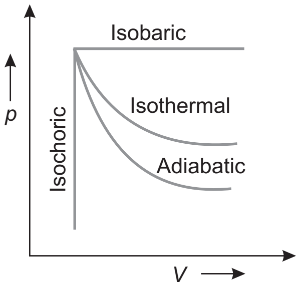


Fig. 5.2 *pV* graph for various thermodynamic processes

(e) Cyclic Process

When a system is undergone a number of different states and finally returns to its initial state, the process is called **cyclic**. For such a process, change in internal energy and enthalpy is zero *i.e.,*

$$dE \text{ or } dU = 0$$

and $$dH = 0$$

e.g., in a process shown below, the system returns to the original state *A* after successive changes.

$$A(p_1, V_1, T_1) \longrightarrow B(p_2, V_2, T_1) \longrightarrow C(p_2, V_3, T_2) \longrightarrow A(p_1, V_1, T_1)$$

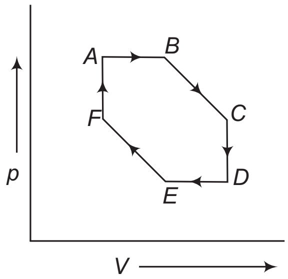
(f) Reversible Process

A reversible system is defined as a system where change takes place infinitesimally slow and the direction of which at any point can be reversed by infinitesimal change in the state of the system. Reversible process is an ideal process and here every intermediate state is in equilibrium with others, if any.

(g) Irreversible Process

An irreversible process is one, the direction of which cannot be reversed by small change in variables. All natural processes are generally irreversible and the net work done in an irreversible process is somewhat less than that in reversible process, *i.e.*, $W_{\text{irr}} < W_{\text{rev}}$.

Sample **Problem 1** *Identify the adiabatic steps in the following cyclic process.*



Temperature at A, B and F is T_1 and at C, D and E is T_2. Given $T_1 > T_2$

(a) $F \rightarrow A$; $D \rightarrow E$ (b) $B \rightarrow C$; $E \rightarrow F$
(c) $B \rightarrow C$; $C \rightarrow D$ (d) $A \rightarrow B$; $E \rightarrow E$

Interpret (*b*) (i) $A \rightarrow B$ (Temperature and pressure are constant).

∴ It is isothermal and isobaric process.

(ii) $B \rightarrow C$ It is adiabatic expansion in which temperature falls from T_1 and T_2.

(iii) $C \rightarrow D$ (Temperature and volume are constant)

∴ This process is isothermal and isochoric.

(iv) $D \rightarrow E$ (Temperature and pressure are constant)

∴ It is isothermal and isobaric contraction.

(v) $E \rightarrow F$ (It is adiabatic compression in which temperature increases from T_2 to T_1).

(vi) $F \rightarrow A$ (Temperature and volume are constant).

∴ It is isothermal and isochoric process.

Thermodynamic Equilibrium

It is an equilibrium that involves following three equilibria

(i) Mechanical equilibrium, *i.e.,* when no work is done on the system or by the system.

(ii) Thermal equilibrium, *i.e.,* temperature remains constant throughout the system including the surroundings.

(iii) Chemical equilibrium, *i.e.,* composition of the system remains constant and definite.

5.2 Work

If an object is displaced through a distance *dx* by a force *F*, the amount of work done is given by

$$W = F \times dx$$

i. e., it is the product of two factors

(i) Intensity factor, *F*

(ii) Capacity factor, *dx*

Work done is a path function, not a state function, as depends upon the path followed. Work done on the system increases the energy of the system and is taken as negative while work done by the system is taken as positive.

i.e., work done by the system = – ve
work done on the system = + ve

Different Types of Work

Work can be defined in the following ways

(a) Gravitational Work, W_g

$$W_g = mgh$$

where, mg = intensity factor, h = capacity factor

(b) Electrical Work, W_e

$$W_e = VQ \text{ (potential difference)}$$

where, V = intensity factor (quantity of electricity)
Q = capacity factor

(c) Mechanical Work or Pressure-volume Work, W

Let a system expands by which the position moves by a very little distance dx. Then the small work done by the system,

$$dW = -F_{\text{ext}} \cdot dx = -p_{\text{ext}} \cdot A \cdot dx = -p_{\text{ext}} \cdot dV$$

where, A = cross sectional area of piston.
p = pressure (intensity factor)
ΔV = change in volume (capacity factor)

Work Done in Isothermal Irreversible Expansion or Compression

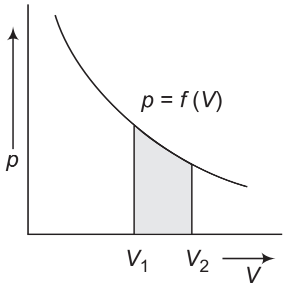


Fig. 5.3 Irreversible work done

In an isothermal irreversible expansion, the total work done by the system can be obtained by integrating $-pdV$ when its volume changes from V_1 to V_2 at constant external pressure, *i.e.*,

$$W = -\int_{V_1}^{V_2} p_{\text{ext}} \cdot dV$$

Geometrically, the magnitude of work done represents the area bounded between the curve $p = f(V)$ and volume axis from V_1 to V_2.

The mechanical work is considered as expansion (if $\Delta V > 0$) or contraction (if $\Delta V < 0$). Thus, $W_{\text{exp}ansion}$ is negative and $W_{\text{contraction}}$ is positive.

Work Done in Isothermal Reversible Expansion or Compression of an Ideal Gas

In reference to the above example, we know that $W = -p \cdot \Delta V$. If the external pressure is not constant and changes in finite number of steps in going from volume V_1 to V_2 then the net work done is the summation of $-p \cdot \Delta V$ terms over all the steps as shown in the Fig. 5.4 and is represented as

$$W = -\Sigma p \cdot \Delta V$$

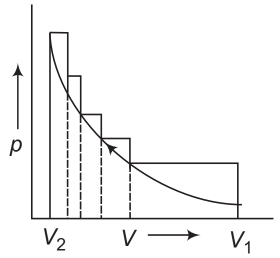


Fig. 5.4 *pV* plot when pressure changes in finite steps during compression from initial volume V_1 to final volume V_2

Further assume that the pressure is not constant but changes during the process in such a manner so that it is always infinitesimally greater than the pressure of the gas, then at each stage of compression the volume decreases by an infinitesimal amount, dV. In such a condition, the work done on the gas can be calculated by the relation

$$W = -\int_{V_1}^{V_2} p_{\text{ex}}\, dV$$

Here, p_{ex} at each state is equal to $(p_{\text{in}} + dp)$ in case of compression. In an expansion process under similar conditions, the external pressure is always less than the pressure of the system *i.e.*, $p_{\text{ex}} = (p_{\text{in}} \pm dp)$. Such processes are called reversible processes.

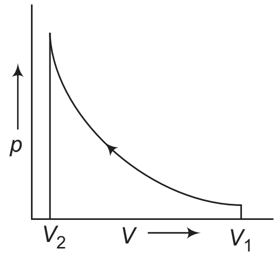


Fig. 5.5 *pV* plot when pressure changes in infinite steps (reversible conditions) during compression from initial volume V_1 to final volume V_2

Thus, the work can be related to internal pressure of the system under reversible conditions as

$$W_{\text{rev}} = -\int_{V_1}^{V_2} p_{\text{ex}}\, dV = -\int_{V_1}^{V_2} (p_{\text{in}} \pm dp) dV$$

Since $dp \times dV$ is very small,

$$W_{\text{rev}} = -\int_{V_1}^{V_2} p_{\text{in}}\, dV$$

Now, the pressure of the gas (p_{in} or p) can be expressed in terms of its volume through gas equation. For n mole of an ideal gas, *i.e.*, $pV = nRT$. $\Rightarrow$ $p = \frac{nRT}{V}$

Therefore, at constant temperature (isothermal process).

$$W_{\text{rev}} = -\int_{V_1}^{V_2} nRT \frac{dV}{V} = -nRT \ln \frac{V_2}{V_1}$$

$$= -2.303 nRT \log \frac{V_2}{V_1} \text{ or } -2.303 nRT \log \frac{p_1}{p_2}$$

W_{rev} is Maximum Work

Work done during isothermal expansion of an ideal gas is given by the equation

$$W = -p_{\text{ex}}\, \Delta V$$

Now, for a given change of volume (ΔV), W can be maximum if p_{ex} is maximum. But for expansion p_{ex} has to be smaller than p_{in}. This means that for getting maximum work, the external pressure has to be infinitesimally smaller than the internal pressure of the gas. These conditions are nearly close to reversibility. Thus, for a given change of volume

$$W_{\text{rev}} = W_{\max}$$

Free Expansion

Expansion of a gas in vacuum ($p_{\text{ex}} = 0$) is called free expansion. No work is done during free expansion (*i.e.*, $W = 0$) of an ideal gas whether the process is reversible or irreversible.

Caution Points

- *(i) The magnitude of work in isothermal irreversible expansion increases as the number of step involved increases.*
- *(ii) The magnitude of work will be more in isothermal irreversible compression than isothermal reversible compression, for the same change in volume. The magnitude of work decreases as the number of steps involved increases.*
- *(iii) The magnitude of work will be more in isothermal reversible expansion of an ideal gas than real gas.*

Work Done in Adiabatic Expansion or Compression Processes

In adiabatic expansion, no heat is allowed to enter or leave the system, hence $q = 0$.

$\therefore$ From first law of thermodynamics $\Delta E = W$. The molar heat capacity at constant volume of an ideal gas is given by $C_V = \left(\frac{dE}{dT}\right)_V$

or $$dE = C_V \cdot dT$$

and for finite changes, $\Delta E = C_V \times \Delta T = W$

(a) Work Done in Reversible Adiabatic Expansion

Let p be the external pressure and ΔV be the increase in volume then work done by the system is $W = -p\Delta V$ and if ΔT is the fall in temperature, then $C_V \Delta T = -p\Delta V$

For very small change in a reversible process and for one mole of a gas,

$$C_V dT = -p\, dV = \frac{-RT}{V} dV \text{ or } C_V \frac{dT}{T} = -R\frac{dV}{V}$$

For a process in which the volume of a gas is V_1 at temperature T_1 and the new volume is V_2 at a temperature T_2,

$$C_V \int_{T_1}^{T_2} \frac{dT}{T} = R \int_{V_1}^{V_2} \frac{dV}{V}$$

On taking log, we get

$$\log \frac{T_1}{T_1} = \frac{R}{C_V} \log \frac{V_1}{V_2}$$

We know that $C_p - C_V = R$ dividing by C_V

$$\frac{C_p}{C_V} - 1 = \frac{R}{C_V}; \gamma - 1 = \frac{R}{C_V} \qquad \left[\frac{C_p}{C_V} = \gamma\right]$$

$$\log \frac{T_2}{T_1} = (\gamma - 1) \log \frac{V_1}{V_2} = \log \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$$

$$T_1 V_1^{\gamma - 1} = T_2 V_2^{\gamma - 1}$$

$$\boxed{TV^{\gamma - 1} = k = \text{constant}}$$

Further, $$\frac{p_1 V_1}{p_2 V_2} = \left(\frac{V_2}{V_1}\right)^{\gamma - 1}$$

or $$\boxed{pV^{\gamma} = \text{constant}}$$

$$p_1 V_1^{\gamma} = p_2 V_2^{\gamma}$$

$$\boxed{\text{Work done} = C_V \times \Delta T = C_V \times (T_2 - T_1) = \frac{R}{\gamma - 1}(T_2 - T_1)}$$

(b) Work Done in Irreversible Adiabatic Expansion

In free expansion, the external pressure is zero, *i.e.*, work done is zero.

$$\therefore \qquad \Delta E = W = 0$$

In intermediate expansion, suppose the pressure is suddenly released to 1 atm and the gas expands adiabatically against the constant pressure. Since this is not a reversible expansion, above equation cannot be used.

Since, $q = 0, \Delta E = W$

$$W = C_V (T_2 - T_1)$$

Let the volume changes from V_1 to V_2 against external pressure, p_{ext},

$$W = - p_{\text{ext}} (V_2 - V_1)$$

$$= - p_{\text{ext}} \left(\frac{RT_2}{p_2} - \frac{RT_1}{p_1} \right)$$

$\therefore$ Work done, $W = - Rp_{\text{ext}} \left(\dfrac{T_2 p_1 - T_1 p_2}{p_1 p_2} \right)$

Caution Points

(*i*) *The temperature of gas decreases in adiabatic expansion i.e., cooling occurs and increases in adiabatic compression (i.e., the system gets warmed).*

(ii) *In any adiabatic process (expansion or compression), the final temperature of the gas in reversible process is lower than that in irreversible process.*

(*iii*) *Isobaric process* $W = - p_{\text{ext}} (V_2 - V_1)$

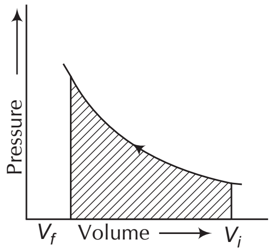
(*iv*) *Isochoric expansion* $W = 0$

Sample **Problem 2** *The pressure-volume work for an ideal gas can be calculated by using the expression* $W = -\int_{V_i}^{V_f} p_{ex} dV$. *The work can also be calculated from the pV –plot by using the area under the curve within the specified limits. When an ideal gas is compressed (a) reversibly and (b) irreversibly from volume* V_i *to* V_f, *choose the correct option.* **[NCERT Exemplar]**

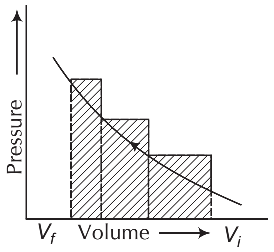
(*a*) W (reversible) = W (irreversible)
(*b*) W (reversible) $<$ W (irreversible)
(*c*) W (reversible) $>$ W (irreversible)
(*d*) W (reversible) = W (irreversible) + $p_{ex} \cdot \Delta V$

Interpret (*b*) W (reversible) $<$ W (irreversible)

This is because area under the curve is always more in irreversible compression as can be seen from Fig. (a) and (b).

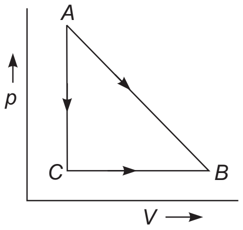


(a) Reversible compression



(b) Irreversible compression

Sample **Problem 3** *Consider the modes of transformations of a gas from state A to state B as shown in the given p-V diagram. Which one of the following is not true?*



(*a*) $\Delta H = q$ along $A \to C$
(*b*) ΔS is same along both $A \to B$ and $A \to C \to B$
(*c*) W is same along both $A \to B$ and $A \to C \to B$
(*d*) $W > 0$ along $A \to B$

Interpret (*c*) Work (W) is a path function, so depends upon the path followed, not only on the initial and final state of the system.

Sample **Problem 4** *A system consisting of 1 mole of an ideal gas undergoes an isothermal expansion at 25°C from 1.0 bar to a lower pressure while generating 100 J of work. What is the final pressure of the system if the external pressure is constant at 0.1 bar?*

(*a*) 1.23 *bar*	(*b*) 0.712 *bar*
(*c*) 0.958 *bar*	(*d*) 0.664 *bar*

Interpret (*b*) $W = - p_{\text{ext}} (V_2 - V_1)$

$$= - p_{\text{ext}} \left(\frac{nRT}{p_2} - \frac{nRT}{p_1} \right)$$

$$= - nRTp_{\text{ext}} \left(\frac{1}{p_2} - \frac{1}{p_1} \right)$$

or, $$-100 = -1 \times 8.314 \times 298 \times 0.1 \left(\frac{1}{p_2} - \frac{1}{1} \right)$$

$\therefore$ $p_2 = 0.712$ bar

Sample **Problem 5** *During an adiabatic expansion, a gas obeys* VT^3 = *constant. The gas must be*

(*a*) *monoatomic*
(*b*) *diatomic*
(*c*) *polyatomic*
(*d*) *either of the above*

Interpret (*c*) VT^3 = constant,

Also $V^{\gamma - 1} T$ = constant for adiabatic expansion.

$$VT^{\frac{1}{\gamma - 1}} = \text{constant or } \frac{1}{\gamma - 1} = 3$$

$\gamma = \dfrac{4}{3}$, *i.e.*, the gas is polyatomic.

5.3 Heat

Heat is defined as the quantity of energy, which flows between system and surroundings on account of temperature difference. It is also a path function, *i.e.,* depends upon the path followed. It is given as

$$H = ms\Delta t$$

where, m = mass of substance, s = specific heat

Δt = temperature difference

Heat flowing into the system is taken as **positive** and heat flowing out of the system is taken as **negative.**

Difference between Heat and Work

When heat is supplied to a gas in a system, the molecules start moving faster with greater randomness in different directions. However, when work is done on the system then initially the molecules start moving down in the direction of the piston. Thus, work is an organised form of energy while heat is a random form of energy.

5.4 Zeroth Law of Thermodynamics

This law was put forward much after the establishment of the first and second laws of thermodynamics. It is placed before the first and second laws as it provides a logical basis for the concept of temperature of a system.

According to this laws, "When two objects (maintained at different temperatures) are brought in thermal contact, they exchange heat with each other until they reach a state of thermal equilibrium". *The heat flows always from the object of higher temperature to the object of lower temperature*. At thermal equilibrium, the temperature of both of them became same.

This idea of thermal equilibrium is called *zeroth law of thermodynamics or law of temperature* or *law of thermal equilibrium*.

This law is also applicable for more than two objects. In such a condition, it states "if each of the two objects is in thermal equilibrium with a third object then they are also in thermal equilibrium with each other."

Check Point 1

1. When an ideal gas expands in vacuum, there is neither absorption nor evolution of heat. Explain, why?
2. Neither heat nor work is a state function but their sum, *i.e.*, $q + W$ is a state function. Explain why?
3. Why does the change in internal energy zero during an isothermal process?
4. Why does work done during a reversible isothermal expansion is more than that in intermediate expansion?

5.5 Internal Energy

Every system is associated with a definite amount of energy, called the internal energy of the system. It is the sum of all forms of **kinetic** and **potential energies** that it can have under specified conditions *i.e.,* translational, vibrational, rotational, chemical bond energy, etc. The **gravitational energy** is usually neglected.

Internal energy is a state function , *i.e.,* depends only upon the state of the system (*i.e.,* conditions of temperature, pressure, etc.) and is independent of the method by which state has been attained. The absolute value of internal energy can't be determined. However, change in internal energy (difference between the internal energies of the products E_f or E_p and that of reactants, E_i or E_R can be determined experimentally using a bomb calorimeter.

$$\Delta E = E_f - E_i$$

Internal energy of a system depends upon the quantity of substance contained in the system. Hence, it is an extensive property.

The internal energy of ideal gases is a function of temperature only. Hence in isothermal processes, as the temperature remains constant, there is no change in internal energy, *i.e.,*

$$\Delta E = 0$$

Caution Point *By convention the internal energy of an element, in most stable form, is zero.*

Units of *E* The units of energy are ergs (CGS units) or joules (SI units).

$$1 \text{ cal} = 4.184 \text{ J}$$

$$1 \text{ cal} = 4.184 \times 10^7 \text{ erg}$$

$$1 \text{ J} = 0.2390 \text{ cal}$$

$$1 \text{ J} = 10^7 \text{ erg}$$

$$1 \text{ J} = 1 \text{ N m (newton-metre)},$$

$$1 \text{ L atm} = 101.3 \text{J}$$

$$= 24.206 \text{ cal},$$

thus, $1 \text{ cal} > 1 \text{ joule} > 1 \text{ erg}$

The change in internal energy can be brought about in two ways:

(i) Either by allowing the heat to flow into the system (absorption) or out of the system (evolution).

(ii) By doing work on the system or the work done by the system.

5.6 First Law of Thermodynamics

The *first law of thermodynamics* given by Helmholtz and Robert Mayer is similar to the *law of conservation of energy*. The law states

1. Energy can neither be created nor destroyed although it can be changed from one form to another.
2. It is impossible to construct a perpetual motion machine which could produce work without consuming energy.
3. The total energy of an isolated system remains constant though it may change from one form to another.
4. Whenever a quantity of one kind of energy disappears, an exactly equivalent quantity of energy in some other form must appear.

Mathematical Expression of First Law of Thermodynamics

Suppose a system consumes heat (q) and work (W) is done on the system. In this process, the internal energy changes from E_1 to E_2 then

$$\Delta E = q + W \quad \text{where, } \Delta E = (E_2 - E_1) = \Delta U$$

It is the mathematical expression of first law of thermodynamics.

(i) *When a system undergoes isothermal change* $\Delta E = 0$, *i.e.,* there is no increase or decrease in the internal energy of the system, then the first law of thermodynamics reduces to

$$0 = q + W$$

or $\quad q = -W$

i.e., heat absorbed from surroundings = Work done by the system

or $\quad W = -q$

Heat given to the surroundings = work done on the system

(ii) *If no work is done*, $W = 0$ and the first law reduces to

$$\Delta E = q$$

i.e., increase in internal energy of the system is equal to the heat absorbed by the system or decrease in internal energy of the system is equal to heat lost by the system.

(iii) *If there is no exchange of heat between the system and surroundings,* $q = 0$, the first law reduces to

$$\Delta E = W$$

i.e., work is done at the expense of internal energy.

(iv) *In case of gaseous system*, if a gas expands against the constant external pressure, p, let the volume change be ΔV, the mechanical work done by the gas is equal to $-p \times \Delta V$

Substituting this value in $\Delta E = q + W$

$$\Delta E = q - p\Delta V$$

when, $\quad \Delta V = 0,$

$$\Delta E = q \text{ or } q_v$$

The symbol q_v indicates the heat change at constant volume.

Caution Point *According to old conventions* $\Delta E = q - W$ *, but according to latest convention, by first law of thermodynamics* $\Delta E = q + W$ (*Work done on the system is taken as positive*)

Sample Problem 6 *Expansion of a gas in vacuum is called free expansion. Calculate the work done and the change in internal energy when 1 L of ideal gas expands isothermally into vacuum until its total volume is 5 L?* **[NCERT Exemplar]**

(a) 0, 4
(b) 0, 0
(c) 0, −5
(d) −5, 0

Interpret (b) $(-W) = p_{\text{ext}}(V_2 - V_1) = 0 \times (5 - 1) = 0$

For isothermal expansion, $q = 0$

By first law of thermodynamics

$$q = \Delta E + (-W)$$

$$\Rightarrow \quad 0 = \Delta E + 0 \quad \text{so} \quad \Delta E = 0$$

Sample Problem 7 *A system undergoes a certain change in state by path I and the corresponding heat absorbed and work done are 10 kcal and 0 erg, respectively. For the same change in state by path II, the respective quantities are 11 kcal and 0.5* W_{max}*, where* W_{max} *represents the work done if the change were reversibly carried out. Find the magnitude of* W_{max} *in erg.*

(a) 2
(b) 8.4×10^7
(c) 8.4×10^{10}
(d) 8.4×10^{-7}

Interpret (c) As internal energy is a state function, its change is independent from path and hence,

$$\Delta U_{\text{I}} = \Delta U_{\text{II}}$$

or, $\quad q_1 + W_1 = q_{\text{II}} + W_{\text{II}}$

or, $\quad 10 + 0 = 11 + 0.5W_{\text{max}}$

$\therefore \quad |W_{\text{max}}| = 2 \text{ kcal} = 2 \times 1000 \times 4.2 \times 10^7$

$$= 8.4 \times 10^{10} \text{ erg}$$

Hot Spot 1

ENTHALPY

Analysis of last year AIEEE or JEE Main examination shown that it is a very important topic. Questions based on the relationship of ΔE and ΔH are frequently asked. Here, the main point is "finding the value of Δn_g.

The total heat content of a system at constant pressure is called the **enthalpy of the system**. Indeed, it is the sum of internal energy and the product of pressure-volume work. It is an extensive quantity and represented by the symbol H.

$$\therefore \qquad H = E + p\Delta V \qquad \text{...(i)}$$

Its units are kcal or kJ/mol.

Suppose a system absorbs heat, q_p and its volume changes from V_1 to V_2 against a constant pressure, p, the work done by the system,

$$(W) = -p\,(V_2 - V_1)$$
$$= -p\Delta V$$

Now applying the first law of thermodynamics,

$$\Delta E = q_p - p\,(V_2 - V_1)$$

i.e.,
$$(E_2 - E_1) = q_p - p\,(V_2 - V_1)$$

or
$$(E_2 + pV_2) - (E_1 + pV_1) = q_p \qquad \text{...(ii)}$$

We know that,

$$E + pV = H \qquad (\textit{i.e.}, \text{ enthalpy of the system})$$

Thus
$$(E_2 + pV_2) = H_2 \text{ and } (E_1 + pV_1) = H_1$$

By putting these values in Eq. (ii), we get

$$H_2 - H_1 = q_p \text{ or } \Delta H = q_p$$

Now in the equation $\Delta E + p\Delta V = \Delta H$

If $\Delta V = 0$, so $\qquad \Delta H = \Delta E$

and as $\qquad \Delta H = q_v$

Hence, $\qquad \Delta E = q_v$

Here, q_v = heat supplied at constant volume

Thus, we can say that **"heat supplied at constant pressure is the measure of enthalpy change, while the heat supplied at constant volume is the measure of internal energy change."**

In other words, the enthalpy change of a reaction can be defined as the amount of heat absorbed or evolved at constant pressure when the quantities of substance indicated by thermochemical equation have completely reacted *e.g.,* in the reaction,

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g); \qquad \Delta H = -890.3 \text{ kJ}$$

Thus, heat of reaction for the above reaction is –890.3 kJ or in other words if 1 mole of CH_4 combines with 2 moles of O_2 in gaseous state, 890.3 kJ of energy is liberated.

Relationship Between ΔH and ΔE

The difference in ΔH and ΔE is insignificant for solids and liquids, however in the case of gases, if pressure and temperature remain constant, then for a given thermochemical equation, (*i.e.*, the chemical reactions in which heat of the reaction and state of the substance taking part are mentioned) change in number of moles,

$$\Delta n_g = n_2 - n_1$$

So, the above equation *i.e.,*

$$\Delta H = \Delta E + p\Delta V$$

can be converted to

$$\Delta H = \Delta E + \Delta n_g RT \qquad (\because\ p\Delta V = \Delta n_g RT)$$

If,

Case I : $\Delta n_g = 0$ then $\Delta H = \Delta E$

Case II : $\Delta n_g < 0$ then $\Delta H < \Delta E$

Case III : $\Delta n_g > 0$ then $\Delta H > \Delta E$

If ΔH is positive, the process will be endothermic, *i.e.,* accompany with the evolution of heat [or the heat content of the products (H_p) is lesser than that of the reactants (H_R)] or product is more stable than reactant. If ΔH is negative, the process will be exothermic, *i.e.,* proceeds with the absorption of heat[or $H_P > H_R$].

Ways of Solving Problems

In order to solve out ΔE and ΔH based problems if

(i) **Pressure and volume are given use the formula**

$$\Delta H = \Delta E + p\Delta V$$

Sample **Problem 8** *The enthalpy change for the reaction of 50 mL of ethylene with 50 mL of* H_2 *at 1.5 atm pressure is –0.31 kJ. The value of ΔE is*

(a) –0.5640 kJ (b) –0.2350 kJ
(c) –0.2835 kJ (d) –0.5032 kJ

Interpret (b) $C_2H_2(g) + H_2(g) \longrightarrow C_2H_4(g)$

$$\Delta H = -0.31 \text{ kJ mol}^{-1}$$
$$p = 1.5 \text{ atm}$$
$$(V_2 - V_1) = (50 - 100)$$
$$\Delta V = -50 \text{ mL} = -0.050 \text{ L}$$
$$\Delta H = \Delta E + p\Delta V$$
$$\Delta E = \Delta H - p\Delta V$$
$$= -0.31 \text{ kJ mol}^{-1} - 1.5 \times (-0.050)$$
$$= -0.235 \text{ kJ}$$

(ii) **Pressure and volume are not given** Calculate Δn_g (or Δn) from balanced equation and then use the formula

$$\Delta H = \Delta E + \Delta n_g RT$$

Sample Problem 9 *The reaction of cyanamide, $NH_2CN(s)$, with dioxygen was carried out in a bomb calorimeter, and ΔU was found to be $-742.7\ kJ\ mol^{-1}$ at 298 K. Calculate the enthalpy change for the reaction at 298 K ($R = 8.314 \times 10^{-3}\ kJ\ K^{-1}\ mol^{-1}$)*

$$NH_2CN(s) + \frac{3}{2}O_2(g) \longrightarrow N_2(g) + CO_2(g) + H_2O(l)$$

[NCERT]

(a) −741.46 (b) −743.9
(c) +741.46 (d) + 743.9

Interpret (a) Use the following steps to solve out such problems.

Step I Write the balanced equation

$$NH_2CN(s) + \frac{3}{2}O_2(g) \longrightarrow N_2(g) + CO_2(g) + H_2O(l)$$

Step II Calculate Δn_g

Difference of moles of gaseous products and reactants,

$$\Delta n_g = n_p - n_r = 2 - \frac{3}{2} = \frac{1}{2} = 0.5 \text{ mol}$$

Step III Calculate ΔH by using the formula $\Delta H = \Delta U + \Delta n_g RT$

$$\Delta H = \Delta U + \Delta n_g RT$$

$$\Delta H = -742.7 \text{ kJ mol}^{-1} + (0.5 \text{ mol} \times 8.314 \times 10^{-3} \text{ kJ mol}^{-1} \times 298 \text{ K})$$

$$\Delta H = (-742.7 \text{ kJ} + 1238.786 \times 10^{-3} \text{ kJ}) \text{ mol}^{-1}$$

$$= -741.46 \text{ kJ mol}^{-1}$$

During calculation always remember the units of different quantities, *i.e.*, ΔH, ΔU and R must be the same.

Caution Point *In the laboratory most of the reactions are carried out at constant pressure, so ΔH is more significant than ΔE.*

Enthalpy Change of a Reaction ($\Delta_r H$)

The heat change during a chemical reaction (when moles of reactants and products being same as indicated by balanced chemical equation) is called **enthalpy** or **heat of reaction.**

$\Delta_r H$ = sum of enthalpies of products − sum of enthalpies of reactants

$$\Delta_r H = \sum_i x_i H_p - \sum_i y_i H_R$$

where, x_i and y_i = stoichiometric coefficients of products and reactants respectively in a balanced equation.

H_p = enthalpy of formation of products

H_R = enthalpy of formation of reactants

e.g., For the reaction,

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

$\Delta_r H$ is written as

$$\Delta_r H = [H_{(CO_2,\,g)} + 2 \times H_{(H_2O,\,l)}] - [H_{(CH_4,\,g)} + 2 \times H_{(O_2,\,g)}]$$

Sample Problem 10 *Enthalpies of formation of CO(g), $CO_2(g)$, $N_2O(g)$ and $N_2O_4(g)$ are −110, −393, 81 and 9.7 kJ mol^{-1} respectively. Find the value of $\Delta_r H$ for the reaction,*

$$N_2O_4(g) + 3CO(g) \longrightarrow N_2O(g) + 3CO_2(g)$$

[NCERT]

(a) −776.4 kJ (b) −778 kJ (c) −777.7 kJ (d) − 760 kJ

Interpret (b) Heat of reaction,

$$\Delta_r H^\circ = \Sigma \Delta_f H^\circ_{\text{products}} - \Sigma \Delta_f H^\circ_{\text{reactants}}$$

$$= [\Delta_f H^\circ (N_2O) + 3\Delta_f H^\circ (CO_2)] - [\Delta_f H^\circ (N_2O_4) + 3\Delta_f H^\circ (CO)]$$

$$= [81 + (3 \times -393)] - [9.7 + (3 \times -110)] \text{ kJ}$$

$$= -777.7 \text{ kJ} \approx 778 \text{ kJ}.$$

Factors Affecting Enthalpy of Reaction

The heat or enthalpy of reaction depends upon the following factors

(i) Physical state of reactants and products
(ii) Allotropic forms of elements involved
(iii) Chemical composition of reactants and products
(iv) Amount of reactants
(v) Temperature
(vi) Medium of reaction

The variation of enthalpy of reaction with temperature is given by **Kirchhoff's equation.**

Consider a process

$$A \longrightarrow B$$

E_A and H_A are the internal energy and enthalpy of A, respectively whereas E_B and H_B are the internal energy and enthalpy of B, respectively.

Hence,

$$\Delta H = H_B - H_A$$

Since enthalpy is a function of temperature and pressure. The above equation can be differentiated *w.r.t.* temperature at constant pressure, *i.e.*,

$$\left[\frac{\delta(\Delta H)}{dT}\right]_p = \left[\frac{\delta(H_B)}{dT}\right]_p - \left[\frac{\delta(H_A)}{dT}\right]_p$$

$$= (C_p)_B - (C_p)_A = \Delta C_p$$

where, ΔC_p = difference in the heat capacity between reactants and products

or $$d(\Delta H) = \Delta C_p \cdot dT$$

Case I **When ΔC_p is constant between two temperature T_1 and T_2.**

$$\therefore \qquad \int_{H_1}^{H_2} d(\Delta H) = \int_{T_1}^{T_2} \Delta C_p \cdot dT$$

or

$$[\Delta H]_{H_1}^{H_2} = \Delta C_p (T)_{T_1}^{T_2}$$

$$\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1) \qquad \text{...(i)}$$

Similarly, we can write,

$$\Delta U_2 - \Delta U_1 = \Delta C_V \cdot (T_2 - T_1) \qquad \text{...(ii)}$$

Eqs. (i) and (ii) are known as **Kirchhoff's equations.**

Case II **ΔC_p varies with temperature**

$$\int d(\Delta H) = \Delta C_p \cdot dT$$

or

$$\Delta H = \int \Delta C_p dT + K$$

where, K is the integration constant,

When $T = 0$, then $\Delta H_0 = K$

$$\therefore \qquad \Delta H = \Delta H_0 + \int \Delta C_p \, dT \qquad \text{...(iii)}$$

where, ΔH_0 refers to the enthalpy change at absolute zero.

or

$$\Delta H = \Delta H_0 + \alpha T + \beta \frac{T^2}{2} + \gamma \frac{T^3}{3} \qquad \text{...(iv)}$$

Eqs. (iii) and (iv) are another forms of Kirchhoff's equation.

Sample **Problem 11** *One mole of an ideal gas with $C_y = 3/2\,R$ is heated at a constant pressure of 1 atm from 25°C to 100°C. The ΔE and ΔH are respectively.*

(*a*) 300, 225 (*b*) 225, 375

(c) 375, 225 (*d*) 225, 300

Interpret (*b*) For ideal gas,

$$\Delta E = n \cdot C_V \cdot \Delta T = 1 \times \left(\frac{3}{2} \times 2\right) \times (100 - 25) = \mathbf{225\ cal}$$

Now,
$$C_p = C_V + R = \frac{3}{2} R + R = \frac{5}{2} R$$

Now,
$$\Delta H = n \cdot C_p \Delta T = 1 \times \left(\frac{5}{2} \times 2\right) \times (100 - 25) = \mathbf{375\ cal}$$

Calculation of Enthalpy of the Reaction

Calorimeter is the apparatus which is used to measure the heat of the reaction experimentally. If we know water equivalent of the calorimeter (W), mass (m) and specific heat (s) of liquid and initial and final temperature of the calorimeter, the heat of the reaction is calculated as

$$Q = (W + m) \times s \times (T_2 - T_1)$$

Two common types of calorimeters are **water calorimeter** and **bomb calorimeter**.

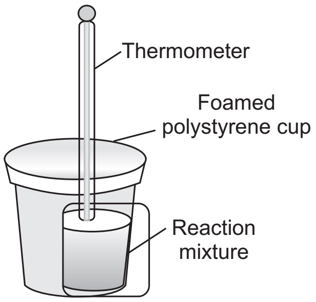


Fig. 5.6 Calorimeter for measuring heat changes at constant pressure (atmospheric pressure)

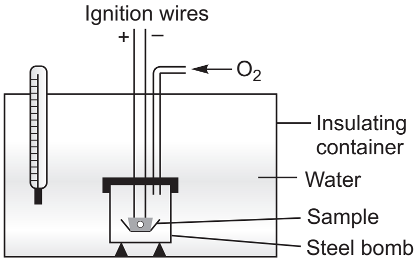


Fig. 5.7 Bomb calorimeter

In **water calorimeter** pressure remains constant, thus it gives the heat at constant pressure, *i.e.*, ΔH. In **bomb calorimeter**, the volume remains constant, thus the heat, measured by it, is called the heat at constant volume (*i.e.*, q_V) or ΔE.

$$\Delta E = \frac{(W + m)\,(T_2 - T_1) \times s}{w_1} \times M \text{ kcal}$$

Here, w_1 = mass of substance taken

and M = molecular mass of the substance

or
$$\Delta E = \frac{C \times \Delta T \times M}{w_1}$$

where, C = thermal capacity of calorimeter

Sample **Problem 12** *0.16 g of methane is subjected to combustion at 27°C in bomb calorimeter system. The temperature of the calorimeter system (including water) was found to rise by 0.5°C. Calculate the heat of combustion of methane (in kJ mol^{-1}) at constant volume. The thermal capacity of the calorimeter system is 17.7 kJ K^{-1}.*

(*a*) –695 (*b*) –1703

(*c*) –890 (*d*) –885

Interpret (*d*) For bomb calorimeter, $\Delta E = \dfrac{C \times \Delta T \times M}{m}$

($\because$ In bomb calorimeter V remains constant)

$$= \frac{17.7 \times 0.5 \times 16}{0.16} = 885 \text{ kJ/mol}$$

Thus, the heat produced is q_V *i.e.*, $q_V = -885$ kJ

Standard Enthalpy of Reaction

A substance is in its **standard state** at 1 atm pressure and 298 K. Hence, when the reaction is carried out at standard conditions, its enthalpy change is called standard enthalpy of the reaction and is denoted by $\Delta_r H^\circ$.

The sign of $\Delta_r H^\circ$ gets reversed on reversing a chemical equation.

Enthalpy of Formation

The enthalpy change when one mole of a compound is formed from its elements in their most stable state of aggregation, is called **enthalpy of formation** and is denoted by $\Delta_f H$ *e.g.,*

$$\text{C(graphite)} + 2H_2(g) \longrightarrow CH_4(g); \quad \Delta_f H = -74.8 \text{ kJ}$$

The above enthalpy change under standard conditions (1 atm and 298 K) is called **standard heat of formation** and is denoted by $\Delta_f H^\circ$.

Enthalpy of formation of an element at standard state (or in its most stable state) by convention is taken as zero, *e.g.,* enthalpy of formation of Mg, Al, Na, H_2, O_2, F_2, etc. is taken as zero.

Sample **Problem 13** *Given,*

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g); \ \Delta_r H^\circ = -92.4 \text{ kJ mol}^{-1}$$

The standard enthalpy of formation of NH_3 *gas is*

[NCERT]

(*a*) $+92.4$ kJ mol^{-1}
(*b*) -92.4 kJ mol^{-1}
(*c*) -46.2 kJ mol^{-1}
(*d*) $+46.2$ kJ mol^{-1}

Interpret (*c*) Given, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

$$\Delta_r H^\circ = -92.4 \text{ kJ mol}^{-1}$$

Chemical reaction for the enthalpy of formation of $NH_3(g)$ is as follows

$$\frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) \longrightarrow NH_3(g)$$

Therefore, $$\Delta_f H^\circ = \frac{-92.4}{2} = -46.2 \text{ kJ mol}^{-1}$$

Enthalpy Change During Phase Transformation

The enthalpy change when one mole of a substance changes from its one state or phase to another, is called enthalpy change during phase transformation.

It can be of following types

(a) Enthalpy of Fusion

The enthalpy change when one mole of a solid substance is converted into its liquid state at its melting point is called the **enthalpy of fusion** ($\Delta_{\text{fus}} H$). Ionic solids have high values of $\Delta_{\text{fus}} H$ as compared to molecular solids.

(b) Enthalpy of Vaporisation

The enthalpy change that accompanies vaporisation of one mole of a liquid at its boiling point is called the *enthalpy of vaporisation* ($\Delta_{\text{vap}} H$). High value of enthalpy of vaporisation shows the presence of stronger forces of attraction.

(c) Enthalpy of Sublimation

It is defined as the enthalpy change when one mole of a solid sublimes (*i.e.,* converts directly into gaseous state) at a temperature below its melting point. It is represented by $\Delta_{\text{sub}} H$.

$$\Delta_{\text{sub}} H = \Delta_{\text{fus}} H + \Delta_{\text{vap}} H$$

Enthalpies for Different Types of Reactions

(a) Enthalpy of Combustion

The amount of heat evolved or absorbed when one mole of the substance is completely burnt in oxygen or air, is called *enthalpy of combustion*. It is denoted by $\Delta_c H$, *e.g.,*

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l); \quad \Delta_c H = -192 \text{ kcal}$$

The value of $\Delta_c H$ *is always negative. This is because heat is evolved during combustion.*

The grading of food articles and various fuels can be done on the basis of the values of enthalpies of combustion If heat of combustion is measured in kcal/g or kJ/g (*i.e.*, calculated for one gram of a substance), it is called the **calorific value.** In other words, *the amount of heat produced in calorie or joule when one gram of a substance (food or fuel) is completely burnt or oxidised,* is called calorific value.

Mathematically,

$$\text{Calorific value} = \frac{\Delta_c H}{\text{mass}}$$

Table 5.1 **Calorific Value of Important Food Stuffs and Fuels**

Fuel	Calorific value (kJ/g)	Food	Calorific value (kJ/g)
Wood	17	Milk	3.1
Charcoal	33	Egg	6.7
Kerosine	48	Rice	16.7
Methane	55	Sugar	17.3
LPG	55	Butter	30.4
Hydrogen	150	Ghee	37.6

Out of the fuels listed, hydrogen has the highest calorific value. However, it is not used as domestic or industrial fuel due to some technical problems. Of the various constituents of our food, fats and carbohydrates serve as the main sources of energy. The calorific value of proteins is quite low.

On combustion, C, H and S of a compounds are oxidised to CO_2, H_2O and SO_2 respectively.

Sample Problem 14 *ΔH for combustion of ethane and ethyne are –341.1 and –310.0 kcal respectively. Which is better gas welder?*

(a) *Ethane* (b) *Ethyne*
(c) *Both have equal capacity* (d) *Data insufficient*

Interpret (*b*) Calorific value = heat produced by 1 g of fuel.

Given, $\Delta_C H$ for $C_2H_6 = -341.1$ kcal

$$\therefore \quad \text{Calorific value} = \frac{-341.1}{30} = -11.37 \text{ kcal/g}$$

Given, $\Delta_C H$ for $C_2H_2 = -310.0$ kcal

$$\therefore \quad \text{Calorific value} = \frac{-310.0}{26} = -11.92 \text{ kcal/g}$$

As the calorific value of C_2H_2 is high as compared to C_2H_6, therefore C_2H_2 is a better gas welder.

(b) Enthalpy of Neutralisation

The enthalpy change when one equivalent of an acid is neutralized by one equivalent of a base in a fairly dilute solution is called the *heat or enthalpy of neutralization*. It is denoted by $\Delta_n H$ *e.g.*,

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O; \quad \Delta_n H = -13.7 \text{ kcal}$$

The heat of neutralisation of a strong acid against a strong base is always constant i.e., 13.7 kcal/equivalent or **57.1 kJ.** This is because it is infact heat of formation of water in case of dilute solution *i.e.*,

$$H^+ + OH^- \longrightarrow H_2O; \quad \Delta H = -13.7 \text{ kcal}$$

For a weak acid against a strong base or a strong acid against a weak base or a weak acid against a weak base, its numerical value is always less than 13.7 kcal due to the fact that here some heat is used up in the ionisation of acid or base. However, **for HF, $\Delta_n H$ is higher due to high heat of hydration of fluoride ion**.

Neutralisation reactions are always exothermic, thus, it always have a negative value.

The heat of neutralisation of an acid or base can be easily determined in the laboratory with the help of polythene or polystyrene bottle. Bottle is fitted with rubber cork through which a thermometer and a stirrer are fitted as shown in the fig. 5.8. 100 mL each of acid and alkali of equal normality are taken in separate bottles. The temperature of each solution is regularly recorded. When constant temperature is attained, the alkali solution is added to the acid solution. The mixture is quickly stirred and the maximum temperature attained is noted.

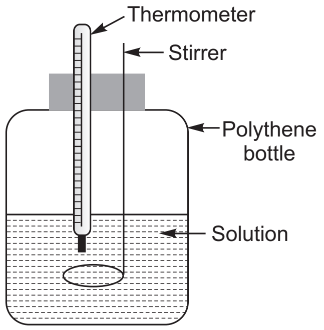


Fig. 5.8 Determination of heat of neutralisation

Calculations

Suppose, the initial temperature of acid and base $= T_1$

Final temperature of solution after mixing $= T_2$

$$\text{Rise in temperature} = T_2 - T_1$$

For the purpose of simplicity, the heat capacity of the bottle may be neglected as it is very small in comparison to that of solution. The specific heat capacity of the solution is assumed to be the same as that of water.

Q = Heat change in reaction

= Mass of solution × sp. heat × $(T_2 - T_1)$

Q is the heat evolved by the neutralisation.

$$\text{Therefore, the enthalpy of neutralisation} = \frac{Q}{100} \times 1000 \times \frac{1}{x}$$

where, x = normality of the acid or base.

Sample Problem 15 *When 50 mL of 1 M HCl (aq) with 50 mL of 1 M NaOH (aq), the enthalpy of neutralisation will be*

(a) *+57.1 kJ* (b) *114.2 kJ*
(c) *–57.1 kJ* (d) *2.9 kJ*

Interpret (*d*)

$$\underset{\substack{(50/1000)\times 1 \\ 0.05\text{ mol/L}}}{HCl} + \underset{\substack{(50/1000)\times 1 \\ 0.05\text{ mol/L}}}{NaOH} \longrightarrow NaCl + H_2O$$

∵ When 1 mole HCl is neutralised by 1 mole NaOH, the enthalpy of neutralisation = –57.1 kJ

∴ When 0.05 mole HCl is neutralised by 0.05 mol NaOH,

$$\Delta_n H = -57.1 \times 0.05$$
$$= 2.85 \approx 2.9 \text{ kJ}$$

(c) Enthalpy of Solution

The enthalpy change when one mole of solute is dissolved completely in excess of solvent is called **enthalpy** or **heat**

of solution. The solvent used here is usually water. It is denoted by $\Delta_{sol}H$, e.g.,

$$NH_4Cl(s) + H_2O(l) \longrightarrow NH_4Cl(aq);$$
$$\Delta_{sol}H = +\ 3.90 \text{ kcal}$$
$$\Delta_{sol}H = \text{hydration energy} - \text{lattice energy}$$

(About lattice energy, you have read in chemical bonding).

(d) Enthalpy of Hydration

The enthalpy change can be defined as **enthalpy** or **heat of hydration** when one mole of anhydrous or partially hydrated salt combines with required number of moles of water to form a specific hydrate. Its symbol is $\Delta_{hyd}H$, e.g.,

$$CuSO_4(s) + 5H_2O(l) \longrightarrow CuSO_4 \cdot 5\ H_2O(s);$$
$$\Delta_{hyd}H = 78.22 \text{ kJ}$$

In general cases, hydration is an exothermic process but there are some cases also where hydration is an endothermic process.

Sample **Problem 16** *At 298 K, the enthalpy of solution of solid magnesium sulphate is* -91.21 *kJ mol*$^{-1}$ *and that of hydrated magnesium sulphate is* 13.81 *kJ mol*$^{-1}$*. The heat of hydration of solid magnesium sulphate is*

(*a*) -91.21 (*b*) -105.02

(*c*) $+105.02$ (*d*) $+91.21$

Interpret (*b*) Given

$$\text{(i) } MgSO_4(s) + 7H_2O \xrightarrow{\text{Excess}} MgSO_4 \cdot 7H_2O(aq)$$
$$\Delta_{sol}H_1 = -91.21 \text{ kJ mol}^{-1}$$
$$\text{(ii) } MgSO_4 \cdot 7H_2O(s) + H_2O \text{ (excess)} \longrightarrow MgSO_4 \cdot 7H_2O(aq)$$
$$\Delta_{sol}H_2 = 13.81 \text{ kJ mol}^{-1}$$

Eq. (i) is infact, involves the following two steps :

$$MgSO_4(s) + 7H_2O \longrightarrow MgSO_4 \cdot 7H_2O(s);$$
$$\Delta_{hyd}H_3 = ?$$
$$MgSO_4 \cdot 7H_2O(s) + H_2O(\text{excess}) \longrightarrow MgSO_4 \cdot 7H_2O(aq);$$
$$\Delta_{sol}H_2 = 13.81 \text{ kJ mol}^{-1}$$

Thus, $\Delta_{sol}H_1 = \Delta_{sol}H_2 + \Delta_{hyd}H_3$

or
$$\begin{aligned}\Delta_{hyd}H_3 &= \Delta_{sol}H_1 - \Delta_{sol}H_2\\ &= -91.21 - 13.81\\ &= -105.02 \text{ kJ mol}^{-1}\end{aligned}$$

(e) Enthalpy of Dilution

The enthalpy change when the solution containing one mole of a substance is diluted from one concentration to another is called **enthalpy** or **heat of dilution.** e.g.,

$$KCl\ (200H_2O) \longrightarrow KCl(300\ H_2O);\ \Delta_{dil}H = x \text{ kJ}$$

If integral heat of solution of the hydrated and anhydrous salt is known, the heat of hydration is obtained by subtracting $\Delta_{hyd}H$ (hydrated salt) from $\Delta_{hyd}H$ (anhydrous salt), e.g.,

$$CuSO_4(\text{anhydrous}) + a\ H_2O(l) \longrightarrow CuSO_4 \cdot a\ H_2O$$
$$\Delta_{hyd}H_{(\text{anhy})} = -66.50 \text{ kJ}$$
$$CuSO_4 \cdot 5H_2O + (a-5)\ H_2O(l) \longrightarrow CuSO_4 \cdot a\ H_2O$$
$$\Delta_{hyd}H_{(\text{Hydrated})} = 11.71 \text{ kJ}$$

Thus, $\Delta_{hyd}H$ of solution $= \Delta_{hyd}H(\text{anhy.}) - \Delta_{hyd}H\ (\text{hydrated})$

(f) Enthalpy of Ionisation

The enthalpy change when one mole of a weak acid or a weak base is completely ionised into its constituents, is called the **enthalpy** or **heat of ionisation.** It is represented by $\Delta_{ion}H$, e.g.,

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq);$$
$$\Delta_{ions}H = -55.43 \text{ kJ mol}^{-1}$$

Heat of ionisation can also be obtained by subtracting the heat of neutralisation of weak acid or a weak base from the heat of neutralisation of strong acid and strong base (*i.e.,* -13.7 kcal or -57.32 kJ)

Since, *heat is required for ionisation process, the enthalpy of ionisation is usually negative.*

(g) Enthalpy of Transition

The enthalpy change when one mole of a substance changes from its one allotropic form into another is called **enthalpy of transition.** It is represented by $\Delta_{transition}H$ or Δ_tH, e.g.,

$$S_{(\text{rhombic})} \longrightarrow S_{(\text{monoclinic})};\qquad \Delta_tH = -13.14 \text{ kJ}$$

(h) Enthalpy of Atomisation

The enthalpy change that accompanies the total separation of all atoms in a chemical substance (either element or molecule or compound) is called the **enthalpy of atomisation.** It is denoted by Δ_aH. e.g.,

$$\text{(i) } CH_4(g) \longrightarrow C(g) + 4H(g);\qquad \Delta_aH = 1665 \text{ kJ mol}^{-1}$$
$$\text{(ii) } Na(s) \longrightarrow Na(g);\qquad \Delta_aH = 108.4 \text{ kJ mol}^{-1}$$

(In this case, enthalpy of atomisation is same as that of sublimation.)

$$\text{(iii) } H_2(g) \longrightarrow 2\ H(g);\qquad \Delta_aH = 435.0 \text{ kJ mol}^{-1}$$

(Here, enthalpy of atomisation is same as the bond dissociation enthalpy.)

Hence, *it can be concluded that in case of diatomic molecule,* ΔH_a = *bond dissociation enthalpy and in case of monoatomic metal, it is equal to sublimation enthalpy.*

Bond Energy and Bond Dissociation Energy

When a bond is formed between two atoms in gaseous state to form a molecule, some heat is always evolved which is called **bond energy** or **bond formation energy.** Infact two terms **bond energy** and **bond dissociation energy** are always confused with each other, but these terms are shown to have different usage. *Bond dissociation energy is the amount of energy required to break/dissociate bond of a particular type present in one molecule of the compound while bond energy is taken as the average value of dissociation energies of same type of bonds present in one mole.*

In case of diatomic molecules, bond energy is equal to the enthalpy of bond dissociation.

$$\text{H—Cl}(g) \longrightarrow \text{H}(g) + \text{Cl}(g);\ \Delta H = +431\ \text{kJ mol}^{-1}$$

However, in case of polyatomic molecules, as

$$\text{CH}_4(g) \longrightarrow \text{C}(g) + 4\text{H}(g); \quad \Delta H = 1664\ \text{kJ mol}^{-1}$$

$$\text{C—H bond energy} = \frac{1}{4}\ \text{of bond dissociation energy}$$

(as there are four C—H bonds in CH_4)

$$= \frac{1664}{4} = 416\ \text{kJ mol}^{-1}$$

As a chemical reaction involves the breaking of old bonds in reactants and formation of new bonds in products, the enthalpy change of a reaction can also be calculated by, the following formula.

$$\Delta_r H = \text{sum of BE of reactants} - \text{sum of BE of products}$$

Sample **Problem 17** *Bond energy of* H—H *bond is* 430 *kJ mol*$^{-1}$ *and that of* Cl—Cl *bond is* 242 *kJ mol*$^{-1}$. *If the heat of formation of* HCl *is* –91 *kJ mol*$^{-1}$, *the bond energy of* H—Cl *is*

(a) 427 *kJ mol*$^{-1}$ (b) 490 *kJ mol*$^{-1}$

(c) 245 *kJ mol*$^{-1}$ (d) 290 *kJ mol*$^{-1}$

Interpret (a) Given, $H_2 + Cl_2 \longrightarrow 2HCl \quad \Delta_f H = -91\ \text{kJ mol}^{-1}$

∵ In this reaction, two moles of HCl are produced,

$$\Delta_r H = 2 \times \Delta_f H = 2 \times -91 = -182\ \text{kJ mol}^{-1}$$

Let the bond energy of H—Cl bond is x.

∴ The bond energy for 2 moles of HCl = $2x$.

For the reaction,

$$\text{H—H} + \text{Cl—Cl} \longrightarrow 2\text{H—Cl}$$

$$\Delta_r H = \Sigma\,\text{BE}_{(\text{reactants})} - \Sigma\,\text{BE}_{(\text{products})}$$

$$-182 = 430 + 242 - 2x$$

$$-182 = 672 - 2x$$

$$\therefore \quad x = \frac{854}{2} = 427\ \text{kJ mol}^{-1}$$

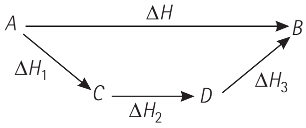
Hot Spot 2

HESS'S LAW of Constant Heat Summation

Analysis of previous years' JEE Main & AIEEE examination reveal that the topic is very important. Many a times questions were see from this topic. The questions are generally numerical type and their level varies from easy to average.

"The total heat change (ΔH) accompanying a chemical reaction is the same whether the reaction takes place in one or more steps" or "Enthalpy change in a particular reaction is always constant and is independent of the path in which the reaction takes place." The above statements are called **Hess's law of constant heat summation.**

Suppose, enthalpy change for direct conversion $A \longrightarrow B$ is ΔH. B can also be prepared from A through intermediates C and D, for which enthalpy changes are ΔH_1, ΔH_2 and ΔH_3 respectively as shown.



Then according to Hess's law

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

e.g., for the formation of CO_2 directly as

$$\text{C} + \text{O}_2(g) \longrightarrow \text{CO}_2(g); \quad \Delta H = -393.5\ \text{kJ}$$

CO_2 can also be prepared as

$$\text{C} + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{CO}(g); \quad \Delta H_1 = -110.5\ \text{kJ}$$

$$\text{CO} + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{CO}_2(g); \quad \Delta H_2 = -283.0\ \text{kJ}$$

Thus, total heat $\Delta H = \Delta H_1 + \Delta H_2$

$$= -110.5 - 283.0 = -393.5\ \text{kJ}$$

Hence, it is clear from the above that ΔH direct and ΔH obtained indirectly are same.

It clearly indicates that when chemical equations are added, subtracted or multiplied, the heat changes can also be added, subtracted or multiplied correspondingly.

Applications of Hess's Law

1. For the determination of enthalpies of formation of compounds.
2. For the determination of enthalpies of extremely slow reactions.
3. For the determination of enthalpies of transformation of one allotropic form into another.
4. For the determination of bond energies.

   $\Delta H_{\text{reaction}} = \Sigma$ Bond energies of reactants − Σ Bond energies of products

   Note In case of atomic species, bond energy is replaced by heat of atomization.
5. For the determination of resonance energy.

When a compound shows resonance, there is considerable difference between the heat of formation as calculated from bond energies and that determined experimentally.

$\therefore$ Resonance energy = Experimental or actual heat of formation − Calculated heat of formation.

Thermochemical Calculations

For making thermochemical calculations, the following points are to be kept in mind :

(i) Write down the required thermochemical equation. For example, if heat of formation of methane is to be determined, write down the following equation :

$$C(s) + 2H_2(g) \longrightarrow CH_4(g); \;\; \Delta H = ?$$

(ii) Try to obtain the required equation from the given data.

There are two ways for doing this.

First way By adding, subtracting and multiplying various the rmochemical equation.

Second way Enthalpy of reaction = Σ enthalpies of products − Σ enthaplies of reactants.

Sample Problem 18 *Calculate the standard enthalpy of formation of* $CH_3OH(l)$ *from the following data :*

[NCERT]

$$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l);$$

$$\Delta_r H^\circ = -726 \text{ kJ mol}^{-1}$$

$$C_{\text{graphite}} + O_2(g) \longrightarrow CO_2(g); \;\; \Delta_c H^\circ = -393 \text{ kJ mol}^{-1}$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l); \;\; \Delta_f H^\circ = -286 \text{ kJ mol}^{-1}$$

(a) −2339 (b) +239

(c) +119.5 (d) −119.5

Interpret (a) Firstly we write the required chemical equation for the formation of 1 mole of methanol (l) and then calculate $\Delta_f H^\circ$ for the formation of methanol by adding all the equation in such a way so that it give the required equation (*i.e.*, apply Hess's law)

Required reaction for the formation of methanol is as follows

$$C(s) + 2H_2(g) + \frac{1}{2}O_2(g) \longrightarrow CH_3OH(l); \quad \Delta_f H^\circ = ?$$

Given, enthalpy for the combustion of methanol

$$\text{(i)}\;\; CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l);$$

$$\Delta_r H^\circ = -726 \text{ kJ mol}^{-1}$$

Enthalpy for the formation of 1 mole of $CO_2(g)$;

$$\text{(ii)}\;\; C(s) + O_2(g) \longrightarrow CO_2(g); \quad \Delta_f H^\circ = -393 \text{ kJ mol}^{-1}$$

Enthalpy for the formation of 1 mole of $H_2O(l)$;

$$\text{(iii)}\;\; H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l); \quad \Delta_f H^\circ = -286 \text{ kJ mol}^{-1}$$

Multiplying Eq. (iii) by 2 [because 2 moles $H_2O(l)$ are formed in Eq. (i)] we get,

$$\text{(iv)}\;\; 2H_2(g) + O_2(g) \longrightarrow 2H_2O(l); \quad \Delta_f H^\circ = -572 \text{ kJ mol}^{-1}$$

Summing up the Eqs. (ii) and (iv), we get

$$\text{(v)}\;\; C(s) + 2H_2(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l);$$
$$\Delta_f H^\circ = -965 \text{ kJ mol}^{-1}$$

Reversing Eq.(i) we get

$$\text{(vi)}\;\; CO_2(g) + 2H_2O(l) \longrightarrow CH_3OH(l) + \frac{3}{2}O_2(g);$$

$$\Delta_f H^\circ = +726 \text{ kJ mol}^{-1}$$

Adding Eqs. (v) and (vi) we get required equation

$$C(s) + 2H_2(g) + \frac{1}{2}O_2(g) \longrightarrow CH_3OH(l);$$

$$\Delta_f H^\circ = -239 \text{ kJ mol}^{-1}$$

Sample Problem 19 *Given,*

$$CCl_4(g) \longrightarrow C(g) + 4Cl(g)$$

Calculate the bond enthalpy of C—Cl *in* $CCl_4(g)$.

$$\Delta_{\text{vap}} H^\circ (CCl_4) = 30.5 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ (CCl_4) = -135.5 \text{ kJ mol}^{-1}$$

$$\Delta_a H^\circ (C) = 715.0 \text{ kJ mol}^{-1},$$

where, $\Delta_a H^\circ$ is enthalpy of atomisation, $\Delta_a H^\circ (Cl_2) = 242 \text{ kJ mol}^{-1}$.

[NCERT]

(a) + 1304 (b) −1304

(c) −326 (d) + 326

Interpret (d) ***Step I*** Write the balanced equation for all the enthalpy changes.

$$\text{(i)}\;\; CCl_4(l) \longrightarrow CCl_4(g); \quad \Delta_{\text{vap}} H^\circ = +30.5 \text{ kJ mol}^{-1}$$

$$\text{(ii)}\;\; C(s) + 2Cl_2(g) \longrightarrow CCl_4(l); \quad \Delta_f H^\circ = -135.5 \text{ kJ mol}^{-1}$$

$$\text{(iii)}\;\; C(s) \longrightarrow C(g); \quad \Delta_a H^\circ = 715.0 \text{ kJ mol}^{-1}$$

$$\text{(iv)}\;\; Cl_2(g) \longrightarrow 2Cl(g); \quad \Delta_a H^\circ = 242 \text{ kJ mol}^{-1}$$

Step II Apply Hess's law to obtain the ΔH for the equation

$$CCl_4(g) \longrightarrow C(g) + 4Cl(g)$$

Multiply Eq. (iv) by 2

(v) $2Cl_2(g) \longrightarrow 4Cl(g)$; $\quad \Delta_a H^\circ = 484.0 \text{ kJ mol}^{-1}$

Add Eqs. (iii) and (v),

(vi) $C(s) + 2Cl_2(g) \longrightarrow C(g) + 4Cl(g)$; $\quad \Delta H = 1199 \text{ kJ mol}^{-1}$

Reverse Eqs. (i) and (ii),

(vii) $CCl_4(g) \longrightarrow CCl_4(l)$; $\quad \Delta H = -30.5 \text{ kJ mol}^{-1}$

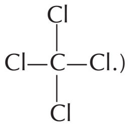
(viii) $CCl_4(l) \longrightarrow C(s) + 2Cl_2(g)$; $\quad \Delta H = +135.5 \text{ kJ mol}^{-1}$

Add Eqs. (vi), (vii) and (viii), we get

$$CCl_4(g) \longrightarrow C(g) + 4Cl(g);\ \Delta H = 1304 \text{ kJ mol}^{-1}$$

Step III Since bond enthalpy is average of all the bonds.

$$\text{Bond enthalpy of C—Cl bond in } CCl_4 = \frac{1304}{4} = 326 \text{ kJ mol}^{-1}$$

(∵ There are four C—Cl bonds in CCl_4,  $\mathrm{Cl{-}\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{C}}{-}Cl}$.)

5.7 Heat Capacity

The quantity of heat required to raise the temperature of system by one degree is called heat capacity of that system. This is denoted by C_V (when volume is constant) and by C_p (when pressure is constant).

Thus, in general we can say

$$\text{Heat capacity} = \frac{dq}{dT}$$

The magnitude of heat capacity depends upon the size, composition and nature of the system. Heat capacity varies directly with the amount of substance. It also affects temperature. If the magnitude of heat capacity is large, there is only a small rise in temperature by a given amount of heat, *e.g.*, Heat capacity of H_2O is large, thus a large amount of heat is required to raise its temperature.

In chemical calculations we often use specific heat capacity and molar heat capacities. **Specific heat** is defined as "the heat required to raise the temperature of one unit mass by 1 degree (either celsius or kelvin)". When the definition is given in terms of mole, it is considered as **molar heat capacity**, *i.e.*, the heat capacity of one mole of a substance.

The specific heat capacity is denoted by c and can be calculated with the help of following formula

$$q = c \times m \times \Delta T$$

where, q = heat required to raise the temperature by 1°C

c = specific heat capacity

m = mass

Δt = temperature change (in °C)

If C is the heat capacity of n mol of the system, then its molar heat capacity C_m is given by $C_m = C/n$.

Relation Between C_p and C_V

Enthalpy of the system

$$H = E + pV$$

From ideal gas equation.

$$pV = nRT$$

where, $n = 1$

$$pV = RT \quad \text{or} \quad H = E + RT$$

On differentiating with respect to T

$$\therefore \qquad \frac{dH}{dT} = \frac{dE}{dT} + R$$

$$\text{or} \qquad C_p = C_V + R$$

$$\text{or} \qquad (C_p - C_V) = R = 1.99 \text{ cal K}^{-1} \text{ mol}^{-1} = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

The difference between C_p and C_V is equal to the work done by 1 mole of a gas in expansion when heated through 1°C.

C_p is Always Greater than C_V

When gas is heated at constant volume, the pressure of a gas has to increase. As the gas is not allowed to expand, therefore in case of C_V heat is required for raising the temperature of one mole of a gas through one degree.

When gas is heated at constant pressure it expands. The gas has done some work against external pressure. More heat is, therefore, supplied to raise its temperature through one degree. Thus, C_p is heat required for the purpose of

(i) increasing temperatures of one mole of gas through one degree.

(ii) for increasing the volume of the gas against external pressure.

C_p/C_V Ratio

The ratio of molar heat capacities at constant pressure to that at constant volume is represented by γ. The value of γ gives information about the atomicity of gases.

$$\frac{C_p}{C_V} = \gamma$$

From the ratio of C_P and C_V, we get idea of atomicity of a gas.

1. For **monoatomic gas,** $C_p = 5$ cal; $C_V = 3$ cal

   hence, $\qquad \gamma = \dfrac{C_p}{C_V} = \dfrac{5}{3} = 1.67$

2. For **diatomic gas,** $C_p = 7$ cal; $C_V = 5$ cal

   hence, $$\gamma = \frac{C_p}{C_V} = \frac{7}{5} = 1.40$$

3. For **triatomic gas,** $C_p = 8$ cal, $C_V = 6$ cal

   hence, $$\gamma = \frac{8}{6} = 1.33$$

4. For any hypothetical process, if type of gas is given (*i.e.*, monoatomic, diatomic etc.) then specific heat can be calculated by the expression :

   $$C = \frac{R}{\gamma - 1} + \frac{R}{1 - x}$$

   provided gas follows $pV^{\gamma} = \text{constant}$

***Sample* Problem 20** *4 moles of an ideal gas having* $\gamma = 1.67$ *are mixed with 2 moles of another ideal gas having* $\gamma = 1.40$. *Find the equivalent values of* γ *for the mixture*.

(*a*) 1.33 (*b*) 1.54 (*c*) 1.67 (*d*) 1.23

Interpret (*b*) $$\gamma_{\text{mix}} = \frac{C_{P_{\text{mix}}}}{C_{V_{\text{mix}}}} = \frac{\left(\dfrac{n_1 C_{p_1} + n_2 C_{p_2}}{n_1 + n_2}\right)}{\left(\dfrac{n_1 C_{V_1} + n_2 C_{V_2}}{n_1 + n_2}\right)}$$

$$= \frac{n_1 \cdot \dfrac{R \cdot \gamma_1}{\gamma_1 - 1} + n_2 \cdot \dfrac{R \cdot \gamma_2}{\gamma_2 - 1}}{n_1 \cdot \dfrac{R}{\gamma_1 - 1} + n_2 \cdot \dfrac{R}{\gamma_2 - 1}}$$

$$= \frac{n_1 \gamma_1 (\gamma_2 - 1) + n_2 \gamma_2 (\gamma_1 - 1)}{n_1 (\gamma_2 - 1) + n_2 (\gamma_1 - 1)}$$

$$= \frac{4 \times 1.67 \times (1.40 - 1) + 2 \times 1.40 \times (1.67 - 1)}{4 \times (1.40 - 1) + 2 \times (1.67 - 1)}$$

$$= 1.547$$

Alternate Method γ_{mix} may also be determined by first calculating $C_{V_{\text{mix}}}$. Try yourself.

Check Point 2

1. Why does the enthalpy of combustion is always negative?
2. Why is the heat of neutralisation between an weak acid and strong base less than 13.7 kcal?
3. HF is a weak acid but its enthalpy of neutralisation is greater than 57.1 kJ. Explain, why?
4. Calculation ΔH is more significant than $\Delta E°$, in laboratories, why?
5. Although the calorific values of hydrogen is very high, yet it is not used as domestic fuel. Explain, why?
6. Why is a large amount of heat required to raise the temperature of water?

5.8 Spontaneous and Non-spontaneous Processes

A physical or chemical change that occurs by its own *i.e.*, without the help of an external source, is called **spontaneous process** or **natural process** or **feasible process or probable** process. For example rolling ball, heat flow, gas flow, etc. There are also some processes which require some initiation before they proceed spontaneously. These processes are also considered as spontaneous processes. Thus, we can say that spontaneous processses are of two types :

1. Spontaneous processes which does not require initiation *e.g.,* sugar dissolution in water, water evaporation from river, ponds, etc.
2. Spontaneous processes where initiation is required, for example,

   $$2H_2(g) + O_2(g) \xrightarrow[\text{spark}]{\text{Electric}} 2H_2O(l)$$

   Here, the reaction is initiated by electric spark, and then proceeds spontaneously.

   $$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$$

   Here, CH_4 burns spontaneously when ignited initially.

Rest of the other processes which require a continuous supply of energy from outside the system are called **non-spontaneous processes.**

The spontaneity of the process can be explained on the basis of change in energy. A spontaneous process generally proceeds with decrease in energy, but it is not the case with all process *e.g.*, melting of ice is an endothermic process.

Besides energy decrease, increase in randomness is another factor which determines the spontaneity of a process. Thus, there are two factors which govern the spontaneity of a process :

(i) Tendency to attain minimum energy state, *i.e.*, tendency to become more and more stabilised.

(ii) Tendency to attain maximum randomness or disorderness.

Both of these factors are equally responsible for spontaneity and both of them are independent of each other. Spontaneous changes are always unidirectional and in case of reversible reactions proceed till equilibrium is achieved.

5.9 Entropy

The extent of randomness in a system may be expressed in terms of entropy, which is defined as, the property of a system which measures the degree of randomness in a system. It is generally denoted by S and is a state function, *i.e.*, change in entropy (ΔS) depends only on the initial and final states of the system.

Thus,

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

Units of entropy are **joule per kelvin per mole.**

For a given substance, the crystalline solid state is most ordered and therefore, has the lowest entropy while gaseous state is most disordered, therefore, has the highest entropy. The liquid state is the intermediate between two. Thus, the order of randomness and thus, the entropy is

$$\text{gas} > \text{liquid} > \text{solid}$$

Some examples in which entropy either increases or decreases are

1. A molecule if kept in a larger volume container will have higher entropy.
2. Decomposition of a compound increases entropy while combination results to decrease in entropy.
3. In case of atoms or molecules belonging to different elements, the one with higher mass have greater entropy, *i.e.*, for inert gases :

   $$S_{\text{He}} < S_{\text{Ne}} < S_{\text{Ar}} < S_{\text{Kr}} < S_{\text{Xe}} < S_{\text{Rn}}$$

   Similarly, for halogens

   $$S_{\text{F}_2} < S_{\text{Cl}_2} < S_{\text{Br}_2} < S_{\text{I}_2}$$
4. The molecules with more atoms of given type or with greater number of chemical bonds or greater capacity to take up energy means greater thermal disorder thus, have greater entropy, *e.g.,*

   $$S_{\text{acetylene}} < S_{\text{ethylene}} < S_{\text{ethane}}$$
5. Vaporisation and fusion results to entropy increase while crystallisation results to decrease in entropy.
6. At absolute zero, entropy of all pure elements and compounds is zero because kinetic energy of constituent atoms is zero.
7. Stretching of rubber band results in increase in entropy while in case of boiling of egg, entropy decreases.

Entropy is also a measure of unavailable energy, the energy which cannot be converted into work by the system. The unavailable energy of any system is given as a product of change in entropy at the temperature at which system absorbs heat, and the temperature at which system loses heat.

Unavailable energy = Change in entropy × temperature

Entropy Change in Reversible Process

Consider an isothermal reversible process. In this process, let the system absorbs q amount of heat from surroundings at temperature T. The increase in the entropy of the system will be

$$\Delta S_{\text{system}} = +\frac{q}{T}$$

On the other hand, surroundings lose the same amount of heat at the same temperature. The decrease in the entropy of the surroundings will be

$$\Delta S_{\text{surroundings}} = -\frac{q}{T}$$

Total change in entropy of the process = entropy change in system + entropy of change in surroundings

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = \frac{q}{T} - \frac{q}{T} = 0$$

When the reversible process is adiabatic, there will be no heat exchange between system and surroundings, *i.e.*, $q = 0$

$$\therefore \quad \Delta S_{\text{system}} = 0,$$

$$\Delta S_{\text{surroundings}} = 0$$

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$$

Entropy Change in Irreversible Processes

Consider a system at higher temperature T_1 and its surroundings at lower temperature T_2. 'q' amount of heat goes irreversibly from system to surroundings.

$$\therefore \quad \Delta S_{\text{system}} = -\frac{q}{T_1}$$

$$\Delta S_{\text{surroundings}} = +\frac{q}{T_2}$$

$$\Delta S_{\text{process}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

$$= -\frac{q}{T_1} + \frac{q}{T_2} = q\left[\frac{T_1 - T_2}{T_1 T_2}\right]$$

But $\quad T_1 > T_2$

$$\therefore \quad T_1 - T_2 = +\text{ve} \text{ or } \Delta S_{\text{process}} > 0$$

Hence, entropy increases in an irreversible process.

Caution Points

(*i*) *A thermodynamically irreversible process is always accompanied by increase in entropy of the universe while in case of reversible process, entropy remains constant.*

(*ii*) *Most of the natural phenomenon are irreversible in nature.*

Entropy and Spontaneity

Positive and negative values of ΔS shows the spontaneous and non-spontaneous processes respectively. For equilibrium when an isolated system is in equilibrium, the entropy is maximum. The mathematical condition for entropy (S) to be maximum is that the change in entropy (ΔS) is zero, *i.e.*, $\Delta S = 0$ (at equilibrium for an isolated system)

Entropy Change During Phase Transition

The change of matter from one state to another is called **phase transition**. The entropy changes at the time of phase change can be summarised as

$$\Delta S_{\text{melting}} = \frac{\Delta H_{\text{fusion}}}{T_m}$$

where, T_m = melting point of substance.

$$\Delta S_{\text{vaporisation}} = \frac{\Delta H_{\text{vaporisation}}}{T_b}$$

where, T_b = boiling point of substance

Similarly, $$\Delta S_{\text{sublimation}} = \frac{\Delta H_{\text{sublimation}}}{T_{\text{sub}}}$$

where, T_{sub} = sublimation temperature

Entropy Change for Ideal Gases

Change in entropy for an ideal gas under different conditions may be calculated as

(i) When the gas changes from initial state (1) to final state (2)

$$\Delta S = 2.303 nC_V \log\left(\frac{T_2}{T_1}\right) + 2.303\, nR\log\left(\frac{V_2}{V_1}\right)$$

(when T and V are variables)

$$\Delta S = 2.303 nC_p \log\left(\frac{T_2}{T_1}\right) + 2.303 nR\log\left(\frac{p_1}{p_2}\right)$$

(when T and p are variables)

(ii) For isothermal process, $\Delta S = nR\ln\frac{V_2}{V_1} = nR\ln\frac{p_2}{p_1}$ $(\because \Delta T = 0)$

(iii) For isobaric process, $\Delta S = nC_p \ln\frac{T_2}{T_1}$ $(\because p_1 = p_2)$

(iv) For isochoric process, $\Delta S = nC_V \ln\frac{T_2}{T_1}$ $(\because V_1 = V_2)$

(v) **Entropy change in mixing of ideal gases** Let n_1 mole of gas A and n_2 mole of gas B are mixed; then total entropy change can be calculated as

$$\Delta S = -2.303\, R[n_1 \log x_1 + n_2 \log x_2]$$

x_1, x_2 are mole fractions of gases A and B,

i.e., $x_1 = \frac{n_1}{n_1 + n_2}$; $x_2 = \frac{n_2}{n_1 + n_2}$

$$\Delta S/\text{mol} = -2.303 R\left[\frac{n_1}{n_1 + n_2}\log x_1 + \frac{n_2}{n_1 + n_2}\log x_2\right]$$

$$\Delta S/\text{mol} = -2.303 R[x_1 \log x_1 + x_2 \log x_2]$$

(vi) Entropy change in adiabatic expansion will be zero, $\Delta S = 0$.

Standard and Molar Entropy Change

If entropy change is measured under standard conditions, it is called **standard entropy change** (ΔS°). Once, we know the entropies of a variety of substances participating in a reaction, we can calculate the standard entropy change, ΔS° as

ΔS° = sum of ΔS° of products − sum of ΔS° of reactants

e. g., in a general reaction,

$$aA + bB \longrightarrow xX + yY$$

$$\Delta S^\circ = [xS^\circ \text{ for } X + yS^\circ \text{ for } Y] - [aS^\circ \text{ for } A + bS^\circ \text{ for } B]$$

The standard entropy of a substance can be calculated with the help of following formula

$$S^\circ = 2.303\, C_p \log T$$

If entropy is defined per unit amount of substance, it is called **molar entropy** (S_m).

Sample Problem 21 *The entropy change can be calculated by using the expression $\Delta S = \frac{q_{rev}}{T}$. When water freezes in a glass beaker, choose the correct statement amongst the following :* **[NCERT Exemplar]**

(a) ΔS (system) decreases but ΔS (surroundings) remains the same

(b) ΔS (system) increases but ΔS (surroundings) decreases

(c) ΔS (system) decreases but ΔS (surroundings) increases

(d) ΔS (system) decreases and ΔS (surroundings) also decreases.

Interpret (c) Freezing is exothermic process. The heat released increases the entropy of surroundings.

Sample Problem 22 *When 36 g of liquid water evaporates at 373 K ($\Delta_{vap}H = 40.63$ kJ mol^{-1}), the entropy change is*

(a) 218 JK^{-1} (b) 315 JK^{-1}

(c) 185 JK^{-1} (d) 268 JK^{-1}

Interpret (a) $\Delta_{\text{vap}}H = 40.63 \text{ kJ mol}^{-1}, T_b = 373 \text{ K}$

$$\Delta_{\text{vap}} S = \frac{\Delta_{\text{vap}}H}{T_b} = \frac{40.63 \times 1000 \text{ J mol}^{-1}}{373 \text{ K}}$$

$$= 109 \text{ JK}^{-1}\text{mol}^{-1}$$

Entropy change for evaporation of 36 g of water

$$= \frac{109}{18} \times 36 = 218 \text{ JK}^{-1}$$

5.10 Second and Third Laws of Thermodynamics

Second Law of Thermodynamics

The second law of thermodynamics can be stated as

1. Whenever a spontaneous process takes place, it is always accompanied by an increase in total entropy of the universe.
2. It is impossible to take heat from a hotter reservoir and completely convert into work by a cyclic process without transferring a part of heat to a cooler reservoir. This statement of second law is called **Kelvin's statement**.
3. It is impossible for a cyclic process to transfer heat from a body at lower temperature to one at a higher temperature without converting some work to heat. This statement of the second law of thermodynamics is known as **Clausius statement**.

The above statements (*i.e.*, the second law) in simplified form can be stated as "for a spontaneous process in an isolated system, the change in entropy is positive."

In statement (i) above, the term universe means the system and the surroundings. Thus,

$$\Delta S_{\text{univ}} = \Delta S_{\text{syst}} + \Delta S_{\text{surr}}$$

Conversion of Heat into Work
(Carnot Cycle)

Carnot in 1824 gave an imaginary reversible cycle which demonstrates the maximum conversion of heat into work. He actually proposed a theoretical heat engine to show that its efficiency was based upon the temperatures, between which it operated. Infact, heat engine is a machine which can do work by using heat that flows out spontaneously from a high temperature source to a low temperature sink.

A Carnot cycle comprises four operations or processes:

(i) Isothermal reversible expansion
(ii) Adiabatic reversible expansion
(iii) Isothermal reversible compression
(iv) Adiabatic reversible compression

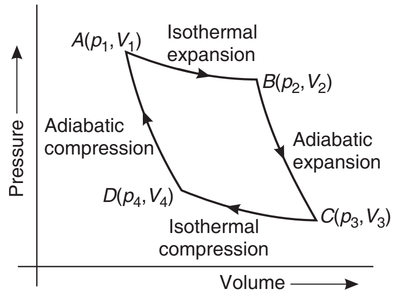


Fig. 5.9 Carnot cycle

(a) Net work done in 1 cycle is

$$W = RT_2 \ln \frac{V_2}{V_1} + RT_1 \ln \frac{V_4}{V_3}$$

(b) Net heat absorbed in the whole cycle is

$$q = R(T_2 - T_1) \ln \frac{V_2}{V_1}$$

The ratio of the work obtained in a cyclic process (W) to the heat taken from a high efficiency reservoir is called the **efficiency of heat engine.** It is denoted by η.

$$\eta = \frac{W}{q_2} = \frac{T_2 - T_1}{T_2} = 1 - \frac{T_1}{T_2}$$

The above relation shows that efficiency depends upon the temperature limits between which the cycle operates. The above relation was stated in the form of **Carnot theorem** by Carnot *i.e.*, **"***Every perfect engine working reversibly between the same temperature limits has the same efficiency, whatever be the working substance.***"**

Sample **Problem 23** *The maximum efficiency of a steam engine operating between* 100°C *and* 25°C *is*

(*a*) 25% (*b*) 22.2% (*c*) 30% (*d*) 20%

Interpret (*d*) $\eta = \frac{T_2 - T_1}{T_2} = \frac{373 - 298}{373} = 0.20$ or 20%

Third Law of Thermodynamics

This law was proposed by German chemist **Walther Nernst.** According to this law, "*The entropy of a perfectly crystalline substance approaches zero as the absolute zero of temperature is approached*"**.** It forms the basis from which entropies at other temperatures can be measured.

$$\lim_{T \to 0} S = 0$$

In case of CO *and* NO *molecules in solid state, there is randomness even at* 0 K *due to their dipole moment hence entropy in such cases is not zero even at* 0 K.

As the temperature is raised, the molecules begin to vibrate. The number of ways in which the vibrational energy can be distributed increases with increase in temperature and the entropy of the solid increases steadily as the temperature increases. At the melting point (mp) of a solid, there is a discontinuous jump in entropy because there are many more ways of arranging the molecules in the liquid than in the solid. An even greater jump in entropy is observed at the boiling point (bp) because molecules in the gas are free to occupy a more larger volume and hence randomness increases.

Check Point 3

1. Why does a real crystal has more entropy than an ideal crystal?
2. Why is entropy of substance taken as zero at absolute zero temperature?
3. How does entropy change when
   (i) temperature increases?
   (ii) pressure decreases?
4. Which of the following will have larger entropy; a mole of ice at 0°C or a mole of water at the same temperature?

Hot Spot 3

GIBBS FREE ENERGY

Analysis of previous years' AIEEE or JEE Main examination papers reveals the importance of Gibbs free energy and its relationship with spontaneity for this examination. The question are generally numerical type and may be direct or indirect.

The maximum amount of energy available to a system, during a process, that can be converted into useful work is called **free energy** or **Gibbs free energy** or **Gibbs energy.** It was called Gibbs free energy in early literature but in accordance with IUPAC recommendations we shall use the term free energy for it.

Gibbs energy is the measure of capacity of a system to do useful work. It is denoted by G and given as

$$G = H - TS$$

where, H = enthalpy of system, S = entropy of system

T = absolute temperature

but we know that, $H = E + pV$

Hence, $G = E + pV - TS$

Similarly, change in free energy is expressed as

$$\Delta G = \Delta E + \Delta(pV) - \Delta(TS)$$

If the process is carried out at constant temperature and pressure, then $\Delta(pV)$ becomes $p\Delta V$ and $\Delta(TS)$ becomes $T\Delta S$.

Hence, $\Delta G = \Delta E + p\Delta V - T\Delta S$ ...(i)

but $\Delta E + p\Delta V = \Delta H$

thus , $\Delta G = \Delta H - T\Delta S$ ...(ii)

The above Eq. (ii) is called **Gibbs Helmholtz equation** and is very useful in predicting the spontaneity of a process.

(i) If ΔG is negative, the process is spontaneous
(ii) If ΔG is positive, the process is non-spontaneous
(iii) If ΔG is zero, the process is in equilibrium state

Gibbs Free Energy as Criteria for Spontaneity

Spontaneity of a process is decided by the value of ΔG. A negative value of ΔG shows a spontaneous process and a positive value shows a non-spontaneous process. Since, the value of ΔG depends upon ΔS and ΔH, these two also play an important role for deciding spontaneity of a process. [$\Delta G = \Delta H - T\Delta S$, Gibbs Helmholtz equation]. For negative value of ΔG, several conditions exist that are mentioned in the table given below :

Table 5.2 **Relationship between ΔG and Spontaneity of a Process**

S. No.	ΔS	ΔH	ΔG	Spontaneous/ Non-spontaneous process
1.	+	–	–ve at all temperatures	Spontaneous at all temperature
2.	–	–	–ve at low temperature but +ve at high temperature	Spontaneous at low temperature but non-spontaneous at high temperature
3.	+	+	+ve at low temperature and –ve at high temperature	Spontaneous at high temperature
4.	+	+	+ve at all temperatures	Non-spontaneous at all temperature

Sample **Problem 24** *For the reaction at 298 K,*

$$2A+B \longrightarrow C$$

$\Delta H = 400$ kJ mol^{-1} and $\Delta S = 0.2$ kJ K^{-1} mol^{-1}

At what temperature will the reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range?

(a) 1000 *K* (b) 1900 *K* (c) 2000 *K* (d) 2200 *K*

Interpret (*d*) In order to solve out such problems following steps are involved.

Step I Write the information that you have.

e.g., In the above question, we have

$$\Delta H = 400 \text{ kJ mol}^{-1}, \Delta S = 0.2 \text{ kJ K}^{-1}\text{mol}^{-1}$$

Process spontaneous, so $\Delta G < 0$

Step II Think which formula you can use for the information given so that you can find spontaneity.

ΔG is helpful in finding spontaneity and is also related to ΔH and ΔS as

$$\Delta G = \Delta H - T\,\Delta S$$

Step III Calculate the value of T by putting the values of ΔH, ΔS and ΔG.

$$0 > \Delta H - T\,\Delta S$$

$$T\,\Delta S > \Delta H, T > \frac{\Delta H}{\Delta S}, T > \frac{400}{0.2}, T > 2000 \text{ K}$$

Sample **Problem 25** *What is the free energy change; ΔG, when 1.0 mole of water at 100°C and 1 atm pressure is converted into steam at 100°C and 1 atm pressure?*

(a) 0 *cal* (b) 10 *cal* (c) 320 *cal* (d) 290 *cal*

Interpret (a) At equilibrium $\Delta G = 0$

Standard Free Energy Change

The free energy change for a process at 298 K and 1 atm pressure in which the reactants in their standard state are converted into products in their standard state, is called **standard free energy change**. It is denoted by $\Delta G°$.

Free energy change when1 mole of the compound is made from its elements in their standard states is called **standard molar free energy of formation of a compound.** For an element, it is taken as zero by convention. Standard free energy for formation of $H^+(aq)$ is zero.

Efficiency of a fuel cell

$$= \frac{\text{total useful work}}{\text{total heat given}} \times 100 = \frac{\Delta G}{\Delta H} \times 100$$

Caution Points

(*i*) *The dependence of free energy on temperature is given by Gibbs-Helmholtz equation :*

$$\Delta G = \Delta H + T \cdot \left[\frac{\partial(\Delta G)}{\partial T}\right]_P$$

(*ii*) *For isothermal expansion or compression of an ideal gas,* $\Delta G = nRT \ln \frac{p_2}{p_1}$

(*iii*) *Process with negative ΔG is called exo-ergonic and positive ΔG, endo-ergonic.*

(*iv*) *$\Delta_f H°$ and $\Delta G°$ of an element is taken as zero but $\Delta S°$ of an element never be equal to zero.*

Relation between Gibbs Free Energy and Equilibrium Constant

$$\Delta G = \Delta G° + RT \ln Q$$

At equilibrium, $\Delta G = 0$ and $Q = K$

on putting the values we get

$$0 = \Delta G° + RT \ln K \text{ or } \Delta G° = RT \ln K$$

Thus the standard free energy $(\Delta G°)$ is related to equilibrium constant K as

$$\Delta G° = -RT \ln K \; i.e., \Delta G° = -2.303\, RT \log K$$

Table 5.3 **Relationship between the Standard Free Energy Change and the Equilibrium Constant**

$\Delta G°$	$\log K$	K	Comment
$\Delta G° = 0$	$\log K = 0$	1	The equilibrium mixture contains comparable amounts of reactants and products ($K = 1$ for 1M concentrations and 1 atm partial pressures)
$\Delta G° < 0$	$\log K > 0$	$K > 1$	The equilibrium mixture is mainly products.
$\Delta G° > 0$	$\log K < 0$	$K < 1$	The equilibrium mixture is mainly reactants.

Relation between Gibbs Free Energy and EMF of the Cell

Any process that occurs spontaneously can be utilised for performance of work. The greater the Gibbs energy change, the greater is the amount of work that can be obtained from the process.

The free energy change (ΔG) is related to the electrical work done in the cell as

$$\Delta G = -nFE_{\text{cell}}$$

where, E = emf of the cell

n = number of moles of electrons involved

F = Faraday's constant *i.e.*, 96500 C

If reactants and products are in their standard state,

$$\Delta G° = -nFE°$$

where, $E°$ = standard cell potential

Check Point 4

1. What is the value of ΔG at melting point of ice?
2. Which one becomes zero at equilibrium from ΔG and $\Delta G°$?
3. An exothermic reaction $A \rightarrow B + C$ is spontaneous in the back direction. What is the sign of ΔS for the forward direction?
4. If for a hypothetical reaction; $A(s) + B(s) \longrightarrow AB(g)$, the heat of the reaction is $+y$, tell under what conditions will the reaction occur spontaneously?

WORKED OUT Examples

Example 1 *56 g of iron reacts with* HCl *in a closed vessel of fixed volume. Again, same amount of* Fe *is made to react in an open beaker at 27°C. The work done (in cal) in both the cases will be respectively*

(a) –600, –600 (b) –600, +600
(c) –300, –600 (d) 0, –600

Solution (*d*) In first case, since the volume is fixed,

$$\Delta V = 0$$
$$W = -p_{ext}\Delta V = 0$$

In second case,

$$W = -p_{ext}\Delta V$$

or $$= -p_{ext} \times \frac{\Delta n_g RT}{p_{ext}} = -\Delta n_g RT \qquad \left(\because \Delta V = \frac{\Delta n_g RT}{p}\right)$$

56 g of Fe = 1 mole of Fe

Thus, $$\underset{1\text{ mol}}{\text{Fe}(s)} + 2\text{HCl}\,(aq) \longrightarrow \text{FeCl}_2(aq) + \underset{1\text{ mol}}{\text{H}_2(g)}$$

$$\Delta n_g = 1 - 0 = 1$$
$$W = -1 \times 2 \times 300 = -600 \text{ cal}$$

Example 2 *Consider a system consisting of one mole of a diatomic gas, contained in a piston. What is the temperature change of the gas, if* $q = 50.0\,J$ *and* $W = -100.0\,J$?

(a) –50 *J* (b) –2.4 *J*
(c) – 5.8 *J* (d) –1.25 *J*

Solution (*b*) According to the first law of thermodynamics,

$$\Delta E = q + W = 50 - 100 = -50 \text{ J}$$

Molar heat capacity at constant volume, $C_V = \left(\frac{\Delta E}{\Delta T}\right)_V$

$$\therefore \qquad \Delta T = \frac{\Delta E}{C_V} = \frac{-50\text{ J}}{\frac{5}{2}R} = \frac{-50}{\frac{5}{2} \times 8.314} = -2.41 \text{ K}$$

Example 3 *1 mole of carbon dioxide gas at 300 K is expanded under adiabatic condition such that its volume becomes 27 times. The work done during the process is (Given,* $\gamma = 1.33$ *and* $C_V = 6$ *cal* mol^{-1} *for* CO_2)

(a) 1200 *cal*
(b) 600 *cal*
(c) 1800 *cal*
(d) –600 *cal*

Solution (*a*) For adiabatic condition, $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$

or $$\frac{T_2}{T_1} = \left(\frac{1}{27}\right)^{1.33-1} = \left(\frac{1}{27}\right)^{0.33}$$

$$= \left(\frac{1}{27}\right)^{1/3} = \frac{1}{3}$$

or $$T_2 = \frac{1}{3} \times T_1$$

$$T_2 = \frac{1}{3} \times 300 = 100 \text{ K}$$

From first law of thermodynamics,

$$\Delta E = q + W$$
$$W = -\Delta E$$

($\because q = 0$ for adiabatic expansion)

$$= -C_V (T_2 - T_1)$$
$$= -6\ (100 - 300) = +1200 \text{ cal}$$

Example 4 *The vapour pressure of benzene is* 0.153×10^5 Nm^{-2} *at 303 K and* 0.520×10^5 Nm^{-2} *at 333 K. The mean latent heat of evaporation of benzene over this temperature range is*

(a) 48.5 *kJ* mol^{-1} (b) 31.8 *kJ* mol^{-1}
(c) 40.5 *kJ* mol^{-1} (d) 34.2 *kJ* mol^{-1}

Solution (*d*) From Clausius-Clapeyron equation,

$$\Delta H_V = \frac{2.303\, RT_1T_2}{(T_2 - T_1)} \log \frac{p_2}{p_1}$$

$$= \frac{2.303 \times 8.314 \times 303 \times 333}{(333 - 303)} \log \frac{0.520 \times 10^5}{0.153 \times 10^5}$$

$$= 34.2 \times 10^3 \text{ J} = 34.2 \text{ kJ mol}^{-1}$$

Example 5 *The heat liberated from the combustion of* 0.5 g *of carbon raised the temperature of* 2000 g *of water from* 24°C *to* 26°C*. The heat of the combustion of carbon is*

(a) –4 *kcal* (b) –8 *kcal*
(c) –62 *kcal* (d) –96 *kcal*

Solution (*d*) The amount of heat liberated by 0.05 g of *C*

$$= ms\Delta t$$
$$= 2000 \times 1 \times (26 - 24)$$
$$= 4000 \text{ cal} = 4 \text{ kcal}$$

$$\text{Calorific value} = \frac{4\text{ kcal}\times 1}{0.5} = 8\text{ kcal per g}$$

∴ Heat of combustion = $-8\times 12 = -96$ kcal per mole

Example 6 *The specific heat of silver is* 0.0565 *cal/g°C. Assuming no heat loss, the final temperature, when* 100 g *of* Ag *at* 40.0°*C is immersed in* 60.0 g *of water at* 10.0°*C, is*

(*a*) 10.15 (*b*) 12.58
(*c*) 40.00 (*d*) 19.16

Solution (*b*) Suppose final temperature is t and $Q = ms\Delta t$

$$\text{Heat lost by silver} = 100\times 0.0565\times(40-t)$$
$$\text{Heat gained by water} = 60\times 1\times(t-10)$$
$$\text{Heat lost by silver} = \text{heat gained by water}$$
$$5.65\times(40-t) = 60\,(t-10)$$
$$\therefore\quad t = 12.58°\text{ C}$$

Example 7 *Standard enthalpy of formation of* $C_3H_7NO_2(g)$, $CO_2(g)$ *and* $H_2O(l)$ *are* −133.57, −94.05 *and* −68.32 *kcal/mol respectively. Standard enthalpy of combustion of* CH_4 *at* 25°*C is* −212.8 *kcal/mol.*

Calculate ΔE *for combustion of* $C_3H_7NO_2(s)$.

(*a*) −372.69 (*b*) −387.70
(*c*) −370.89 (*d*) −372.16

Solution (*b*) $C_3H_7NO_2(s) + \frac{11}{2}O_2(g) \longrightarrow 3CO_2(g) + \frac{1}{2}N_2(g) + \frac{7}{2}H_2O(g)$

$$\Delta H_{\text{comb}} = 3\Delta H_f^\circ(CO_2) + 0 + \frac{7}{2}\Delta H_f^\circ(H_2O) - \Delta H_f^\circ(C_3H_7NO_2) - 0$$
$$= 3(-94.05) + \frac{7}{2}(-68.32) - (-133.57)$$
$$= -387.70\text{ kcal/mol}$$

Example 8 *Find* ΔH *of the following reaction,*

$$OF_2(g) + H_2O(g) \longrightarrow O_2(g) + 2HF(g);$$

Average bond energies of O—F, O—H, O═O, H—F *are* 44, 111, 118 *and* 135 *kcal/mol respectively.*

(*a*) 310 (*b*) −698
(*c*) −78 (*d*) −388

Solution (c) Energy used in bond breaking, *i.e.*, ΔH_1

$$F-O-F \longrightarrow O(g) + 2F(g);\qquad \Delta H = +2\times 44$$
$$H-O-H \longrightarrow O(g) + 2H(g);\qquad \Delta H = +2\times 111$$
$$\therefore\quad \Delta H_1 = 2\times 44 + 2\times 111 = +310\text{ kcal}$$

Energy released in bond formation, *i.e.*, ΔH_2

$$O + O \longrightarrow O_2;\qquad \Delta H = -118$$
$$2[H + F \longrightarrow H-F];\qquad \Delta H = -2\times 135$$
$$\therefore\quad \Delta H_2 = -118 + (-2\times 135) = -388\text{ kcal}$$

Using Hess's Law; $\Delta_r H = H_1 + H_2$

$$= 310 + (-388) = -78\text{ kcal.}$$

Example 9 *Calculate the standard free energy change for the formation of methane at 298 K. The value of* $\Delta_r H^\circ$ *for* $CH_4(g)$ *is* −74.81 *kJ mol*$^{-1}$ *and S values for* C(*graph*), $H_2(g)$ *and* $CH_4(g)$ *are* 5.70, 130.7 *and* 186.3 JK^{-1} mol^{-1} *respectively.*

(*a*) −80.8 (*b*) −98.91
(*c*) −50.74 (*d*) −40.4

Solution (c) For the reaction; $C + 2H_2 \longrightarrow CH_4$

Given, $\Delta H^\circ = -74.81\text{ kJ mol}^{-1}$

ΔS_m° can be calculated as

$$\Delta S_m^\circ = S^\circ_{m\,(\text{product})} - S^\circ_{m\,(\text{reactant})}$$
$$= S_m^\circ CH_4(g) - [S_m^\circ C_{(\text{graph})} + 2S_m^\circ H_2(g)]$$
$$= [186.3 - (5.70 + 2\times 130.7)]\text{ JK}^{-1}\text{ mol}^{-1}$$
$$= -80.8\text{ JK}^{-1}\text{ mol}^{-1}$$
$$= -80.8\times 10^{-3}\text{ JK}^{-1}\text{ mol}^{-1}$$

Since, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$= -74.81 - [(298)\times(-80.8\times 10^{-3})]$$
$$= -74.81 + 24.07\text{ kJ mol}^{-1}$$
$$= -50.74\text{ kJ mol}^{-1}$$

Example 10 *What is the equilibrium constant, K for the following reaction at 400 K?*

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

$\Delta H = 77.2$ kJ mol^{-1} *and* $\Delta S = 122$ JK^{-1} mol^{-1} *at* 400 *K*.

(*a*) −3.708 (*b*) 1.95×10^{-4}
(*c*) 2.8×10^4 (*d*) 1.67×10^{-5}

Solution (*b*) $\Delta G = \Delta H - T\Delta S$

$$= 77.2 - 400\times 122\times 10^{-3}$$
$$= +28.4\text{ kJ mol}^{-1} = 28400\text{ J mol}^{-1}$$

Further, $\Delta G = -2.303\,RT\log K$

or $28400 = -2.303\times 8.314\times 400\times\log K$

$$\log K = -\frac{28400}{2.303\times 8.314\times 400}$$
$$\log K = -3.708$$
$$K = \text{Antilog}\,(-3.708) = 1.95\times 10^{-4}$$

Start Practice for JEE Main

Round I (Topically Divided Problems)

Fundamentals of Thermodynamics

1. Identify the intensive quantity from the following.

(a) Enthalpy and temperature
(b) Volume and temperature
(c) Enthalpy and volume
(d) Temperature and refractive index

2. If a refrigerator's door is opened then, we get

(a) room heated
(b) room cooled
(c) more amount of heat is passed out
(d) no effect on room

3. In ... process, work is done at the expense of internal energy.

(a) isothermal (b) isochoric
(c) adiabatic (d) isobaric

4. Choose the correct answer. A thermodynamic state function is a quantity **[NCERT]**

(a) used to determine heat changes
(b) whose value is independent of path
(c) used to determine pressure-volume work
(d) whose value depends on temperature only.

5. Thermodynamics is not concerned about...... . **[NCERT Exemplar]**

(a) energy changes involved in a chemical reaction
(b) the extent to which a chemical reaction proceeds
(c) the rate at which a reaction proceeds
(d) the feasibility of a chemical reaction

6. Which of the following statements is correct? **[NCERT Exemplar]**

(a) The presence of reacting species in a covered beaker is an example of open system
(b) There is an exchange of energy as well as matter between the system and the surroundings in a closed system
(c) The presence of reactants in a closed vessel made up of copper is an example of a closed system
(d) The presence of reactants in a thermos flask or any other closed insulated vessel is an example of a closed system

Work, Heat and First Law of Thermodynamics

7. Which of the following expressions represents the first law of thermodyamics?

(a) $\Delta E = -q + W$ (b) $\Delta E = q - W$
(c) $\Delta E = q + W$ (d) $\Delta E = -q - W$

8. If a gas at constant temperature and pressure expands then its

(a) internal energy increases and then decreases
(b) internal energy increases
(c) internal energy remains the same
(d) internal energy decreases

9. At 27° C, one mole of an ideal gas is compressed isothermally and reversibly form a pressure of 2 atm to 10 atm. The values of ΔE and q are $(R = 2)$

(a) 0, −965.84 cal
(b) −965.84 cal, −865.58 cal
(c) +865.58 cal, −865.58 cal
(d) −865.58 cal, −865.58 cal

10. In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process? **[NCERT]**

(a) −464 J (b) + 464 J
(c) +307 J (d) −307 J

11. The change in internal energy for an isolated system at constant volume is **[NCERT Exemplar]**

(a) zero (b) − 2.18 erg
(c) +4.27 erg (d) +2.78 erg

12. In an adiabatic process, no transfer of heat takes place between system and surroundings. Choose the correct option for free expansion of an ideal gas under adiabatic condition form the following. **[NCERT Exemplar]**

(a) $q = 0$, $\Delta T \neq 0$, $W = 0$ (b) $q \neq 0$, $\Delta T = 0$, $W = 0$

(c) $q = 0$, $\Delta T = 0$, $W = 0$ (d) $q = 0$, $\Delta T = 0$, $W \neq 0$

13. In a closed insulated container, a liquid is stirred with a paddle to increase its temperature. In this process, which of the following is true?

(a) $\Delta E = W \neq 0, Q = 0$ (b) $\Delta E \neq 0, Q = W = 0$

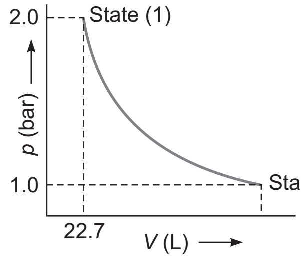
(c) $\Delta E = W = Q = 0$ (d) $\Delta E = 0, Q \neq 0, W = 0$

14. How many joules of heat are absorbed when 70.0 g of water is completely vaporised at its boiling point?

(a) 23352 J (b) 7000 J

(c) 15813 J (d) 158200 J

15. 1.0 mole of a monoatomic idea gas is expanded from state (1) to state (2) as shown in the figure. Calculate the work done for the expansion of gas from state (1) to state (2) at 298 K **[NCERT Exemplar]**



(a) −1717.46 J (b) +1717.46 J

(c) −1908.2 J (d) +1908.2 J

16. An ideal gas is allowed to expand against a constant pressure of 2 bar from 10 L to 50 L in one step. The amount of work done by the gas is *x*. If the same expansion were carried out reversibly, will the work done be higher or lower than the earlier case? **[NCERT Exemplar]**

(a) Lower (b) Higher

(c) Same as before (d) Can't anything

Enthalpy $\Delta_f H$ and $\Delta_r H$

17. The enthalpy of reaction for the reaction :

$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$ is $\Delta_r H^\ominus = -572 \text{kJ mol}^{-1}$

What will be the standard enthalpy for the of formation of $H_2O(l)$? **[NCERT Exemplar]**

(a) -572 kJ mol^{-1}

(b) + 57 kJ mol^{-1}

(c) +286 kJ mol^{-1}

(d) -286 kJ mol^{-1}

18. Which of the following equations correctly represents the standard heat of formation (ΔH_f°) of methane?

(a) C(diamond) + $2H_2 \longrightarrow CH_4(g)$

(b) C(graphite) + $2H_2(g) \longrightarrow CH_4(l)$

(c) C(graphite) + $2H_2(g) \longrightarrow CH_4(g)$

(d) C(graphite) + $4H \longrightarrow CH_4(g)$

19. ΔU° of combustion of methane is $-X$ kJ mol^{-1}. The value of ΔH° is **[NCERT]**

(a) $= \Delta U^\circ$ (b) $> \Delta U^\circ$

(c) $< \Delta U^\circ$ (d) $= 0$

20. For the reactions $A \to B$; $\Delta H = +24$ kJ/mol and $B \to C$; $\Delta H = -18$ kJ/mol, the decreasing order of enthalpy of *A*, *B* and *C* follows the order

(a) *A, B, C* (b) *B, C, A*

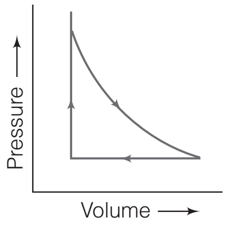
(c) *C, B, A* (d) *C, A, B*

21. If the combustion of 1 g of graphite produces 20.7 kJ of heat, what will be the molar enthalpy change? **[NCERT Exemplar]**

(a) -2.48 kJ mol^{-1} (b) -248 kJ mol^{-1}

(c) -2.48 J mol^{-1} (d) -248 J mol^{-1}

22. A sample of 1.0 mole of a monoatomic ideal gas is taken through a process of expansion and compression as shown in the figure. What will be the value of ΔH for the process as a whole? **[NCERT Exemplar]**



(a) −3.150 (b) −2.303

(c) +2.303 (d) 0

23. The enthalpies of the elements in their standard states are assumed to be

(a) zero at 298 K

(b) unit at 298 K

(c) zero at all temperatures

(d) zero at 273 K

24. For the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$; ΔH is

(a) $\Delta E - 2RT$ (b) $\Delta E - RT$

(c) $\Delta E + RT$ (d) $\Delta E + 2RT$

25. What is Δn_g for the combustion of 1 mole of benzene, when both the reactants and products are gas at 298 K?

(a) 0 (b) 1

(c) 0.5 (d) 1.5

26. The ΔH_f° of O_3, CO_2, NH_3 and HI are 142.2, –393.3, –46.2 and + 25.9 kJ per mol respectively. The order of their increasing stabilities will be

(a) O_3, CO_2, NH_3, HI (b) CO_2, NH_3, HI, O_3
(c) O_3, HI, NH_3, CO_2 (d) NH_3, HI, CO_2, O_3

27. Two moles of an ideal gas is expanded isothermally and reversibly from 1 L to 10 L at 300 K. The enthalpy change (in kJ) for the process is

(a) 11.4 (b) –11.4 (c) 0 (d) 4.8

Different Enthalpies, Hess's Law and Bond Energy

28. 50 mL of water takes 5 min to evaporate from a vessel on a heater connected to an electric source which delivers 400 W. The enthalpy of vaporisation of water is

(a) 40.3 kJ per mol (b) 43.2 kJ per mol
(c) 16.7 kJ per mol (d) 180.4 kJ per mol

29. Hess's law is applicable for the determination of heat of

(a) reaction (b) formation
(c) transition (d) All of these

30. Enthalpy of combustion of carbon to CO_2 is $-393.5\text{ kJ mol}^{-1}$. Calculate the heat released upon the formation of 35.2 g of CO_2 from carbon and dioxygen gas. (Molar mass of $CO_2 = 44\text{ g mol}^{-1}$). [NCERT]

(a) 13.851 kJ (b) 138.5 kJ
(c) 31.48 J (d) 314.8 kJ

31. Consider the reaction given below. On the basis of these reactions find out which of the algebric relations given in options (a) to (d) is correct?

(I) $C(g) + 4H(g) \longrightarrow CH_4(g); \Delta_r H = x\text{ kJmol}^{-1}$

(II) $C\text{ (graphite, s)} + 2H_2(g) \longrightarrow CH_4(g);$

$\Delta_r H = y\text{ kJ mol}^{-1}$ [NCERT Exemplar]

(a) $x = y$ (b) $x = 2y$
(c) $x > y$ (d) $x < y$

32. What would be the heat released when an aqueous solution containing 0.5 mole of HNO_3 is mixed with 0.3 mole of OH^-? (Enthalpy of neutralization is –57.1 kJ)

(a) 28.5 kJ (b) 17.1 kJ
(c) 45.7 kJ (d) 1.7 kJ

33. $C_{\text{diamond}} + O_2 \longrightarrow CO_2;$ $\Delta H = -395.3\text{ kJ/ mol}$

$C_{\text{graphite}} + O_2 \longrightarrow CO_2;$ $\Delta H = -393.4\text{ kJ / mol}$

$C_{\text{graphite}} \longrightarrow C_{\text{diamond;}}$ $\Delta H = ?$

(a) –3.8 (b) –1.9
(c) +3.8 (d) +1.9

34. Given,

(i) $S + O_2 \longrightarrow SO_2,$ $\Delta H = -298.2\text{ kJ}$

(ii) $SO_2 + \frac{1}{2}O_2 \longrightarrow SO_3,$ $\Delta H = -98.7\text{ kJ}$

(iii) $SO_3 + H_2O \longrightarrow H_2SO_4,$ $\Delta H = -130.2\text{ kJ}$

(iv) $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O,$ $\Delta H = -287.3\text{ kJ}$

The enthalpy of formation of H_2SO_4 is

(a) –715.4 kJ (b) –814.4 kJ
(c) –554 kJ (d) –455.3 kJ

35. Enthalpy of sublimation of a substance is equal to [NCERT Exemplar]

(a) enthalpy of fusion + enthalpy of vaporisation
(b) enthalpy of fusion
(c) enthalpy of vaporisation
(d) twice the enthalpy of vaporisation

36. The net enthalpy change of a reaction is the amount of energy required to break all the bonds in reactant molecules minus amount of energy required to form all the bonds in the product molecules. What will be the enthalpy change for the following reaction?

$$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$$

Given that bond energy of H_2, Br_2 and HBr is $435\text{ kJmol}^{-1}, 192\text{ kJmol}^{-1}$ and 368 kJmol^{-1} respectively.

(a) $+109\text{ kJ mol}^{-1}$ (b) -109 kJ mol^{-1}
(c) $+493\text{ kJ mol}^{-1}$ (d) -493 kJ mol^{-1}

37. The enthalpy of vaporisation of CCl_4 is 30.5 kJ mol^{-1}. Calculate the heat required for the vaporisation of 284 g of CCl_4 at constant pressure. (Molar mass of $CCl_4 = 154\text{g mol}^{-1}$). [NCERT Exemplar]

(a) 56.2 kJ (b) 52.5 kJ
(c) 18.4 kJ (d) 30.5 kJ

38. In a calorimeter, the temperature of the calorimeter increases by 6.12 K, the heat capacity of the system is 1.23 kJ/g/deg. What is the molar heat of decomposition for NH_4NO_3?

(a) –7.53 kJ/mol
(b) –398.1 kJ/mol
(c) –16.1 kJ/mol
(d) –602 kJ/mol

39. Which is the best definition of heat of neutralization?

(a) The heat absorbed when one gram molecule of an acid is neutralized by one gram molecule of a base in dilute solution at a stated temperature
(b) The heat set free or absorbed when one gram atom of an acid is neutralized by one gram atom of a base at a stated temperature

(c) The heat set free or absorbed when a normal solution containing one gram-equivalent of an acid is neutralized by a normal solution containing one gram-equivalent of a base at a stated temperature

(d) The heat set free when one gram-equivalent of an acid is neutralized by one gram-equivalent of a base in dilute solution at a stated temperature

40. 18.0 g water completely vaporises at 100°C and 1 bar pressure and the enthalpy change in the process is 40.79 kJ mol^{-1}. What will be the enthalpy change for vaporising two moles of water under the same conditions and what is the standard enthalpy of vaporisation for water? **[NCERT Exemplar]**

(a) 81.58 kJ, 81.58 kJ (b) 40.79kJ, 40.79 kJ
(c) 40.79 kJ,81.58 kJ (d) 81.58kJ, 40.79 kJ

41. The absolute enthalpy of neutralisation of the reaction

$\text{MgO}(s) + 2\text{HCl}(aq) \longrightarrow \text{MgCl}_2(aq) + \text{H}_2\text{O}(l)$ will be

(a) greater than -57.33 kJ mol^{-1}
(b) 57.33 kJ mol^{-1}
(c) less than -57.33 kJ mol^{-1}
(d) -57.33 kJ mol^{-1}

42. The heat of formations of $\text{CO}(g)$ and $\text{CO}_2(g)$ are –26.4 kcal and –94.0 kcal respectively. The heat of combustion of carbon monoxide will be

(a) –67.6 kcal (b) 36.5 kcal
(c) –36.5 kcal (d) –46.5 kcal

43. Enthalpy of solution of NaOH (solid) in water is – 41.6 kJ mol^{-1}. When NaOH is dissolved in water, the temperature of water

(a) increases (b) decreases
(c) does not change (d) fluctuates indefinitely

44. The enthalpy of dissolution of $\text{BaCl}_2(s)$ and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}(s)$ are –20.6 and 8.8 kJ per mol respectively. The enthalpy of hydration for

$\text{BaCl}_2(s) + 2\text{H}_2\text{O} \longrightarrow \text{BaCl}_2 \cdot 2\text{H}_2\text{O}(s)$ is

(a) 29.4 kJ (b) –29.4 kJ
(c) –11.8 kJ (d) 38.2 kJ

45. Given that, $\text{C}(g) + 4\text{H}(g) \longrightarrow \text{CH}_4(g)$; $\Delta H = -166$ kJ. The bond energy C—H will be

(a) –416 kJ/mol (b) –41.6 kJ/mol
(c) 832 kJ/mol (d) None of these

46. If enthalpies of methane and ethane are respectively 320 and 360 cal then the bond energy of C—C bond is

(a) 80 cal (b) 40 cal (c) 60 cal (d) 120 cal

47. The heat of atomisation of $\text{PH}_3(g)$ is 228 kcal per mol and that of $\text{P}_2\text{H}_4(g)$ is 335 kcal per mol. The energy of P—P bond is

(a) 102 kcal/mol (b) 31 kcal/mol
(c) 26 kcal/mol (d) 204 kcal/mol

48. The heat evolved in the combustion of methane is given by the following equation

$$\text{CH}_4(g) + 2\text{O}_2(g) \longrightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l); \quad \Delta H = -890.3 \text{ kJ}$$

How many gram of methane would be required to produce 445.15 kJ of heat of combustion?

(a) 4 g (b) 8 g (c) 12 g (d) 16 g

49. Diborane is a potential rocket fuel which undergoes combustion according to the equation

$$\text{B}_2\text{H}_6(g) + 3\text{O}_2(g) \longrightarrow \text{B}_2\text{O}_3(g) + 3\text{H}_2\text{O}(g)$$

Calculate the enthalpy change for the combustion of diborane.

Given

(i) $2\text{B}(s) + \frac{3}{2}\text{O}_2(g) \longrightarrow \text{B}_2\text{O}_3(s); \Delta H = -1273$ kJ/mol
(ii) $\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{H}_2\text{O}(l); \Delta H = -286$ kJ/mol
(iii) $\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g); \quad \Delta H = 44$ kJ/mol
(iv) $2\text{B}(s) + 3\text{H}_2(g) \longrightarrow \text{B}_2\text{H}_6(g); \Delta H = 36$ kJ/mol

(a) +2035 kJ/mol (b) –2035 kJ/mol
(c) +2167 kJ/mol (d) –2167 kJ/mol

50. The standard molar heat of formation of ethane, CO_2 and water (l) are respectively –21.1, –94.1 and – 68.3 kcal. The standard molar heat of combustion of ethane will be

(a) –372 kcal (b) 162 kcal (c) –240 kcal (d) 183.5 kcal

51. Combustion of glucose takes place according to the equation

$$\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{CO}_2 \longrightarrow 6\text{CO}_2 + 6\text{H}_2\text{O}; \ \Delta H = -72 \text{ kcal}$$

How much energy will be required for the production of 1.6 g of glucose? (Molecular mass of glucose = 180)

(a) 0.064 kcal (b) 0.64 kcal (c) 6.4 kcal (d) 64 kcal

Heat Capacity, Entropy, Second and Third Law of Thermodynamics

52. The enthalpy of vaporisation of a substance is 840 J/mol and its boiling point is –173K. Its entropy of vaporisation is

(a) 4.8 J/mol/K (b) 12 J/mol/K
(c) 210/mol/K (d) 49 J/mol/K

53. Maximum entropy will be in which of the following?

(a) Ice (b) Liquid water
(c) Snow (d) Water vapour

54. The molar heat capacity of water at constant pressure is 75 JK^{-1} mol^{-1}. When 1.0 kJ of heat is supplied to 100 g of water which is free to expand the increase in temperature of water is

(a) 2.4 K (b) 3.6 K (c) 4.8 K (d) 1.2 K

55. For an isolated system, $\Delta U = 0$, what will be ΔS ? **[NCERT]**

(a) 0 (b) > 0
(c) < 0 (d) ≥ 0

56. For the reaction, $2Cl(g) \longrightarrow Cl_2(g)$, what are the signs of ΔH and ΔS ? **[NCERT]**

(a) +,+ (b) +, –
(c) –, – (d) –, +

57. The entropy change in surroundings when 1.00 mole of $H_2O(l)$ is formed under standard conditions is

$$\Delta_f H^\circ = -286 \text{ kJ mol}^{-1}.$$ **[NCERT]**

(a) 856.5 JK^{-1} mol^{-1} (b) 765 JK^{-1} mol^{-1}
(c) 1050 JK^{-1} mol^{-1} (d) 959.7 JK^{-1} mol^{-1}

58. The standard molar entropy of $H_2O(l)$ is 70 JK^{-1} mol^{-1}. Standard molar entropy of $H_2O(s)$ is **[NCERT Exemplar]**

(a) more than 70 JK^{-1} mol^{-1}
(b) less than 70 JK^{-1} mol^{-1}
(c) equal to 70 JK^{-1} mol^{-1}
(d) None of the above

59. Heat capacity (C_p) is an extensive property but specific heat (C) is an intensive property. What will be the relation between C_p and C for 1 mole of water? **[NCERT Exemplar]**

(a) + 4.18 JK^{-1} (b) – 4.18 JK^{-1}
(c) – 75.3 JK^{-1} (d) + 75.3 JK^{-1}

60. Which one of the following has ΔS° greater than zero?

(a) $CaO + CO_2(g) \rightleftharpoons CaCO_3(s)$
(b) $NaCl(aq) \rightleftharpoons NaCl(s)$
(c) $NaNO_3(s) \rightleftharpoons Na^+(aq) + NO_3^-(aq)$
(d) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

61. Mark the correct statement.

(a) For a chemical reaction to be feasible, ΔG should be zero
(b) Entropy is a measure of order in a system
(c) For a chemical reaction to be feasible, ΔG should be positive
(d) The total energy of an isolated system is constant

62. The entropy values (in JK^{-1} mol^{-1}) of $H_2(g)$ = 130.6 $Cl_2(g)$ = 223.0 and $HCl(g)$ = 186.7 J mol^{-1} K^{-1} at 298 K and 1 atm pressure, then entropy change for the reaction

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) \text{ is}$$

(a) +540.3
(b) +727.3
(c) −166.9
(d) +19.8

63. A container has hydrogen and oxygen mixture in the ratio of 1 : 1 by weight, then

(a) internal energy of the mixture decreases
(b) internal energy of the mixture increases
(c) entropy of the mixture increases
(d) entropy of the mixture decreases

64. Equal volumes of monoatomic and diatomic gases at same initial temperature and pressure are mixed. The ratio of specific heats of the mixture (C_p/C_V) will be

(a) 1 (b) 2
(c) 1.67 (d) 1.2

65. If a gas has 2 atm and 5 atm pressure at 30°C and 27°C respectively. Then it will

(a) cool on expansion
(b) warm on expansion
(c) no change on expansion
(d) None of the above

Gibbs Free Energy and Spontaneity

66. The free energy change for a reversible reaction at equilibrium is

(a) large, positive (b) small, negative
(c) small, positive (d) zero

67. In which of the following conditions a chemical reaction cannot occur?

(a) ΔH and ΔS increase and $T\Delta S > \Delta H$
(b) ΔH and ΔS decrease and $\Delta H > T\Delta S$
(c) ΔH increases and ΔS decreases
(d) ΔH decreases and ΔS increases

68. The equilibrium constant for a reaction is 10. What will be the value of ΔG°? $R = 8.314$ JK^{-1} mol^{-1}, $T = 300$ K. **[NCERT]**

(a) −574.414 J mol^{-1} (b) 5744.14 J mol^{-1}
(c) −57.4414 J mol^{-1} (d) 57441.4 J mol^{-1}

69. Calculate the free energy change of

$$2CuO(s) \longrightarrow Cu_2O(s) + \frac{1}{2} O_2(g)$$

Given, ΔH = 145.6 kJ per mol

ΔS = 116 J per mol per K

(a) 113.8 kJ per mol
(b) 221.5 kJ per mol
(c) 55.4 kJ per mol
(d) 145.6 kJ per mol

70. For a reaction at 25°C, enthalpy and entropy changes are -11.7×10^3 J mol^{-1} and -105 J mol^{-1} K^{-1} respectively. What is the Gibbs free energy?

(a) 15.05 kJ (b) 19.59 kJ
(c) 2.55 kJ (d) 22.55 kJ

Round II (Mixed Bag)

Only One Correct Option

1. When one mole of monoatomic ideal gas at T temperature undergoes adiabatic change under a constant external pressure of 1 atm, change in volume is from 1 L to 2 L. The final temperature in kelvin would be

(a) $\frac{T}{2^{(2/3)}}$ (b) $T + \frac{2}{3 \times 0.0821}$

(c) T (d) $T - \frac{2}{3 \times 0.0821}$

2. If 900 J/g of heat is exchanged at boiling point of water then increase in entropy is

(a) 43.4 J/mol (b) 87.2 J/mol

(c) 900 J/mol (d) zero

3. Calculate the enthalpy change on freezing of 1.0 mole of water at 10.0°C to ice at – 10.0° C.

$$\Delta_{\text{fus}}H = 6.03 \text{ kJ mol}^{-1} \text{ at } 0°\text{C}.$$
$$C_p[H_2O(l)] = 75.3 \text{ J mol}^{-1} \text{ K}^{-1}$$
$$C_p[H_2O(s)] = 36.8 \text{ J mol}^{-1} \text{ K}^{-1}$$

[NCERT]

(a) -753 J mol^{-1} (b) -368 J mol^{-1}

(c) $-7.151 \text{ kJ mol}^{-1}$ (d) $-6.03 \text{ kJ mol}^{-1}$

4. Given that $dE = TdS - pdV$ and $H = E + pV$. Which one of the following relations is true?

(a) $dH = TdS - Vdp$ (b) $dH = SdT + Vdp$

(c) $dH = -SdT - Vdp$ (d) $dH = dE - pdV$

5. The free energy change for the following reactions are given below.

$$C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(l); \quad \Delta G° = -1234 \text{ kJ}$$
$$C(s) + O_2(g) \longrightarrow CO_2(g)\,; \quad \Delta G° = -394 \text{ kJ}$$
$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)\,; \quad \Delta G° = -237 \text{ kJ}$$

What is the standard free energy change for the reaction?

$$H_2(g) + 2C(s) \longrightarrow C_2H_2(g)$$

(a) – 209 kJ (b) – 2259 kJ

(c) + 2259 kJ (d) 209 kJ

6. The value of $\log_{10} K$ for a reaction $A \rightleftharpoons B$ is (Given, $\Delta_r H°_{298\text{ K}} = -54.07 \text{ kJ mol}^{-1}$, $\Delta_r S°_{298\text{ K}} = 10 \text{ kJ}^{-1} \text{ mol}^{-1}$ and $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$,

(a) 5 (b) 10

(c) 95 (d) 100

7. In an isobaric process, the ratio of heat supplied to the system $(d\theta)$ and work done by the system (dW) for diatomic gas is

(a) 1 : 1 (b) 7 : 2

(c) 7 : 5 (d) 5 : 7

8. A cylinder of gas is assumed to contain 11.2 kg of butane (C_4H_{10}). If a normal family needs 20000 kJ of energy per day, the cylinder will last in (Given that ΔH for combustion of butane is –2658 kJ)

(a) 20 days (b) 25 days

(c) 26 days (d) 24 days

9. The direct conversion of A to B is difficult, hence it is carried out by the following shown path

$$\begin{tikzcd} C \arrow[r] & D \arrow[d] \\ A \arrow[u] & B \end{tikzcd}$$

Given,
$$\Delta S_{(A \to C)} = 50 \text{ eu}$$
$$\Delta S_{(C \to D)} = 30 \text{ eu}$$
$$\Delta S_{(D \to B)} = 20 \text{ eu}$$

where eu is entropy unit, then $\Delta S_{(A \to B)}$ is

(a) +100 eu (b) +60 eu

(c) –100 eu (d) –60 eu

10. For the reaction $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$, ΔH, and ΔS are –283 kJ and -87 JK^{-1}, respectively. It was intended to carry out this reaction at 1000, 1500, 3000 and 3500 K. At which of these temperatures would this reaction be thermodynamically spontaneous?

(a) 1500 and 3500 K

(b) 3000 and 3500 K

(c) 1000, 1500 and 3000 K

(d) 1500,3000 and 3500 K

11. The heat of neutralisation of a strong acid and a strong alkali is 57.0 kJ mol^{-1}. The heat released when 0.5 mole of HNO_3 solution is mixed with 0.2 mole of KOH is

(a) 57.0 kJ (b) 11.4 kJ

(c) 28.5 kJ (d) 34.9 kJ

12. The enthalpy of combustion of H_2, cyclohexene (C_6H_{10}) and cyclohexane (C_6H_{12}) are –241, –3800 and –3920 kJ per mol respectively. Heat of hydrogenation of cyclohexene is

(a) 121 kJ/mol (b) –121 kJ/mol

(c) +242 kJ/mol (d) –242 kJ/mol

13. Heat of dissociation of benzene to elements is 5335 kJ/ mol. The bond enthalpies of $-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$; $\overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}$ and $-\overset{|}{\underset{|}{C}}-H$ bonds are 347.3, 615 and 412.2 kJ respectively. Resonance energy of benzene is
- (a) 1.15 kJ
- (b) 15.1 kJ
- (c) 974.2 kJ
- (d) 1511 kJ

More than One Correct Option

14. Which of the following statements is/are correct?
- (a) Heat, like work is a way of transferring energy
- (b) Heat is not a property of the system, whereas the temperature is a property of the system
- (c) Heat is manifested only at the boundary of system and surroundings
- (d) None of the above

15. Thermodynamics mainly deals with **[NCERT Exemplar]**
- (a) interrelation of various forms of energy and their transformation from one form to another
- (b) energy changes in the processes which depend only on initial and final states of the microscopic systems containing a few molecules
- (c) how and at what rate these energy transformations are carried out
- (d) the system in equilibrium state or moving from one equilibrium state to another equilibrium state

16. The spontaneity means, having the potential to proceed without the assistance of external agency. The processes which occur spontaneously are **[NCERT Exemplar]**
- (a) flow of heat from colder to warmer body
- (b) gas in a container contracting into one corner
- (c) gas expanding to fill the available volume
- (d) burning carbon in oxygen to give carbon dioxide

17. A sample containing 1.0 mole of an ideal gas is expanded isothermally and reversibly to ten times of its original volume, in two separate experiments. The expansion is carried out at 300 K and at 600 K respectively. Choose the correct option. **[NCERT Exemplar]**
- (a) Work done at 600 K is 20 times the work done at 300 K
- (b) Work done at 300 K is twice the work done at 600 K
- (c) Work done at 600 K is twice the work done at 300 K
- (d) $\Delta E = 0$ in both cases

18. Consider the following reaction between zinc and oxygen and choose the correct options out of the options given beolw : **[NCERT Exemplar]**

$$2\,\text{Zn}(s) + \text{O}_2(g) \longrightarrow 2\,\text{ZnO}(s); \quad \Delta H = -693.8 \text{ kJ mol}^{-1}$$

- (a) The enthalpy of two moles of ZnO is less than the total enthalpy of two moles of Zn and one mole of oxygen by 693.8 kJ
- (b) The enthalpy of two moles of ZnO is more than the total enthalpy of two moles of Zn and one mole of oxygen by 693.8 kJ
- (c) 693.8 kJ mol^{-1} energy is evolved in the reaction
- (d) 693.8 kJ mol^{-1} energy is absorbed in the reaction

Assertion and Reason

Directions (Q. Nos. 19 to 23) *Each of these questions contains two statements : Statement* I (*Assertion*) *and Statement* II (*Reason*). *Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes* (*a*), (*b*), (*c*), (*d*) *given below :*
- (a) Statement I is true; Statement II is true; Statement II is a correct explanation for Statement I.
- (b) Statement I is true; Statement II is true; Statement II is not a correct explanation for Statement I.
- (c) Statement I is true; Statement II is false.
- (d) Statement I is false; Statement II is true.

19. **Statement I** Absolute values of internal energy of substance can't be determined.

Statement II It is impossible to determine exact values of constituent energies of the substances.

20. **Statement I** The mass and volume of a substance are the extensive properties and are proportional to each other.

Statement II The ratio of mass of a sample to its volume is an intensive property.

21. **Statement I** Zeroth law can also be termed as law of thermal equilibrium.

Statement II Two objects in thermal equilibrium with the third one, are in thermal equilibrium with each other.

22. **Statement I** Combustion of all organic compounds is an exothermic reaction.

Statement II The enthalpies of all elements in their standard state are zero. **[NCERT Exemplar]**

23. **Statement I** A liquid crystallises into a solid and is accompanied by decrease in entropy.

Statement II In crystals, molecules organise in an ordered manner. **[NCERT Exemplar]**

Comprehension Based Questions

Directions (Q. Nos. 24 to 26) The first law of thermodynamics was given as $Q = \Delta E + (-W)$; where Q is the heat given to a system and ΔE represents increase in internal energy and $-W$ is work done by the system. Various processes such as isothermal, adiabatic, cyclic, isobaric and isochoric process in terms of first law of thermodynamics leads for important results. The molar heat capacity for 1 mole of monoatomic gas is $3/2R$ at constant volume and $5/2R$ at constant pressure.

24. Which of the following statements are correct?

(1) Both work and heat appears at the boundaries of system.

(2) Heat given to a system is given positive sign.

(3) Heat given to a system is equal to increase in internal energy under isothermal conditions.

(4) Heat given to a system is used to increase internal energy under isochoric conditions.

(5) Both work and heat are not state functions but their sum $(q + W)$ is a state function.

(a) 1, 2, 4, 5
(b) 1, 3, 4, 5
(c) 1, 2, 3, 4
(d) 2, 3, 4, 5

25. A system is allowed to move from state A to B following path ACB by absorbing 80 J of heat energy. The work done by the system is 30 J. The work done by the system in reaching state B from A is 10 J through path ADB. Which statements are correct?

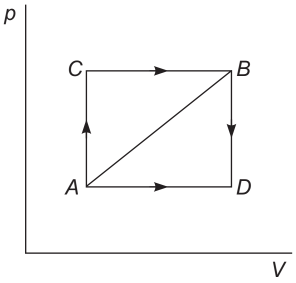
(1) Increase in internal energy from state A to state B is 50 J.

(2) If path ADB is followed to reach state B, $\Delta E = 50$ J.

(3) If work done by the system in path AB is 20 J, the heat absorbed during path $AB = 70$ J.

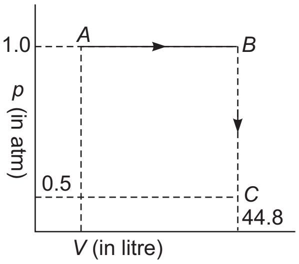
(4) The value $E_C - E_A$ is equal to $E_D - E_B$.

(5) Heat absorbed by the system to reach B from A through path ADB is 60 J.



(a) 1,5 (b) 1, 3, 5
(c) 1, 2, 3, 5 (d) 1, 4, 5

26. 1 mole of a monoatomic gas is expanded through path ABC as shown in the figure.



Select the correct statements.

(1) If specific heat of gas are 0.125 and 0.075 cal/g, the mol. wt. of gas = 40.

(2) Temperature at point A, B, C are 273, 546 and 273 K respectively.

(3) ΔE for the process A to B is 2.27 kJ.

(4) ΔE for the process B to C is 3.44 kJ.

(5) ΔE for the overall cycle $A \rightarrow B \rightarrow C \rightarrow A$ is 3.4 kJ.

(a) 1, 2, 3, 4 (b) 3, 4, 5
(c) 1, 3, 4 (d) 1, 2, 5

Directions (Q. Nos. 27 and 28) The bond dissociation energy of a diatomic molecule is also called bond energy. However, the bond dissociation energy depends upon the nature of bond and also the molecule in which the bond is present.

The bond energy of N—H bond in NH_3 is equal to one-third of the energy of dissociation of NH_3 because there are three N—H bonds and those of C—H bond in CH_4 is equal to one-fourth of the energy of dissociation of CH_4.

Heat of a reaction = Bond energy of reactants − Bond energy of products

27. The enthalpy changes for the reaction

$$H_2O(g) \longrightarrow H(g) + OH(g)$$

and

$$OH(g) \longrightarrow O(g) + H(g)$$

are 501.87 kJ mol^{-1} and 423.38 kJ mol^{-1}. The bond enthalpy of O—H bond is

(a) −462.625 kJ mol^{-1} (b) 462.625 kJ mol^{-1}
(c) −713.54 kJ mol^{-1} (d) 713.54 kJ

28. Find the bond enthalpy of S—S bond from the following data.

C_2H_5—S—$C_2H_5(g)$ $\Delta H_f^\circ = -147.23$ kJ mol^{-1}

C_2H_5—S—S—$C_2H_5(g)$ $\Delta H_f^\circ = -201.92$ kJ mol^{-1}

S$(g)\Delta H_f^\circ = -222.80$ kJ mol^{-1}

(a) − 227.49 kJ mol^{-1} (b) 277.49 kJ mol^{-1}
(c) −349.15 kJ mol^{-1} (d) 349.15 kJ mol^{-1}

Directions (Q. Nos. 29 to 31) In a fuel cell (device used for producing electricity directly from a chemical reaction), methanol is used as a fuel and oxygen gas is used an an oxidizer. The standard enthalpy of combustion of methanol is $-726\ \text{kJ mol}^{-1}$. The standard free energies of formation of $CH_3OH(l), CO_2(g)$ and $H_2O(l)$ are –166.3, –394.4 and $-237.1\ \text{kJ mol}^{-1}$ respectively.

29. The standard free energy change of the reaction will be

(a) $-597.8\ \text{kJ mol}^{-1}$ (b) $-298.9\ \text{kJ mol}^{-1}$

(c) $-465.2\ \text{kJ mol}^{-1}$ (d) $-702.3\ \text{kJ mol}^{-1}$

30. The efficiency of the fuel cell will be

(a) 96.7% (b) 66.2%

(c) 41.3% (d) 85.1%

31. The standard internal energy change of the cell reaction will be

(a) $-727.24\ \text{kJ mol}^{-1}$

(b) $-724.76\ \text{kJ mol}^{-1}$

(c) $-728.48\ \text{kJ mol}^{-1}$

(d) $-723.42\ \text{kJ mol}^{-1}$

Previous Years' Questions

32. The incorrect expression among the following is **[AIEEE 2012]**

(a) $\dfrac{\Delta G_{\text{system}}}{\Delta S_{\text{total}}} = -T$

(b) In isothermal process, $W_{\text{reversible}} = -nRT \ln \dfrac{V_f}{V_i}$

(c) $\ln K = \dfrac{\Delta H^\circ - T\Delta S^\circ}{RT}$

(d) $K = e^{-\Delta G^\circ/RT}$

33. The entropy change involved in the isothermal reversible expansion of 2 moles of an ideal gas from a volume of $10\ \text{dm}^3$ to volume of $100\ \text{dm}^3$ at 27°C is **[AIEEE 2011]**

(a) $38.3\ \text{J mol}^{-1}\text{K}^{-1}$ (b) $35.8\ \text{J mol}^{-1}\text{K}^{-1}$

(c) $32.3\ \text{J mol}^{-1}\text{K}^{-1}$ (d) $42.3\ \text{J mol}^{-1}\text{K}^{-1}$

34. The value of enthalpy change (ΔH) for the reaction

$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$; at 27° C is $-1366.5\ \text{kJ mol}^{-1}$. The value of internal energy change for the above reaction at this temperature will be **[AIEEE 2011]**

(a) –1371.5 kJ (b) –1369.0 kJ

(c) –1364.0 kJ (d) –1361.5 kJ

35. Consider the reaction,

$4NO_2(g) + O_2(g) \longrightarrow 2N_2O_5(g)$; $\Delta_r H = -111$ kJ. If $N_2O_5(s)$ is formed instead of $N_2O_5(g)$ in the above reaction, the $\Delta_r H$ value will be

(Given, ΔH of sublimation for N_2O_5 is $54\ \text{kJ mol}^{-1}$) **[AIEEE 2011]**

(a) –165 kJ

(b) + 54 kJ

(c) + 219 kJ

(d) –219 kJ

36. The standard enthalpy of formation of NH_3 is $-46.0\ \text{kJ mol}^{-1}$. If the enthalpy of formation of H_2 from its atoms is $-436\ \text{kJ mol}^{-1}$ and that of N_2 is $-712\ \text{kJ mol}^{-1}$, the average bond enthalpy of N—H bond in NH_3 is **[AIEEE 2010]**

(a) $-964\ \text{kJ mol}^{-1}$ (b) $+352\ \text{kJ mol}^{-1}$

(c) $+1056\ \text{kJ mol}^{-1}$ (d) $-1102\ \text{kJ mol}^{-1}$

37. For a particular reversible reaction at temperature T, ΔH and ΔS were found to be both positive. If T_e is the temperature at equilibrium, the reaction would be spontaneous when **[AIEEE 2010]**

(a) $T_e > T$ (b) $T > T_e$

(c) T_e is 5 times T (d) $T = T_e$

38. On the basis of the following thermochemical data $[\Delta_f G^\circ\ H^+(aq) = 0]$

$$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq);\ \Delta H = 57.32\ \text{kJ}$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l);\Delta H = -286.02\ \text{kJ}$$

The value of enthalpy of formation of OH^- ion at 25° C is

(a) –22.88 kJ (b) –228.88 kJ

(c) +228.88 kJ (d) –343.52 kJ

39. Standard entropy of X_2, Y_2 and XY_3 are 60, 40 and $50\ \text{JK}^{-1}\text{mol}^{-1}$, respectively. For the reaction, $\frac{1}{2}X_2 + \frac{3}{2}Y_2 \longrightarrow XY_3$, $\Delta H = -30$ kJ, to be at equilibrium, the temperature will be **[AIEEE 2008]**

(a) 1250 K (b) 500 K (c) 750 K (d) 1000 K

40. Assuming that water vapour is an ideal gas, the internal energy change (ΔE) when 1 mole of water is vaporised at 1 bar pressure and 100° C, (Given, molar enthalpy of vaporisation of water at 1 bar and $373\ \text{K} = 41\ \text{kJ mol}^{-1}$ and $R = 8.3\ \text{J mol}^{-1}\ \text{K}^{-1}$) will be **[AIEEE 2007]**

(a) $4.100\ \text{kJ mol}^{-1}$ (b) $3.7904\ \text{kJ mol}^{-1}$

(c) $37.904\ \text{kJ mol}^{-1}$ (d) $41.00\ \text{kJ mol}^{-1}$

41. Identify the correct statement regarding a spontaneous process. **[AIEEE 2007]**

(a) For a spontaneous process in an isolated system, the change in entropy is positive
(b) Endothermic processes are never spontaneous
(c) Exothermic processes are always spontaneous
(d) Lowering of energy in the reaction process is the only criterion for spontaneity

42. In conversion of limestone to lime, $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$ the values of ΔH° and ΔS° are $+179.1$ kJ mol^{-1} and 160.2 J/K respectively at 298 K and 1 bar. Assuming that ΔH° and ΔS° do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is **[AIEEE 2007]**

(a) 1008 K
(b) 1200 K
(c) 845 K
(d) 1118 K

43. An ideal gas is allowed to expand both reversibly and irreversibly in an isolated system. If T_i is the initial temperature and T_f is the final temperature, which of the following statements is correct? **[AIEEE 2006]**

(a) $(T_f)_{\text{irrev}} > (T_f)_{\text{rev}}$
(b) $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process
(c) $(T_f)_{\text{rev}} = (T_f)_{\text{irrev}}$
(d) $T_f = T_i$ for both reversible and irreversible processes

44. The enthalpy changes for the following processes are listed below :

$$Cl_2(g) \longrightarrow 2Cl(g), 242.3 \text{ kJ mol}^{-1}$$
$$I_2(g) \longrightarrow 2I(g), 151.0 \text{ kJ mol}^{-1}$$
$$ICl(g) \longrightarrow I(g) + Cl(g), 211.3 \text{ kJ mol}^{-1}$$
$$I_2(s) \longrightarrow I_2(g), 62.76 \text{ kJ mol}^{-1}$$

Given that the standard states for iodine and chlorine are $I_2(s)$ and $Cl_2(g)$, the standard enthalpy for the formation of $ICl(g)$ is **[AIEEE 2006]**

(a) -14.6 kJ mol^{-1}
(b) -16.8 kJ mol^{-1}
(c) $+16.8$ kJ mol^{-1}
(d) $+244.8$ kJ mol^{-1}

45. The standard enthalpy of formation (ΔH_f°) at 298 K for methane, $CH_4(g)$ is -74.8 kJ mol^{-1}. The addition information required to determine the average energy for C—H bond formation would be **[AIEEE 2006]**

(a) the dissociation energy of H_2 and enthalpy of sublimation of carbon
(b) latent heat of vaporisation of methane
(c) the first four ionisation energies of carbon and electron gain enthalpy of hydrogen
(d) the dissociation energy of hydrogen molecule, H_2

46. An ideal gas expands in volume from 1×10^{-3} m^3 to 1×10^{-2} m^3 at 300 K against a constant pressure of 1×10^5 Nm^{-2}. The work done is **[AIEEE 2004]**

(a) -900 J
(b) -900 kJ
(c) 270 kJ
(d) 900 kJ

47. The internal energy change when a system goes from state A to B is 40 kJ/mol. If the system goes from A to B by a reversible path and returns to state A by an irreversible path, what would be the net change in internal energy? **[AIEEE 2003]**

(a) 40 kJ
(b) > 40 kJ
(c) < 40 kJ
(d) Zero

48. If at 298 K the bond energies of C—H, C—C, C=C and H — H bonds are respectively 414, 347, 615 and 435 kJ mol^{-1}, the value of enthalpy change for the reaction,

$H_2C{=}CH_2(g) + H_2(g) \longrightarrow H_3C - CH_3(g)$ at 298 K will be **[AIEEE 2003]**

(a) + 250 kJ
(b) -250kJ
(c) + 125 kJ
(d) -125 kJ

49. In an irreversible process taking place at constant T and p and in which only pressure-volume work is being done, the change in Gibbs free energy (dG) and change in entropy (dS), satisfy the criteria **[AIEEE 2003]**

(a) $(dS)_{V,E} < 0, (dG)_{T,p} < 0$
(b) $(dS)_{V,E} > 0, (dG)_{T,p} < 0$
(c) $(dS)_{V,E} = 0, (dG)_{T,p} = 0$
(d) $(dS)_{V,E} = 0, (dG)_{T,p} > 0$

50. Heat required to raise the temperature of 1 mole of a substance by 1° is called **[AIEEE 2002]**

(a) specific heat
(b) molar heat capacity
(c) water equivalent
(d) specific gravity

Answers

Round I

1. (d)	**2.** (a)	**3.** (c)	**4.** (b)	**5.** (c)	**6.** (c)	**7.** (c)	**8.** (c)	**9.** (a)	**10.** (c)
11. (a)	**12.** (c)	**13.** (a)	**14.** (d)	**15.** (a)	**16.** (b)	**17.** (d)	**18.** (c)	**19.** (c)	**20.** (b)
21. (b)	**22.** (d)	**23.** (a)	**24.** (a)	**25.** (c)	**26.** (b)	**27.** (c)	**28.** (b)	**29.** (d)	**30.** (d)
31. (c)	**32.** (b)	**33.** (d)	**34.** (b)	**35.** (a)	**36.** (b)	**37.** (a)	**38.** (d)	**39.** (d)	**40.** (d)
41. (c)	**42.** (a)	**43.** (a)	**44.** (c)	**45.** (b)	**46.** (b)	**47.** (b)	**48.** (b)	**49.** (b)	**50.** (a)
51. (b)	**52.** (a)	**53.** (d)	**54.** (a)	**55.** (b)	**56.** (c)	**57.** (d)	**58.** (b)	**59.** (d)	**60.** (c)
61. (d)	**62.** (d)	**63.** (c)	**64.** (d)	**65.** (b)	**66.** (d)	**67.** (c)	**68.** (b)	**69.** (a)	**70.** (b)

Round II

1. (a)	**2.** (a)	**3.** (c)	**4.** (a)	**5.** (d)	**6.** (b)	**7.** (b)	**8.** (c)	**9.** (b)	**10.** (c)
11. (b)	**12.** (b)	**13.** (c)	**14.** (a,b,c)	**15.** (a,d)	**16.** (c,d)	**17.** (c,d)	**18.** (a,c)	**19.** (a)	**20.** (b)
21. (a)	**22.** (b)	**23.** (a)	**24.** (a)	**25.** (c)	**26.** (a)	**27.** (b)	**28.** (b)	**29.** (d)	**30.** (a)
31. (b)	**32.** (c)	**33.** (a)	**34.** (c)	**35.** (d)	**36.** (b)	**37.** (b)	**38.** (b)	**39.** (c)	**40.** (c)
41. (a)	**42.** (d)	**43.** (a)	**44.** (c)	**45.** (a)	**46.** (a)	**47.** (d)	**48.** (d)	**49.** (b)	**50.** (b)

the Guidance

Round I

1. When a gas undergoes adiabatic expansion, $dq = 0$, it gets cooled due to loss of kinetic energy.

2. In such a condition, the compressor has to run for longer time, releasing more heat to the surroundings.

3. We know that $\Delta E = q + W$

If heat supplied from the surrounding, $q = 0$

$\therefore \quad \Delta E = W$

i.e., work is done at the expense of only internal energy and $q = 0$ for adiabatic process.

4. A thermodynamic state function is a quantity whose value is independent of path. Its value depends only upon the state of the system.

5. Thermodynamics deals with the energy changes, feasibility and extent of a reaction, but not with the rate and mechanism of a process.

6. Presence of reaction species in a covered beaker-Closed system. Exchange of matter as well as energy - Open system

Presence of reactant in a closed vessel - Closed system

Presence of reactants in thermos flask - Isolated system.

8. We know that internal energy of a gas depends upon its pressure and temperature. Thus, if a gas expands at constant temperature and pressure then its internal energy remains same.

9. $W = 2.303 nRT \log \frac{p_2}{p_1} = 2.303 \times 1 \times 2 \times 300 \log \frac{10}{2} = 965.84$

At constant temperature, $\Delta E = 0$

$$\Delta E = q + W;$$
$$q = -W = -965.84 \text{ cal}$$

10. Given, $q = +701 \text{ J}$ (heat is absorbed, hence q is positive)

$W = -394 \text{ J}$ (work is done by the system, hence W is negative)

By first law of thermodynamics,

Internal energy change, $\Delta E = q + W$

$= +701 \text{ J} + (-394 \text{ J}) = +307 \text{ J}.$

Hence, internal energy of the system increases by 307 J.

11. For isolated system there is no transfer of energy as heat or work so according to the first law of thermodynamics,

$$\Delta U = q + W$$
$$\Delta U = 0 + 0 = 0$$

12. Free expansion $W = 0$

Adiabatic process, $q = 0$

$\Delta U = q + W = 0$, this means that internal energy remains constant. Therefore, $\Delta T = 0$

In ideal gas there is no intermolecular attraction. Hence, when such a gas expands under adiabatic conditions into a vacuum, no heat is absorbed or evolved since no external work is done to separate the molecules.

13. As the system is closed and insulated, no heat enter or leave the system, *i.e.,* $q = 0$

$$\Delta E = q + W = W$$

and $\quad \Delta E \neq 0$ as ΔT is not zero.

14. Since the process involves phase change, heat absorbed,

$Q = \text{mass} \times \text{latent heat of vaporisation}$

Given, $\quad \text{mass} = 70.0 \text{ g} = 0.07 \text{ kg}$

$L_y = 2260 \text{ kJ/kg}$

$\therefore \quad Q = 0.07 \times 2260 \text{ kJ} = 158.2 \text{ kJ} = 158200 \text{ J}$

15. It is clear from the figure that the process has been carried out in infinite steps, hence it is isothermal reversible expansion.

$$W = -2.303nRT \log \frac{V_2}{V_1}$$

But, $\quad p_1V_1 = p_2V_2$

$\Rightarrow \quad \frac{V_2}{V_1} = \frac{p_1}{p_2} = \frac{2}{1} = 2$

$\therefore \quad W = -2.303nRT \log \frac{p_1}{p_2}$

$$= -2.303 \times 1 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 298\text{K} \times \log 2$$

$$= -2.303 \times 8.314 \times 298 \times 0.3010 \text{ J} = -1717.46 \text{ J}$$

16. $W = -p_{ex}(V_f - V_t) = -2 \times 40 = -80 \text{ L bar} = -8 \text{ kJ}$

The negative sign shows that work is done by the system on the surrounding. Work done will be more in the reversible expansion because internal pressure and external pressure are almost same at every step.

17. According to the definition of standard enthalpy of formation, the enthalpy change for the following reaction will be standard enthalpy of formation of $H_2O(l)$.

$$H_2O(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l).$$

or the standard enthalpy of formation of $H_2O(l)$ will be half of the enthalpy of the given equation *i.e.*, $\Delta_r H^\ominus$ is also halved.

$$\Delta_f H^\ominus_{H_2O}(l) = \frac{1}{2} \times \Delta_r H^\ominus = \frac{-572 \text{ kJ mol}^{-1}}{2}$$

$$= -286 \text{ kJ/mol}.$$

18. Standard heat of formation of methane is represented by C(graphite) + $2H_2(g) \longrightarrow CH_4(g)$ because the elements taken are in their standard state.

19. $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

$$\Delta n_g = (n_p - n_r) = 1 - 3 = -2$$
$$\Delta H^\circ = \Delta U^\circ + \Delta n_g RT$$
$$\Delta H^\circ = -X - 2RT$$

Hence, $\quad \Delta H^\circ < \Delta U^\circ$

20. $A \longrightarrow B, \Delta H = +24 \text{ kJ/mol}$

$\Rightarrow \quad H_B - H_A = +24 \quad \ldots$(i)

$BC, \; \Delta H = -18 \text{ kJ/mol}$

$\Rightarrow \quad H_C - H_B = -18 \quad \ldots$(ii)

or $\quad H_B - H_C = +18$

From Eqs. (i) and (ii), we have

$$H_C - H_A = 6$$

$\therefore \quad H_B > H_C > H_A$

21. Molar enthalpy change for the combustion of graphite, ΔH = enthalpy of combustion of 1g graphite × molar mass

$$\Delta H = -20.7 \text{ kJ g}^{-1} \times 12 \text{ g mol}^{-1}$$

$$\Delta H = -2.48 \times 10^2 \text{ kJ mol}^{-1}$$

Negative sign in the value of ΔH indicates that the reaction is exothermic.

22. The net enthalpy change, ΔH for a cyclic process is zero as enthalpy change is a state function.

24. $\Delta H = \Delta E + \Delta n_g RT$

Since, $\quad \Delta n_2 = 2 - 4 = -2$

Therefore, $\quad \Delta H = \Delta E - 2RT$

25. $C_6H_6(g) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(g)$

$$\Delta n = 6 + 3 - 1 - \frac{15}{2} = +0.5$$

26. Energy absorbed $\propto \frac{1}{\text{stability of compound}}$

Energy released $\propto$ stability of compound

Thus, the order of stability is

$$142.2 > 25.9 > -46.2 > -393.2$$

i.e., $\quad O_3 > HI > NH_3 > CO_2$

27. $\Delta H = nC_P \Delta T$

The process is isothermal therefore,

$$\Delta H = 0.$$

28. Work done in 1 s = 400 J

Hence, work in 5 min (300 s)

$$= 400 \times 300 = 120 \text{ kJ}$$

$$\Delta H^\circ_{vap} = \frac{120 \text{ kJ}}{50/18} = 43.2 \text{ kJ/mol}$$

30. The reaction for the combustion of carbon into CO_2 is

$$\underset{44 \text{ g}}{C(s) + O_2(g) \longrightarrow CO_2(g)}; \quad \Delta H = -393.5 \text{ kJ mol}^{-1}$$

Heat released in the formation of 44g CO_2 = 393.5kJ

Heat released in the formation of 35.2g CO_2

$$= \frac{393.5 \text{ kJ} \times 35.2 \text{ g}}{44 \text{ g}} = 314.8 \text{ kJ}$$

32. 0.5 mol $HNO_3 \equiv$ 0.5 mol H^+ and 0.3 mol OH^-

$$0.5\, H^+(aq) + 0.3 OH^-(aq) \longrightarrow 0.5\, H_2O(l)$$

$$\Delta H = 0.3 \times 57.1$$
$$= 17.13 \text{ kJ}$$

33. By (ii) – (i) C(graphite) $\longrightarrow$ C(diamond);

$$\Delta H = -393.4 - (-395.3) = +1.9$$

34. For the equation,

$$H_2 + S + 2O_2 \longrightarrow H_2SO_4$$

Eqs. (i) + (ii) + (iii) + (iv)

$$\Delta H = -287.3 + (-298.2) + (-98.7) + (-130.2)$$
$$= -814.4 \text{ kJ}$$

36. $\Delta_r H^\ominus$ = Bond energy of H_2 + Bond energy of $Br_2 - 2 \times$ Bond energy of HBr $= 435 + 192 - (2 \times 368)$ kJ mol^{-1}

$$\Rightarrow \qquad \Delta_r H^\ominus = -109 \text{ kJ mol}^{-1}$$

37. $q_p = \Delta H = -30.5 \text{ kJ mol}^{-1}$

$\therefore$ Heat required for vaporisation of 284 g of

$$CCl_4 = \frac{284 \text{ g}}{154 \text{ g mol}^{-1}} \times 30.5 \text{ kJ mol}^{-1}$$

$$= 56.2 \text{ kJ}$$

38. Molecular weight of NH_4NO_3 = 80 g mol^{-1}

$\therefore$ Molar heat of decomposition,

$$H = ms\Delta t = 80 \times 1.23 \times 6.12$$

$$= 602 \text{ kJ/mol}$$

40. $18.0 \text{ g } H_2O = 1 \text{ mol } H_2O$

Enthalpy change for vaporising 1 mole of H_2O = 40.79 kJ

$\therefore$ Enthalpy change for vaporising 2 moles of

$$H_2O = 2 \times 40.79 \text{ kJ} = 81.58 \text{ kJ}$$

Standard enthalpy of vaporisation at 100° C and 1 bar pressure,

$$\Delta_{vap} H^\circ = +\, 40.79 \text{ kJ mol}^{-1}$$

41. Heat of neutralisation will be less than −57.33 kJ/mol because some amount of this energy will be required for the dissociation of weak base (MgO).

42. $C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g); \ \Delta H_1 = -26.4$ ...(i)

$C(s) + O_2(g) \longrightarrow CO_2(g); \ \Delta H_2 = -94.0$ ...(ii)

We have to find ΔH for the reaction

$$CO + \frac{1}{2} O_2 \longrightarrow CO_2; \qquad \Delta H_1 = ?$$

Eqs. (ii) − (i), we get

$$\Delta H = -94 - (-26.4) = -67.6 \text{ kcal}$$

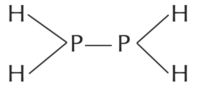
43. Since, process is exothermic, heat is evolved, due to this temperature of water increases.

45. Bond energy of C—H bond $= \frac{-166}{4} = -\ 41.5$ kJ / mol

47. ***Step I*** P—H bond energy from bond dissociation energy of $PH_3(g)$ containing 3 such P—H bonds

$$= \frac{228}{3} = 76 \text{ kcal/mol}$$

Step II The structure of P_2H_4 is



i.e., it contains four P—H bonds and one P—P bond, so P—P bond energy can be calculated by $4 \times$ P — H + P — P = bond dissociation energy of P_2H_4.

$\therefore$ P—P bond energy = 335 − 4(76)

= 31 kcal per mol

48. CH_4 required $= \frac{445.15 \times 16}{890.3} = 8$ g

49. For the equation

$$B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(g) + 3H_2O(g)$$

Eqs. (i) + 3(ii) + 3(iii) − (iv)

$$\Delta H = -1273 + 3(-286) + 3(44) - 36$$

$$= -1273 - 858 + 132 - 36$$

= −2035 kJ/mol

50. Given, (i) $2C + 3H_2 \longrightarrow C_2H_6; \qquad \Delta H = -21.1$

(ii) $C + O_2 \longrightarrow CO_2; \qquad \Delta H = -94.1$

(iii) $H_2 + \frac{1}{2} O_2 \longrightarrow H_2O; \qquad \Delta H = -68.3$

Eqs. 2 (ii) + 3 (iii) − (i)

$$C_2H_6 + \frac{3}{2} O_2 \longrightarrow 2CO_2 + 3H_2O$$

$$\Delta x = 2(-94.1) + 3(-68.3) - (-21.1)$$

$$= -\ 372 \text{ kcal}$$

51. ΔH per 1.6 g $= \frac{72 \times 1.6}{180} = 0.64$ kcal

52. Entropy of vaporisation $= \frac{\Delta H_{vap}}{\text{boling point}} = \frac{840}{173} = 4.8$ J/mol/K

54. Heat capacity of water per gram $= \frac{75}{18} = 4.17$ J

$$Q = mst = 100 \times 4.17 \times t = 1000$$

$$t = \frac{1000}{100 \times 4.17} = 2.4 \text{ K}$$

55. For an isolated system, $\Delta U = 0$ and for a spontaneous process, total entropy change must be positive.

Moreover $\Delta S = \frac{q_{rev}}{T} = \frac{\Delta H}{T} = \frac{\Delta U + p\Delta V}{T} = \frac{p\Delta V}{T} \quad (\because \Delta U = 0)$

i.e., $T\Delta S$ or $\Delta S > 0$

56. In the given reaction, a molecule of Cl_2 is formed from its two gaseous atoms and the energy is released with the formation of bond. Hence, ΔH is negative In this reaction, randomness (entropy) also decreases because 2 moles atoms of Cl have more randomness than one mole molecules of chlorine. Hence, ΔS is negative.

57. Enthalpy change for the formation of 1 mole of $H_2O(l)$.

$$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l); \qquad \Delta_f H^\circ = -286 \text{ kJ mol}^{-1}$$

Energy released in the above reaction is absorbed by the surroundings. It means $q_{surr} = +286 \text{ kJ mol}^{-1}$

$$\Delta S = \frac{q_{surr}}{T} = +\frac{286 \text{ kJ mol}^{-1}}{298 \text{ K}}$$

$$= 0.9597 \text{ kJ K}^{-1} \text{mol}^{-1}$$

$$= 959.7 \text{ JK}^{-1} \text{mol}^{-1}$$

58. Less, because ice is more ordered than $H_2O(l)$.

59. For water, molar heat capacity, $C_p = 18 \times$ specific heat, C

Specific heat, $C = 4.18\ \text{Jg}^{-1}\text{K}^{-1}$ (for water)

Heat capacity, $C_p = 18 \times 4.18\ \text{JK}^{-1} = 75.3\ \text{JK}^{-1}$

62. $\Delta S° = 2S°_{HCl} - (S°_{H_2} + S°_{Cl_2})$

$$= 2 \times 186.7 - (130.6 + 223.0) = 19.8\ \text{JK}^{-1}\text{mol}^{-1}$$

63. Mixing of gases increase the entropy.

64. For monoatomic gas, $\gamma_1 = \dfrac{C_p}{C_v} = 1.67$

For diatomic gas, $\gamma_2 = \dfrac{C_p}{C_v} = 1.40$

$\therefore \quad \gamma_1 : \gamma_2 = \dfrac{1.67}{1.40} = 1.19 : 1$

65. Joule-Thomson coefficient $\mu = \dfrac{dT}{dp} = \dfrac{27 - 30}{5 - 2} = -1$

For all negative values of μ, the gas warms on expansion.

67. If $\Delta H = +$ ve and $\Delta S = -$ ve then the reaction is non-spontaneous.

68. $\Delta G° = -2.303RT \log K_c$

Given, $R = 8.314\ \text{JK}^{-1}\text{mol}^{-1}$, $T = 300\ K, K_c = 10$

$\Delta G° = -2.303 \times 8.314\ \text{JK}^{-1}\text{mol}^{-1} \times 300\ \text{K} \times \log 10\ (\log 10 = 1)$

$$= -5744.14\ \text{J mol}^{-1}$$

69. Use $\Delta G = \Delta H - T\Delta S$

$$\Delta G = 145.6 - 273 \times 0 \cdot 116$$

$$= 113.93\ \text{KJ/mol}$$

70. $\Delta G = \Delta H - T\Delta S$,

$$T = 25 + 273 = 298\ \text{K}$$

$$= -11.7 \times 10^3 - 298 \times (-105)$$

$$= 19590\ \text{J} = 19.59\ \text{kJ}$$

Round II

1. $\dfrac{T}{T_{\text{final}}} = \left(\dfrac{V_2}{V_1}\right)^{\gamma - 1}$

$$\frac{T}{T_{\text{final}}} = \left(\frac{2}{1}\right)^{(5/3 - 1)} = 2^{(2/3)}$$

$$T_{\text{final}} = \frac{T}{2^{(2/3)}}$$

2. $\Delta S_{\text{vap}} = \dfrac{(900 \times 18)}{373} = 43.4\ \text{JK}^{-1}\text{mol}^{-1}$

3. Enthalpy change for the conversion of 1 mole liquid water at 10° C into 1 mole liquid water at 0° C,

$$\Delta H_1 = C_pH_2O(l) \times \Delta T$$

$$= -75.3\ \text{J mol}^{-1}\text{K}^{-1} \times 10\text{K} = -753\ \text{J mol}^{-1}$$

Enthalpy of fusion,

$$\Delta H_2 = \Delta H_{\text{freezing}} = -\Delta H_{\text{fusion}} = -6.03\ \text{kJ mol}^{-1}$$

Enthalpy change for the conversion of 1 mole of ice at 0° C to 1 mole of ice at 10° C,

$$\Delta H_3 = C_pH_2O(s) \times \Delta T = -36.8\ \text{J mol}^{-1}\text{K}^{-1} \times 10\text{K}$$

$$= -368\ \text{J mol}^{-1}$$

$$\Delta H_{\text{total}} = -(0.753 + 6.03 + 0.368)\ \text{kJ mol}^{-1} = -7.151\ \text{kJ mol}^{-1}$$

Note Heat is evolved in the process of cooling (freezing) so such step will have a negative sign with ΔH.

4. Given, $dE = TdS - pdV \quad \ldots\text{(i)}$

$H = E + pV \quad \ldots\text{(ii)}$

Differentiating Eq. (ii)

$dH = dE + pdV + Vdp \quad \ldots\text{(iii)}$

From Eq. (i) and (iii), we get

$$dH = TdS - Vdp$$

5. $C_2H_2(g) + \dfrac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(l); \quad \ldots\text{(i)}$

$\Delta G° = -1234\ \text{kJ}$

$C(s) + O_2(g) \longrightarrow CO_2(g); \quad \Delta G° = -394\ \text{kJ} \ldots\text{(ii)}$

$H_2(g) + \dfrac{1}{2}O_2(g) \longrightarrow H_2O(l); \quad \Delta G° = -237\ \text{kJ} \ldots\text{(iii)}$

Eq. 2(ii) + (iii) – (i)

$$2C(s) + H_2(g) \longrightarrow C_2H_2(g)$$

$$\Delta G° = 2(-394) + (-237) - (-1234)$$

$$\Delta G° = 209\ \text{kJ}$$

6. $A \rightleftharpoons B$

$$\Delta G° = \Delta H° - T\Delta S°$$

$$\Delta G° = -2.303\ RT \log k$$

$$\log k = \frac{\Delta H° - T\Delta S°}{-2.303RT}$$

$$= \frac{-54.07 \times 10^3 - 298 \times 10}{-2.303 \times 8.314 \times 298} = 10$$

7. $-\dfrac{dQ}{dW} = \dfrac{dQ}{dQ - dE};$

$[\because\ dE = dW + dQ : -dW = dQ - dE]$

$$= \frac{nC_p\,dT}{nC_pdT - nC_vdT} = \frac{C_p}{(C_p - C_v)}$$

$= \dfrac{7}{2}$ for diatomic gas

8. Cylinder contains 11.2 kg or 193.10 mole butane.

[$\because$ Molecular mass of butane = 58]

$\because$ Energy released by 1 mole of butane = −2658

$\therefore$ Energy released by 193.10 mole of butane

$$= -2658 \times 193.10$$
$$= 5.13 \times 10^5 \text{ kJ}$$

$\therefore$ cylinder will last in $\dfrac{5.13 \times 10^5}{20000} = 25.66$ or 26 days

9. $\Delta S_{A \to B} = \Delta S_{(A \to C)} + \Delta S_{(C \to D)} + \Delta S_{(D \to B)}$

$$= \Delta S_{(A \to C)} + \Delta S_{(C \to D)} - \Delta S_{(B \to D)}$$
$$= 50 + 30 - 20$$
$$= 60 \text{ eu}$$

10. $\because$ $\Delta G = \Delta H - T \cdot \Delta S$

For a spontaneous reaction ΔG should be negative

$$\Delta H = -238 \text{ kJ}, \quad \Delta S = -87 \text{ kJ}^{-1}$$

Hence, reaction will be spontaneous when $\Delta H > T \cdot \Delta S$. Therefore, at 1000, 1500 and 3000 K the reaction would be spontaneous.

11. 0.2 mole will neutralize 0.2 mole of HNO_3

Heat evolved = 57 × 0.2 = 11.4 kJ

12. Given, (i) $H_2 + \frac{1}{2} O_2 \longrightarrow H_2O; \qquad \Delta H = -241$ kJ

(ii) $C_6H_{10} + \frac{17}{2} O_2 \longrightarrow 6CO_2 + 5H_2O; \Delta H = -3800$ kJ

(iii) $C_6H_{12} + 9O_2 \longrightarrow 6CO_2 + 6H_2O; \Delta H = -3920$ kJ

Required reaction is

$$C_6H_{10} + H_2 \longrightarrow C_6H_{12}$$

So, Eq. (i) + (ii) − (iii) gives

$$C_6H_{10} + 9O_2 \longrightarrow C_6H_{12}$$
$$\Delta H = -241 - 3800 - (-3920)$$
$$= -121 \text{kJ mol}^{-1}$$

13. First we calculate the expected bond dissociation energy of benzene molecule as

$3 \times$ C—C + $3 \times$ C═C + $6 \times$ C—H

$\therefore$ Calculated value = 3 (347.3) + 3(615) + 6(412.2)

= 5360.1

Resonance energy = experimental value − calculated value

= 6335 − 5360.1

= 974.2 kJ/mol

14. Heat is not a state function, while temperature is a state function. Heat flowing into the system is positive and heat flowing out of the system is negative.

15. Thermodynamics deals with interrelation of various forms of energy and their transformation into each other. It also deals with thermal or mechanical equilibrium. However, it does not tell anything about the rate of reaction.

16. Flowing of heat from warmer to colder body, expanding of gas and burning of carbon to give carbon dioxide, all are spontaneous process.

17. $$\frac{W_{600\text{K}}}{W_{300\text{K}}} = \frac{1 \times R \times 600\, K \ln \frac{10}{1}}{1 \times R \times 300 K \ln \frac{10}{1}} = \frac{600}{300} = 2$$

For isothermal expansion of ideal gases, $\Delta E = 0$

Since temperature is constant this means there is no change in internal energy. Therefore, $\Delta E = 0$

18. Negative value of ΔH shows that the process is exothermic *i.e.,* proceed with the evolution of heat. For exothermic process,

$$E_{\text{product}} < E_{\text{reactant}}$$

$\therefore$ Enthalpy of two moles of ZnO is then the total enthalpy of two moles of Zn and one mole of O_2 by 693.8 kJ.

19. It is the fact that absolute values of internal energy of substances cannot be determined. It is also true that determination of exact values of constituent energies of the substance is impossible.

20. The mass and volume depend upon the quantity of matter so these are extensive properties while ratio of mass to its volume *i.e.,* density does not depend upon the quantity of matter so this ratio is an intensive property.

21. Zeroth law of temperature can also be summarized as two objects at different temperatures in thermal contact with each other tend to move towards the same temperature.

22. During combustion, energy is released so it is always an exothermic process.

The enthalpy of all the elements in their standard state are zero

23. When a liquid crystallises, entropy decreases because in crystalline form the molecules are more ordered as compared to a liquid.

24. $Q = \Delta E + p\Delta V$ and $\Delta E = Q + W$ = state function

At T = constant $Q = p\Delta V$

25. $ACB = AC + BC$

$ADB = AD + BD$

Heat absorbed 80 J.

Work done by the system = 10 J $\therefore W = -10$ J

$\therefore \qquad W = -30$ Also $W = -10$ J

$\therefore \qquad E_B - E_A = 50$ J $\therefore$ $Q = 50 + 10 = 60$ J

26. $C_p - C_v = \dfrac{R}{M}$

At $A, p = 1$ atm, $V = 22.4$ L

$\therefore \qquad 0.125 - 0.075 = \dfrac{2}{M} \times 273 \qquad [\therefore T = 273 \text{ K}]$

$\therefore \qquad M = 40$

At $B, p = 1$ atm. $V = 44.8$ L

$$\therefore \qquad T = 546\text{ K}$$

At $C, p = 0.5$ atm., $\quad V = 44.8$ L

$$\therefore \qquad T = 273\text{ K}$$

Also at constant V

$$\Delta E = p \times \Delta E \ \Delta U = C_v \times \Delta T$$
$$= 1 \times 22.4\text{ L atm.,}$$
$$= \frac{1 \times 22.4}{0.0821} \times 8.314\text{ J}$$
$$= 0.075 \times 40 \times 4.12$$
$$= 2268.37\text{ J} = 2.27\text{ kJ}$$

27. The enthalpy of dissociation of the O—H bond depends on the molecular species from which H-atom is being separated.

$$H_2O(g) \longrightarrow H(g) + OH(g); \quad \Delta H^\circ = 501.87\text{ kJ mol}^{-1}$$

However to break O—H bond in hydroxyl a different quantity of heat (423.38kJ mol^{-1}) is

$$\text{BE(O–H)} = \frac{501.87\text{ kJmol}^{-1} + 423.38\text{ kJmol}^{-1}}{2}$$
$$= 462.625\text{ kJ mol}^{-1}$$

28. $\text{BE(S – S)} = \Delta H_{\text{vap}}(s) - \Delta H_f^\circ$

$$= \Delta H_{\text{vap}}(s) - \{H_f^\circ(C_2H_5S — SC_2H_5)\} - H_f^\circ(C_2H_5S — C_2H_5)$$
$$= 222.80 - \{-201.92 - (-147.23)\}$$
$$= 277.49\text{ kJ mol}^{-1}$$

29. Reaction for the combustion of methanol is

$$2CH_3OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 4H_2O(l)$$

$$\Delta_r G^\circ = \left[2\Delta G^\circ_{CO_2} + 4\Delta G^\circ_{H_2O}\right] - \left[2 \times \Delta G^\circ_{CH_3OH} + 3 \times \Delta G^\circ_{O_2}\right]$$
$$= [-2 \times 394.4 + 4 \times (-237.1)] - [2 \times (-166.3) + 3 \times 0]$$
$$= -1737.2 + 332.6$$
$$= -1404.6$$
$$\Delta_f G^\circ_{CH_3OH} = \frac{-1404.6}{2} = -702.3\text{ kJ mol}^{-1}$$

30. Efficiency of fuel cell $= \dfrac{\Delta G}{\Delta H} \times 100$

$$= \frac{702.3}{726} \times 100 = 96.7\%$$

31. $\Delta n_g = 1 - \dfrac{3}{2} = \dfrac{2-3}{2} = \dfrac{-1}{2} = -0.5$

$$\Delta H = \Delta E + \Delta n_g RT$$
$$-726 = \Delta E - (0.5) \times 8.314 \times 298 \times 10^{-3}$$
$$\Delta E = -726 + 1.24$$
$$= -724.76\text{ kJ mol}^{-1}$$

32. (a) $\Delta G = \Delta H - T\Delta S$

For a system, total entropy change $= \Delta S_{\text{total}}$

$$\Delta H_{\text{total}} = 0$$
$$\therefore \qquad \Delta G_{\text{system}} = -T\Delta S_{\text{total}}$$
$$\frac{\Delta G_{\text{system}}}{\Delta S_{\text{total}}} = -T$$

Thus, (a) is correct.

(b) For isothermal reversible process, $\Delta E = 0$

By first law of thermodynamics

$$\Delta E = Q + W$$
$$\therefore \qquad W_{\text{reversible}} = -Q = -\int_{V_i}^{V_f} p\,dV$$
$$W_{\text{reversible}} = -nRT \ln \frac{V_f}{V_i}$$

Thus, (b) is correct.

(c) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$\Delta G^\circ = -RT \log K$$
$$\therefore \qquad -RT \log K = \Delta H^\circ - T\Delta S^\circ$$
$$\therefore \qquad \log K = -\left(\frac{\Delta H^\circ - T\Delta S^\circ}{RT}\right)$$

Thus, (c) is incorrect.

(d) $\Delta G^\circ = -RT \log K$

$$\therefore \qquad \log K = -\frac{\Delta G^\circ}{RT}$$
$$\therefore \qquad K = e^{-\Delta G^\circ/RT}$$

Thus, (d) is also correct.

33. Entropy change for of isothermal expansion of n moles of an ideal gas from volume V_1 to volume V_2 is

$$\Delta S = 2.303\, nR \log \frac{V_2}{V_1}$$
$$= 2.303 \times 2 \times 8.3143 \log \frac{100}{10}$$
$$= 38.296\text{ J mol}^{-1}\text{ K}^{-1}$$

34. Relation between ΔH (enthalpy change) and ΔE (internal energy change) is

$$\Delta H = \Delta E + \Delta n_g RT$$

where, Δn_g = moles of gaseous products – moles of gaseous reactants

$$= 2 - 3 = -1$$
$$\Rightarrow \qquad -1366.5 = \Delta E - 1 \times 8.314 \times 10^{-3} \times 300$$
$$\therefore \qquad \Delta E = -1364.0\text{ kJ mol}^{-1}$$

35. $4NO_2(g) + O_2(g) \longrightarrow 2N_2O_5(g); \ \Delta_r H = -111\text{ kJ}$

$$2N_2O_5(g) \longrightarrow 2N_2O_5(s), \quad \Delta_s H = (-54 \times 2)\text{ kJ}$$
$$4NO_2(g) + O_2(g) \longrightarrow 2N_2O_5(s),$$
$$\Delta_r H = -219\text{ kJ}$$

Note ΔH_r sublimation of $N_2O_5(s)$ t is 54 kJ mol^{-1}.
Thus, for reverse process, it is –54 kJ mol^{-1}.

36. Given, $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)$

$$\Delta H_f^\circ = -46.0 \text{ kJ mol}^{-1}$$

$$2H(g) \longrightarrow H_2(g); \quad \Delta H_f^\circ = -436 \text{ kJ mol}^{-1}$$

$$2N(g) \longrightarrow N_2(g); \quad \Delta H_f^\circ = -712 \text{ kJ mol}^{-1}$$

$$-46 = 3\text{N—H} - \left[-\frac{1}{2}\times 712 - \frac{3}{2}436\right]$$

$$= 3\text{N—H} - \left[\frac{-1}{2}\times 712 - \frac{3}{2}436\right]$$

$$= 3\text{N—H} - [-1010]$$

$$3\text{N—H} = 1056 \text{ kJ mol}^{-}$$

$$\text{N—H} = \frac{1056}{3} = 352 \text{ kJ mol}^{-1}$$

37. $\Delta G = \Delta H - T\Delta S$

At equilibrium, $\Delta G = 0$ for a reaction to be spontaneous ΔG should be negative, so T should be greater than T_e.

38. Consider the heat of formation of H_2O

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H = -286.20 \text{ kJ}$$

$$\Delta H_r = \Delta H_f\,(H_2O, l) - \Delta H_f\,(H_2, g) - \frac{1}{2}\Delta H_f\,(O_2, g)$$

$$-286.20 = \Delta H_f\,(H_2O, l) - 0 - 0$$

$$\Delta H_f\,(H_2O, l) = -286.20$$

Now, consider the ionization of H_2O

$$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq); \quad \Delta H = 57.32 \text{ kJ}$$

$$\Delta H_r = \Delta H_f\,(H^+, aq) + \Delta H_f\,(OH^-, aq) - \Delta H_f\,(H_2O, l)$$

$$57.32 = 0 + \Delta H_f\,(OH^-, aq) - (-286.20)$$

Thus, $\Delta H_f\,(OH^- aq) = 57.32 - 286.20$

$$= -228.88 \text{ kJ.}$$

39. $\frac{1}{2}X_2 + \frac{3}{2}Y_2 \longrightarrow XY_3$

$$\Delta S_{\text{reaction}} = S_{\text{products}} - S_{\text{reactants}}$$

$$\Delta S_{\text{reaction}} = 50 - \left(\frac{3}{2}\times 40 + \frac{1}{2}\times 60\right) = -40 \text{ J mol}^{-1}$$

$$\Delta G = \Delta H - T\Delta S$$

At equilibrium as $\Delta G = 0$

$\therefore \qquad \Delta H = T\Delta S$

$\Rightarrow \qquad T = \frac{\Delta H}{\Delta S} = \frac{30\times 10^3}{40} = 750 \text{ K}$

40. $H_2O(l) \longrightarrow H_2O(g)$

$$\Delta n_g = 1 - 0 = 1$$

$$\Delta E = \Delta H - \Delta n_g RT$$

$$= 41 - 1\times 8.3\times 373\times 10^{-3} \qquad (R = 8.3\times 10^{-3})$$

$$= 37.9 \text{ kJ mol}^{-1}$$

41. In an isolated system where either mass and energy are not exchanged with surrounding for the spontaneous process, the change in entropy is positive.

42. We know that, $\Delta S = \frac{\Delta H}{T}$

$$\Delta S = 160.2 \text{ J/K}$$

$$\Delta H = 179.1\times 10^3 \text{ J/mol}$$

$$T = \frac{179.1\times 10^3 \text{ J/mol}}{160.2 \text{ J/K}}$$

$$= 1117.97 \text{ K} \approx 1118 \text{ K}$$

43. $T_{f\,(\text{irreversible})} > T_{f\,(\text{reversible})}$

It is an adiabatic expansion and W (rev) is maximum.

44. $\frac{1}{2}I_2(s) + \frac{1}{2}Cl_2(g) \longrightarrow ICl(g)$

$$\Delta H = \left[\frac{1}{2}\Delta H_{s\to g} + \frac{1}{2}\Delta H_{\text{diss}}(Cl_2) + \frac{1}{2}\Delta H_{\text{diss}}(I_2)\right] - \Delta H_{ICl}$$

$$= \left(\frac{1}{2}\times 62.76 + \frac{1}{2}\times 242.3 + \frac{1}{2}\times 151.0\right) - 211.3$$

$$= 228.03 - 211.3$$

$$\Delta H = 16.73$$

45. Carbon is found in solid state. The state of substance affects the enthalpy change.

$$C(s) \longrightarrow C(g) \text{ sublimation}$$

and $\quad H_2(g) \longrightarrow 2H(g)$ dissociation

are required for C—H bond.

46. Work done due to change in volume against constant pressure is

$$W = -p(V_2 - V_1)$$

$$= -1\times 10^5 \text{ Nm}^{-2}(1\times 10^{-2} - 1\times 10^{-3})\text{m}^3$$

$$= -900 \text{ Nm} = -900 \text{ J} (1 \text{ Nm} = 1 \text{ J})$$

47. $\Delta E = 0$, in a cyclic process.

48. $CH_2{=}CH_2 + H_2 \longrightarrow CH_3{-}CH_3$

$$\Delta H = (BE)_{\text{reactants}} - (BE)_{\text{products}}$$

$$= 4(BE)_{C-H} + (BE)_{C=C} + (BE)_{H-H} - [6(BE)_{C-H} + (BE)_{C-C}]$$

$$= [4\times 414 + 615 + 435] - [6\times 414 + 347]$$

$$= -125 \text{ kJ}$$

49. An irreversible process

$\Rightarrow$ spontaneous process

$\Rightarrow (dS)_{V,E}$ (change in entropy) $= +$ ve > 0

$\Rightarrow (dG)_{T,p}$ (change in Gibbs free energy) $-$ve $\Rightarrow < 0$

50. The amount of heat required to raise the temperature of one mole of a substance through 1° C is called molar heat capacity.

$$C = \frac{q}{T_2 - T_1}$$

6 Equilibrium

JEE Main MILESTONE

- Concept of Dynamic Equilibrium
- Equilibria Involving Physical Processes
- Equilibria Involving Chemical Processes
- Law of Mass Action or Law of Chemical Equilibrium
- Reaction Quotient or Mass Action Ratio
- Relation Between Vapour Density and Degree of Dissociation
- Le-Chatelier's Principle
- Electrolytes and Non-electrolytes
- Arrhenius Theory of Electrolytic Ionisation
- Various Concepts of Acids and Bases
- Ionisation of Water
- Relation Between K_a and K_b
- pH Scale
- pK Value
- Common Ion Effect
- Salt Hydrolysis
- Buffer Solution

6.1 Concept of Dynamic Equilibrium

When the equilibrium is attained in a chemical reaction all the observable properties of the system like concentration, colour etc., become constant.

It leads us to think that the reaction stops altogether at equilibrium. But this is not true. At equilibrium, the rate of forward reaction becomes equal to the rate of backward reaction so that there is no net change in the concentration of various species. In other words, the equilibrium state is a dynamic balance between the forward and the backward reaction.

On carrying chemical reactions in a closed vessel at a particular temperature, initially the reactant concentration keep on decreasing and product concentration keep on increasing. After sometime, a stage is reached at which there is no net reaction. This stage is called ***state of equilibrium.***

When such a stage is achieved between ions and undissociated electrolytes, it is termed as ***ionic equilibrium.***

6.2 Equilibria Involving Physical Processes

The equilibrium which develops between different phases or physical properties is termed as physical equilibria.

Some of such example are

Solid-Liquid Equilibria

On heating a pure solid substance under atmospheric pressure, it gradually starts converting into the liquid. At a certain temperature, these two phases coexist, which is called the normal *melting point* or *freezing point* of the substance *e.g.,*

Ice and water kept in a perfectly insulated thermos flask at 0°C and the atmospheric pressure are in equilibrium state. There is no change in the mass of ice and water, as the rates of transfer of molecules from ice into water and of reverse transfer from water into ice are equal. This represents a dynamic equilibrium between ice and water, *i.e.*,

$$H_2O(s) \rightleftharpoons H_2O(l)$$

or Rate of melting $\rightleftharpoons$ Rate of freezing

Caution Point *During melting of ice, the volume decreases from 1.09 mL to 1.01 mL per gram.*

Liquid-Gas Equilibria

On heating a pure liquid, it starts to convert into its vapours. If the process is carried out in a closed vessel, the vapours get condensed to give liquid. After some time a stage is reached, at which the rate of evaporation becomes equal to the rate of condensation and the volume of liquid water and vapour become constant. Such a condition, represents liquid-gas equilibria.

$$H_2O(l) \rightleftharpoons H_2O(g); \qquad 373\text{ K; 1 atm pressure}$$

Rate of evaporation = Rate of condensation

Caution Point *The temperature at which a pure liquid starts to convert into its vapours is called its boiling point. At this temperature, the vapour pressure of the liquid becomes equal to the atmospheric pressure. That's why this temperature changes with change in altitude.*

Solid-Vapour Equilibria

Such equilibrium exists only in case of sublimates (the substance which on heating directly vapourised without liquefication). *e.g.,* If a sublimate like solid iodine is heated in a closed vessel, after sometime the vessel gets filled up with violet vapour and the intensity of colour increases with time. After sometime, the intensity of colour becomes constant and at this stage the rate of sublimation of solid becomes equal to the rate of condensation of vapour into solid. This stage is referred to the equilibrium state, *i.e.,*

Rate of sublimation $\rightleftharpoons$ Rate of condensation

or $I_2(s) \rightleftharpoons I_2\text{ (vap)}$

Dissolution of Gases into Liquids

(Henry's Law)

Dissolution of a gas into a liquid is governed by Henry's law, which states that *the mass of a gas dissolved in a given mass of a solvent at any temperature is proportional to the pressure of the gas above the solvent.*

$$m \propto p$$

$$m = k_H p$$

where k_H is the proportionality constant, called the Henry's law constant and depends upon the temperature. Thus, on increasing the temperature, the amount of dissolved gas decreases.

General Characteristics of Equilibria Involving Physical Processes

For the physical processes following characteristics are common to the system at equilibrium

1. At equilibrium, at all the measurable properties of the system remain constant.
2. Equilibrium is possible only in a closed system at a given temperature.
3. Equilibrium is dynamic in nature, *i.e.,* the opposing processes do not stop but take place at the same rate.
4. The physical equilibrium is characterised by constant value of one of its parameter at a given temperature. *e.g.,* for the dissolution of CO_2 in water, at equilibrium

$$CO_2(g) \rightleftharpoons CO_2(aq)$$

$\frac{[CO_2(aq)]}{[CO_2(g)]}$ is constant at a given temperature.

This constant is called the equilibrium constant. Greater the value of equilibrium constant, greater is the extent to which CO_2 dissolves in water.

6.3 Equilibria Involving Chemical Processes

Analogous to the physical system, chemical reactions also attain a state of equilibrium. When opposing processes take place in a chemical reaction, the reaction is said to be a reversible reaction. In other words, reactions, which proceed in both the directions and do not reach to completion, are known as **reversible reactions.** It is represented by putting a double headed arrow ($\rightleftharpoons$) between the reactants and the products, one arrow pointing towards the products and the other pointing towards the reactants.

Some examples of such reactions are as follows

(i) $3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$

(ii) $2HI \rightleftharpoons H_2 + I_2$

Caution Point *Any reaction in which one of the product is gas, but carried out in closed container, i.e., leaving no scope for gas to escape out, can be reversible in nature.*

A reversible reaction is called *homogeneous*, if contains only one phase or called *heterogeneous*, if have more than one phase *e.g.,*

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

(Homogeneous with only gaseous phase)

$$MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g)$$

(Heterogeneous with solid and gaseous phase)

Irreversible Reactions

The reactions, which move in one direction only, *i.e.,* the reactants are almost completely converted into products are called **irreversible reactions.**

Some examples of such reactions are

(i) $BaCl_2 + Na_2SO_4 \longrightarrow BaSO_4 \downarrow + 2NaCl$ (Precipitation reactions)

(ii) $2KClO_3 \xrightarrow{\Delta} 2KCl + 3O_2$ (Decomposition reactions)

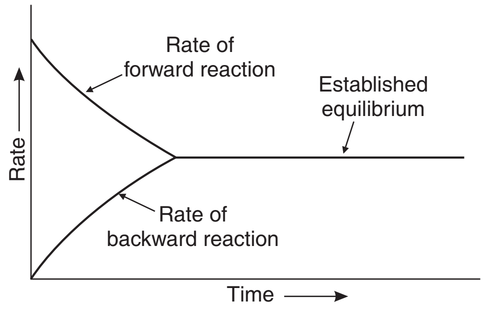
Concept of Chemical Equilibrium

The state of reversible reactions at which the concentration of the reactants and products do not change with time is known as **chemical equilibrium.**

At equilibrium state,

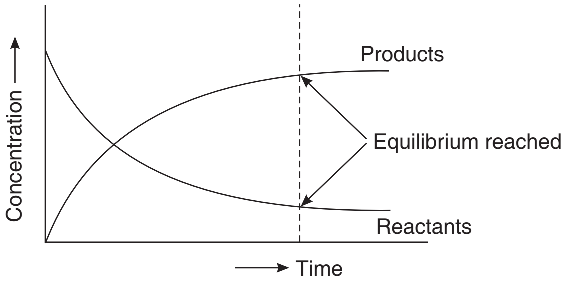
Rate of forward reaction = Rate of backward reaction.

This can be seen in a graphical mode as



Further more, the true equilibrium of a reaction can be attained from both the sides, *i.e.,* the equilibrium concentrations of reactants and products will always be the same whether we begin with the reactants or the products.

The variation of concentration of reactants and products in a reversible reaction can be seen as:



Variation of the concentration of the reactants and products

The equilibrium state is dynamic and not static in nature. It means that the reaction does not stop but both the opposing reactions are going on continuously with same speeds. At this state, the number of moles of substances produced per second in the forward reaction is equal to the number of moles of substances which disappear per second in the backward direction.

Characteristics of Chemical Equilibrium

1. In chemical equilibrium, at a given temperature, the measurable properties like pressure, concentration, density or colour remain constant.
2. Chemical equilibrium can be attained from either side.
3. Chemical equilibrium can be attained in a lesser time by the use of a catalyst, however a catalyst does not change the chemical equilibrium as it affects the rate of both (forward and reverse reaction) to the same extent.
4. Chemical equilibrium is dynamic in nature (*i.e.,* the reaction does not stop but continues in both the directions with same speed).
5. The chemical equilibrium will continue indefinitely if the conditions such as temperature and concentration are not changed.

6.4 Law of Mass Action or Law of Chemical Equilibrium

According to this law, "The rate at which a substance reacts is directly proportional to its active mass and the rate at which a chemical reaction proceeds is proportional to the product of active masses of reacting substances with each concentration term raised to the power of stoichiometric coefficient of that species in the chemical equation".

The term active mass means the molar concentration, *i.e.*, number of moles per litre. It is expressed by enclosing the formula of substance in square brackets as [ ]. Thus, active mass of H_2 can be represented as $[H_2]$.

Sample **Problem 1** *The active mass of* 64 *g of* HI *in a* 2 *L flask would be*

(*a*) 0.25 (*b*) 0.50
(*c*) 25 (*d*) 32

Interpret (*a*) Moles of HI $= \frac{64}{128}$

(Molar mass of HI $= 1 + 127 = 128$ g mol^{-1})

$$\therefore \quad [HI] = \frac{\frac{64}{128}}{2} = 0.25 \text{ mol / L}$$

Caution Point *Active masses of pure solids and liquids are taken as unity because their concentration (or density) remain same throughout the reaction. This is because Gibbs' function for pure solid and liquid are defined at stipulated pressure of* 1.00 *bar and as the p of system changes, Gibbs function remain constant.*

Hot Spot 1

EXPRESSION for Equilibrium Constant from Law of Mass Action

It is an important topic for JEE Main examination. The questions may be based on expression of K or numerical type. The level of question is easy to moderate.

Consider a homogeneous reversible reaction,

$$aA + bB \rightleftharpoons cC + dD$$

According to law of mass action,

Rate of forward reaction,

$$R_f \propto [A]^a[B]^b$$

or $$R_f = k_f[A]^a[B]^b$$

Rate of backward reaction,

$$R_b \propto [C]^c[D]^d$$

or $$R_b = k_b[C]^c[D]^d$$

where, k_f and k_b are the rate constants for forward and backward reactions respectively.

At equilibrium,

rate of forward reaction = rate of backward reaction

i.e., $$k_f[A]^a[B]^b = k_b[C]^c[D]^d$$

or, $$\frac{k_f}{k_b} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad \text{or} \quad K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

where, $K_c = \frac{k_f}{k_b}$ = constant and is known as **equilibrium constant.** It has a definite value for every chemical reaction at a particular temperature regardless of the concentration of reactants.

If K_c is expressed in terms of mole fraction, it is denoted by K_x.

$$K_x = \frac{(\chi_C)^c(\chi_D)^d}{(\chi_A)^a(\chi_B)^b}$$

In terms of partial pressures, equilibrium constants is denoted by K_p.

$$K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b}$$

Sample Problem 2 *Write the expression for the equilibrium constant, K_c for each of the following reactions.*

(i) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$

(ii) $2Cu(NO_3)_2(s) \rightleftharpoons 2CuO(s) + 4NO_2(g) + O_2(g)$

(iii) $CH_3COOC_2H_5(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + C_2H_5OH(aq)$

(iv) $Fe^{3+}(aq) + 3OH^-(aq) \rightleftharpoons Fe(OH)_3(s)$

(v) $I_2(s) + 5F_2 \rightleftharpoons 2IF_5$ **[NCERT]**

Interpret K_c shows the ratio of the product of concentrations of the products to the product of concentrations of the reactants, each raised to the power equal to the corresponding stoichiometric coefficient.

(i) $K_c = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$

(ii) $K_c = [NO_2]^4[O_2]$

(because molar concentrations of pure solids are constant)

(iii) $K_c = \frac{[CH_3COOH(aq)][C_2H_5OH(aq)]}{[CH_3COOC_2H_5(aq)][H_2O(l)]}$

(iv) $K_c = \frac{1}{[Fe^{3+}(aq)]\cdot[OH^-(aq)]^3}$ because $[Fe(OH)_3(s)] = 1$

(v) $K_c = \frac{[IF_5]^2}{[F_2]^5}$ (because $[I_2(s) = 1]$)

Sample Problem 3 *Nitric oxide reacts with* Br_2 *and gives nitrosyl bromide as per reaction given below*

$$2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$$

When 0.087 *mole of* NO *and* 0.0437 *mole of* Br_2 *are mixed in a closed container at constant temperature,* 0.0518 *mole of* NOBr *is obtained at equilibrium. The equilibrium amount of* NO *and* Br_2 *are respectively.* **[NCERT]**

(*a*) 0.0352, 0.0178 (*b*) 0.0872, 0.0259

(*c*) 0.0518, 0.0259 (*d*) 0.0259, 0.0518

Interpret (*a*) In order to solve such problems, following steps are involved

Step I Set up a balance sheet using symbols for the expected equilibirum amounts of reactants and products.

	2NO	+ Br_2	$\longrightarrow$ 2NOBr
Initial moles	0.087	0.0437	0 (as no reaction occur)
At equilibrium moles	$(0.087 - 2x)$	$(0.0437 - x)$	$2x$

[Remember! multiply the value of x with the stoichiometric coefficient of the molecule.]

Step II Compare with the given information

Given equilibrium moles of NOBr = 0.0518

$\therefore$ $$2x = 0.0518$$

and $$x = \frac{0.0518}{2} = 0.0259$$

Step III Put the value of x to obtained equilibrium concentration of other species.

Moles of NO at equilibrium $= (0.087 - 2x)$

$$= 0.087 - 0.0518 = 0.0352 \text{ mol}$$

Moles of Br_2 at equilibrium $= (0.0437 - x)$

$$= 0.0437 - 0.0259 = 0.0178 \text{ mol}$$

Sample Problem 4 *Dihydrogen gas used in Haber's process is produced by reacting methane from natural gas with high temperature steam. The first stage of two stage reaction involves the formation of* CO *and* H_2*. In second stage,* CO *formed in first stage is reacted with more steam in water gas shift reaction,*

$$CO\,(g) + H_2O\,(g) \rightleftharpoons CO_2(g) + H_2(g)$$

If a reaction vessel at 400°C is charged with an equimolar mixture of CO and steam such that $p_{CO} = p_{H_2O} = 4.0$ *bar, what will be the partial pressure of* H_2 *(in bar) at equilibrium?* $K_p = 10.1$ *at 400°C.*

[NCERT]

(a) 12.71
(b) 3.17
(c) 5.32
(d) 3.04

Interpret (*d*) First find the equilibrium concentration in terms of partial pressure and then put these values in K_p expression to find partial pressure of H_2.

	$CO\,(g)$	$+\ H_2O\,(g)$	$\rightleftharpoons\ CO_2(g)$	$+\ H_2(g)$
Initial pressure	4.0 bar	4.0 bar	0	0
At equili.	$(4.0 - p)$	$(4.0 - p)$	p	p

$$K_p = \frac{p_{CO_2} \cdot p_{H_2}}{p_{CO} \cdot p_{H_2O}} = \frac{p \cdot p}{(4-p)\,.\,(4-p)}$$

$$10.1 = \frac{p^2}{(4-p)^2}$$

$$\sqrt{10.1} = \frac{p}{(4-p)}$$

$$3.17 = \frac{p}{(4-p)}$$

$$p = 12.71 - 3.17\,p$$

$$4.17p = 12.71$$

$$p = \frac{12.71}{4.17} = 3.04 \text{ bar}$$

Hence, $p_{H_2} = 3.04$ bar

Relationship Between K_p, K_c and K_x

Consider a gaseous phase reaction,

$$n_1A + n_2B + \ldots\ldots \rightleftharpoons m_1C + m_2D + \ldots\ldots$$

According to law of mass action,

$$K_p = \frac{p_C{}^{m_1} p_D{}^{m_2}}{p_A{}^{n_1} p_B{}^{n_2}} \quad \ldots(\text{i})$$

In terms of molar concentration,

$$K_c = \frac{[C]^{m_1}[D]^{m_2}}{[A]^{n_1}[B]^{n_2}} \quad \ldots(\text{ii})$$

Since for gases, $pV = nRT$

or, $p = \dfrac{n}{V} RT = CRT \quad [C = \text{concentration}]$

$\therefore \quad p_A = C_ART,\ p_B = C_BRT$

$\quad\ \ p_C = C_CRT,\ p_D = C_DRT$

Using these expressions in Eq. (i), we get

$$K_p = \frac{(C_CRT)^{m_1}(C_DRT)^{m_2}}{(C_ART)^{n_1}(C_BRT)^{n_2}}$$

or, $$K_p = \frac{C_C^{m_1} \cdot C_D^{m_2} (RT)^{m_1 + m_2}}{C_A^{n_1} \cdot C_B^{n_2} (RT)^{n_1 + n_2}}$$

or, $$K_p = \frac{C_C^{m_1} C_D^{m_2}}{C_A^{n_1} C_B^{n_2}} (RT)^{(m_1 + m_2) - (n_1 + n_2)}$$

or, $$K_p = \frac{C_C^{m_1} C_D^{m_2}}{C_A^{n_1} C_B^{n_2}} (RT)^{\Delta n_g} \quad \ldots(\text{iii})$$

[$\because\ \Delta n_g = (m_1 + m_2) - (n_1 + n_2)$ or Δn_g = moles of gaseous products − moles of gaseous reactants]

From Eqs. (i) and (iii)

$$\boxed{K_p = K_c (RT)^{\Delta n_g}}$$

We know that partial pressure,

$$p = \text{mole fraction } (\chi) \times \text{total pressure } (p)$$

For the above reaction

$$p_n = \chi_A p,\ p_B = \chi_B p,\ p_c = \chi_C p \text{ and } p_D = \chi_D p$$

So, $$K_p = \frac{p_C^{m_1} \cdot p_D^{m_2}}{p_A^{n_1} \cdot p_B^{n_2}}$$

$$= \frac{(\chi_C p)^{m_1} (\chi_D p)^{m_2}}{(\chi_A p)^{n_1} (\chi_B p)^{n_2}}$$

$$= \frac{\chi_C^{m_1} \cdot \chi_D^{m_2}}{\chi_A^{n_1} \cdot \chi_B^{n_2}} \cdot \frac{p^{(m_1 + m_2)}}{p^{(n_1 + n_2)}}$$

$$= K_x \cdot p^{(m_1 + m_2) - (n_1 + n_2)}$$

$$K_p = K_x p^{\Delta n_g}$$

So, like $$K_p = K_c (RT)^{\Delta n_g}$$

$$K_p = K_x (RT)^{\Delta n_g}$$

If, $\Delta n_g = 0$ then $K_p = K_c$
If, $\Delta n_g = +$ ve then $K_p > K_c$
If, $\Delta n_g = -$ ve then $K_p < K_c$

Sample Problem 5 *The value of* K_c *for each of the following equilibria are respectively.* **[NCERT]**

(i) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g);\ K_p = 1.8 \times 10^{-2}$ *at 500 K*

(ii) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g);\ K_p = 167$ *at 1073 K*

(*a*) $4.38 \times 10^{-4}, 2.89$ (*b*) $4.3 \times 10^{-5}, 2.89$

(*c*) $4.38 \times 10^{-4}, 1.89$ (*d*) $4.3 \times 10^{-5}, 1.89$

Interpret (*c*) (i) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g);$

$$K_p = 1.8 \times 10^{-2} \text{ at } 500\text{ K}$$

$$\Delta n_g = n_p - n_r = 3 - 2 = 1$$

$$K_c = \frac{K_p}{(RT)^{\Delta n_g}} = \frac{1.8 \times 10^{-2}}{0.0821 \times 500} = 4.38 \times 10^{-4}$$

(ii) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g);\ K_p = 167$ at 1073 K

$$\Delta n_g = n_p - n_r = 1$$

$$K_c = \frac{K_p}{(RT)^{\Delta n_g}} = \frac{167}{0.0821 \times 1073} = 1.89$$

Hot Spot 2

CHARACTERISTICS OF Equilibrium Constant

Calculation of equilibrium constant of a reaction from the equilibrium constant(s) of other reaction(s) is also an important topic of this chapter for JEE Main examination. Questions based on this topic are generally easy.

Main characteristics of equilibrium

1. The value of equilibrium constant does not depend on
   - (i) Initial concentrations of reactants
   - (ii) The presence of a catalyst
   - (iii) The direction from which the equilibrium has been attained
   - (iv) Presence of inert materials
   - (v) Nature and number of steps in the reaction as long as stoichiometry is constant.
2. If the equation is divided by a factor '*n*', the new equilibrium constant is n^{th} root of the previous value.
3. If the equation is multiplied by a factor '*n*', the new equilibrium constant is n^{th} power of the previous value. *e.g.,* For the reaction

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3 \qquad K_c = \frac{1}{5}$$

therefore for the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$$K_c' = (K_c)^2 = \left(\frac{1}{5}\right)^2 = 0.04$$

4. If the equation representing equilibrium constant is reversed, the new equilibrium constant is inverse of the first value, *e.g.,* For the following equilibrium, $K_c = 6.3 \times 10^{14}$ at 1000 K

$$NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g)$$

both the forward and reverse reactions in the equilibrium are elementary bimolecular reactions. We have to find the value of K_c for the reverse reaction.

For the reaction, $NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g);$

$$K_c = 6.3 \times 10^{14} \text{ at } 1000\text{ K}$$

$$K_c = \frac{[NO_2][O_2]}{[NO][O_3]} = 6.3 \times 10^{14} \qquad \text{...(i)}$$

For reverse reaction,

$$NO_2(g) + O_2(g) \rightleftharpoons NO(g) + O_3(g)$$

$$K_c' = \frac{[NO][O_3]}{[NO_2][O_2]} \qquad \text{...(ii)}$$

From Eqs. (i) and (ii), we get

$$K_c' = \frac{1}{K_c} = \frac{1}{6.3 \times 10^{14}} = 1.587 \times 10^{-15}$$

5. If two equations are added, their equilibrium constants are multiplied and if they are subtracted, their equilibrium constants are divided (Always remember, equilibrium constants are never added or subtracted).

Sample **Problem 6** *K_{a_1}, K_{a_2} and K_{a_3} are the respective ionisation constants for the following reactions.*

$$H_2S \rightleftharpoons H^+ + HS^-$$

$$HS^- \rightleftharpoons H^+ + S^{2-}$$

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

The correct relationship between K_{a_1}, K_{a_2} and K_{a_3} is

[NCERT Exemplar]

(*a*) $K_{a_3} = K_{a_1} \times K_{a_2}$ (*b*) $K_{a_3} = K_{a_1} + K_{a_2}$

(*c*) $K_{a_3} = K_{a_1} - K_{a_2}$ (*d*) $K_{a_3} = K_{a_1} / K_{a_2}$

Interpret (*a*) For the reaction,

$$H_2S \rightleftharpoons H^+ + HS^-$$

$$K_{a_1} = \frac{[H^+][HS^-]}{[H_2S]}$$

For the reaction,

$$HS^- \rightleftharpoons H^+ + S^{2-}$$

$$K_{a_2} = \frac{[H^+][S^{2-}]}{[HS^-]},$$

When the above two reactions are added,

$$K_{a_3} = \frac{[H^+]^2[S^{2-}]}{[HS^-]} = K_{a_1} \times K_{a_2}$$

∵ When two reactions are added, their equilibrium constants are multiplied.

6. The value of equilibrium constant changes with change of temperature. If K_1 and K_2 be the equilibrium constants of a reaction at absolute temperatures T_1 and T_2 and ΔH is the heat of reaction at constant pressure then

$$\log K_2 - \log K_1 = -\frac{1}{2.303\,R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]\Delta H$$

or
$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Case I If $\Delta H = 0$, *i.e.*, neither heat is absorbed nor evolved then $\log K_2 - \log K_1 = 0 \Rightarrow K_2 = K_1$

Thus, **equilibrium constant remains same at all temperatures.**

Case II If $\Delta H > 0$, *i.e.*, the reaction is endothermic.

Let $T_2 > T_1$, then $\frac{1}{T_2} - \frac{1}{T_1} < 0$

or $\log K_2 - \log K_1 > 0$

$\Rightarrow$ $K_2 > K_1$

Hence, **the value of equilibrium constant rises with rise in temperature.**

Case III If $\Delta H < 0$, *i.e.*, the reaction is exothermic.

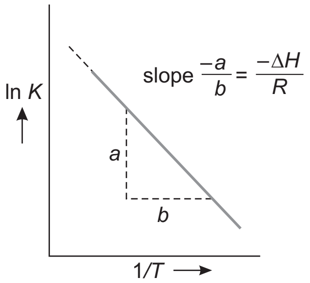
Let $T_2 > T_1$, then $\log K_2 - \log K_1 < 0 \Rightarrow K_2 < K_1$

Therefore, **the value of equilibrium constant is lowered with rise in temperature.**

The other form of the above equation is

$$\ln K = -\frac{\Delta H}{R} \times \frac{1}{T} + \text{constant}$$

(It is the equation of straight line).



Graph of ln K vs $\frac{1}{T}$

The slope of the line allows us to calculate ΔH and the intercept on the ln K axis gives the value of the constant.

The temperature dependence of K_c and K_p can be drawn by **van't Hoff equation** directly as :

(i) $$\frac{\Delta H}{RT^2} = \frac{d(\ln K_p)}{dT}$$

here, ΔH = enthalpy change of reaction at constant pressure

(ii) $$\frac{\Delta E}{RT^2} = \frac{d(\ln K_c)}{dT}$$

here, ΔE = heat of reaction at constant volume.

Sample **Problem 7** *The equilibrium constant for the reaction* $H_2(g) + S(s) \rightleftharpoons H_2S(g)$ *is 18.5 at 925 K and 9.25 at 1000 K respectively. The enthalpy of the reaction is*

(a) 2 kJ mol^{-1} (b) +71 kJ mol^{-1}
(c) −71 kJ mol^{-1} (d) 75 kJ mol^{-1}

Interpret (c) We know that,

$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\log \frac{9.25}{18.5} = \frac{\Delta H}{2.303 \times 8.314} \times \frac{75}{925 \times 1000}$$

$$-0.3010 = \frac{\Delta H \times 75}{2.303 \times 8.314 \times 925 \times 1000}$$

or $$\Delta H = -71080.57 \text{ J mol}^{-1}$$

$$= -71.08 \text{ kJ mol}^{-1}$$

Units of K_c and K_p

If number of moles of reactants and products are equal (*i.e.*, $\Delta n_g = 0$) *e.g.*,

$$2NO \rightleftharpoons N_2 + O_2$$

then, K_p as well as K_c have no units.

If a reaction proceeds with increase in number of moles, (*i.e.*, $\Delta n > 0$)

e.g., $$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$
$$N_2O_4 \rightleftharpoons 2NO_2$$

then, unit of K_p is (atmosphere)$^{\Delta n_g}$ and unit of K_c is (mol per litre)$^{\Delta n_g}$.

If the reaction shows a decrease in the number of moles (*i.e.*, $\Delta n_g < 0$).

e.g., $$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

then, unit of K_p is (atmosphere)$^{\Delta n_g}$ and that of K_c is (litre per mol)$^{\Delta n_g}$.

Significance of Equilibrium Constants (K_p and K_c)

1. Greater the value of equilibrium constant, greater will be the tendency of the reaction to go in forward direction.
2. Greater the equilibrium constant of a reaction, greater will be the stability of the products and unstability of the reactants.
3. If the value of K is greater than 10^3, products predominates, if value of K is less than 10^{-3}, reactant predominates, if it is in between 10^3 to 10^{-3}, considerable amount of both is present.

Sample **Problem 8** *Predict which of the following reaction will have appreciable concentration of reactants and products?* **[NCERT]**

(a) $Cl_2(g) \rightleftharpoons 2Cl(g); \quad K_c = 5 \times 10^{-39}$

(b) $Cl_2(g) + 2NO(g) \rightleftharpoons 2NOCl(g); \quad K_c = 3.7 \times 10^8$

(c) $Cl_2(g) + 2NO_2(g) \rightleftharpoons 2NO_2(g); \quad K_c = 1.8$

(d) *All have appreciable concentration of reactants and products.*

Interpret (c) For this reaction, value of K is in between 10^{-3} to 10^3, thus in it considerable amount of both (reactants and products) are present.

Relationship Between *K* and Standard Gibbs Free Energy

Gibbs free energy change and reaction quotient are related as

$$\Delta G = \Delta G^\circ + 2.303RT \log Q_c$$

At equilibrium, $\Delta G = 0$ and $Q_c = K_c$

On putting values,

$$\Delta G^\circ = -2.303\, RT \log K_c$$

or $$\Delta G^\circ = -2.303\, RT \log K_p \quad \text{(for ideal gases)}$$

Significance of ΔG°

(i) If $\Delta G^\circ < 0, \log K > 0, \Rightarrow K > 1$

Hence, forward reaction is spontaneous.

(ii) If $\Delta G^\circ > 0, \log K < 0 \Rightarrow K < 1$

Hence, the backward reaction is favoured.

(iii) If $\Delta G^\circ = 0, \log K = 0 \Rightarrow K = 1$

Hence, it represents equilibrium.

(iv) If ΔG° is large positive number, $K >> 1$, the forward reaction is nearly complete.

(v) If ΔG° is a very small positive number, $K << 1$, the reverse reaction is nearly complete.

Check Point 1

1. The nature of equilibrium state is dynamic. Explain this.
2. Explain why pure liquids and solids can be ignored while writing the equilibrium expression?
3. Write the equilibrium constant expressions for the following reactions
   (i) $Ag_2O(s) + 2HNO_3(aq) \rightleftharpoons 2AgNO_3(aq) + H_2O(l)$
   (ii) $BaCO_3(s) \rightleftharpoons BaO(s) + CO_2(g)$
   (iii) $CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(g)$
4. Explain why K_p is equal to K_c when Δn_g is zero?
5. Explain how does equilibrium constant affect spontaneity of a chemical reaction?

6.5 Reaction Quotient or Mass Action Ratio

Reaction quotient is the ratio of the molar concentration or partial pressure of the product species to that of reactant species at any stage in the reaction.

For a reaction,

$$A + B \rightleftharpoons C + D$$

$$Q = \frac{[C][D]}{[A][B]}$$

Reaction quotient, Q is denoted as Q_c or Q_p depending upon whether the concentration is taken in terms of moles per litre or partial pressure respectively. With the help of reaction quotient we can predict the direction of reaction.

(i) If $Q = K$, the reaction is in equilibrium.

(ii) If $Q > K$, the reaction moves from right to left, (*i.e.,* in backward direction).

(iii) If $Q < K$, the reaction moves from left to right (*i.e.,* in forward direction).

Sample **Problem 9** *A mixture of* 1.57 *moles of* N_2, 1.92 *moles of* H_2 *and* 8.13 *moles of* NH_3 *is introduced into a* 20 *L reaction vessel at* 500 *K. At this temperature, the equilibrium constant,* K_c *for the reaction,* $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ *is* 1.7×10^2. **[NCERT]**

The true statement is

(a) *the reaction is at equilibrium*

(b) *the reaction goes in the direction of reactants*

(c) *the reaction goes in the direction of products*

(d) *None of the above*

Interpret (*b*) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Given, $[NH_3] = \frac{8.13}{20} M = 0.4065 M$; $[N_2] = \frac{1.57}{20} M = 0.0785 M$

$$[H_2] = \frac{1.92}{20} M = 0.096 M$$

$$Q_c = \frac{[0.4065 M]^2}{[0.0785 M][0.096 M]^3} = 2.379 \times 10^3 M^{-2}$$

$Q_c \neq K_c$, so the reaction mixture is not in equilibrium. $Q_c > K_c$, it indicates that the reaction will proceed in the direction of reactants.

6.6 Relation Between Vapour Density and Degree of Dissociation

Consider the following reversible chemical equation

$$A \rightleftharpoons yB$$

Initial moles : 1 $\quad 0$

At equilibrium $(1 - x)$ $\quad yx$ (x = degree of dissociation)

Number of moles of A and B at equilibrium

$$= 1 - x + yx$$
$$= 1 + x(y - 1)$$

If initial volume of 1 mole of A is V then volume of equilibrium mixture of A and B is $[1 + x(y - 1)]V$.

Now, molar density before dissociation,

$$D = \frac{\text{molecular weight } (m)}{\text{volume } (V)}$$

Molar density after dissociation,

$$d = \frac{m}{[1 + x(y - 1)]V}$$

$$\therefore \quad \frac{D}{d} = [1 + x(y - 1)] \text{ and } x = \frac{D - d}{d(y - 1)}$$

where, y = number of moles of products from one mole of reactant

$\frac{D}{d}$ = van't Hoff factor

Also, $D \times 2$ = molecular weight (theoretical value)

$d \times 2$ = molecular weight of the mixture (abnormal value)

e.g., (i) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

$$y = 2, \text{ and thus, } x = \frac{D - d}{d}$$

(ii) $2NO_2 \rightleftharpoons N_2O_4$

$$y = \frac{1}{2}, \text{ and thus, } x = \frac{2(d - D)}{d}$$

Sample **Problem 10** *Calculate the degree of dissociation, if vapour density of the equilibrium mixture of* NO_2 *and* N_2O_4 *is found to be 40 for the reaction,*

$$N_2O_4 \rightleftharpoons 2NO_2$$

(*a*) 1.25
(*b*) 0.15
(*c*) 1.50
(*d*) 2.50

Interpret (*b*) Theoretical molecular weight $= 2 \times D = 92$

$$D = \frac{92}{2} = 46$$

Hence, $$x = \frac{D - d}{d} = \frac{46 - 40}{40} = 0.15$$

6.7 Le-Chatelier's Principle

In 1884, French chemist **Henry Le-Chatelier** proposed a general principle which applies to all systems in equilibrium. The principle commonly called Le-Chatelier's principle and states that *when a change is brought about on a system in equilibrium, the system tends to adjust itself to reduce the effect of change.*

or

If a system in equilibrium is subjected to a change of concentration, pressure or temperature, the equilibrium shifts in the direction that tends to undo the effect of the change.

Factors Affecting Equilibrium Concentration

Various factors that affect the state of equilibrium are as follows.

(a) Change in Concentration

If concentration of the reactants is increased or product is removed, the equilibrium will shift in the forward direction. On the other hand, if concentration of the products is increased, the equilibrium will shift in the backward direction.

(b) Change in Pressure

If a system in equilibrium consists of gases, the concentration of all the components may be altered by changing the pressure as the pressure at equilibrium is determined by the total number of molecules it contain.

As a general rule, the increase of pressure on a chemical equilibrium shifts it in that direction in which the number of gaseous molecules decreases and *vice-versa*. Thus,

if $\Delta n_g = 0$, no effect on equilibrium due to pressure change.

if $\Delta n_g > 0$, the increase in pressure favours backward reaction.

if $\Delta n_g < 0$, the increase in pressure favours forward reaction.

(c) Change in Temperature

When temperature is raised, the equilibrium is shifted in the direction in which heat is absorbed. Thus, for an exothermic reaction, the increase in temperature favours backward reaction and for an endothermic reaction, the forward reaction is favoured by increase in temperature.

(d) Effect of Catalyst

Catalyst increases (or decreases) both forward and backward reactions equally, therefore equilibrium will be attained in less (or more) time. So, only the time required to reach the equilibrium state is changed by the presence of catalyst. Thus, a catalyst does not affect equilibrium constant.

(e) Effect of Addition of Inert Gas

(i) If keeping pressure of the system constant, an inert gas is added, it will increase the volume of the system. Therefore, the equilibrium will shift in a direction in which there is increase in number of moles of gases.

(ii) If keeping volume of the system constant, an inert gas is added, the relative molar concentration of the substance will not change. Hence, the equilibrium position of the reaction remains unaffected.

Table 6.1 **Effect of Varying Conditions of the Equilibrium, $aA + bB \rightleftharpoons cC + dD, \Delta n_g = (c + d) - (a + b)$**

S. No.	Change imposed on the system in equilibrium	Equilibrium position moves	Equilibrium constant	Any other points
1.	Conc. of *A* and/or *B* increased	To right	No change	No change
2.	Conc. of *C* and/or *D* increased	To left	No change	No change
3.	Pressure increased	To right if $(c + d) < (a + b)$, *i.e.*, $\Delta n_g = -\text{ve}$ To left if $(c + d) > (a + b)$, *i.e.*, $\Delta n_g = +\text{ ve}$ No change if $(c + d) = (a + b)$, *i.e.*, $\Delta n_g = 0$	No change No change No change	Very little effect, if any, on reactions in liquid solution
4.	Temperature increased	To left if $\Delta H = -\text{ve}$ (exothermic) To right if $\Delta H = +\text{ve}$ (endothermic)	Value decreased Value increased	Equilibrium achieved faster
5.	Addition of catalyst	No change	No change	Equilibrium achieved faster
6.	Addition of inert gas			
	(i) At constant *p*	To the direction of increasing gaseous moles	No change	No change
	(ii) At constant *V*	No effect	No change	No change

Applications of Le-Chatelier's Principle

This principle is applicable to physical as well as chemical equilibria.

Some of its applications are mentioned below.

(a) Formation of HI

$$H_2 + I_2 \rightleftharpoons 2HI, \quad \Delta H = -12.4 \text{ kcal}$$

The favourable conditions for forward reaction are

(i) high concentration of H_2 or/and I_2.

(ii) unaffected by pressure change (as $\Delta n_g = 0$)

(iii) low reaction temperature (as the reaction is exothermic).

(iv) no effect of addition of inert gas.

(b) Haber's Process of Synthesis of Ammonia

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -22.4 \text{ kcal}$$

The favourable conditions are

(i) high concentration of N_2 or/and H_2

(ii) high pressure (as $\Delta n_g = -2$)

(iii) low temperature (as the reaction is exothermic)

Although the low temperature favour the formation of NH_3, yet an optimum temperature is set, as the rate of reaction is very slow at low temperature. A temperature of 500° C is selected and a pressure of 200 atm is applied in practice. To enhance the rate of reaction, catalyst, finely divided iron containing molybdenum (acts as promoter) is used.

(c) Manufacture of Nitric Acid (Birkeland-Eyde Process)

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \; \Delta H = +\, 43.2 \text{ kcal}$$

The factors favouring formation of NO are

(i) increase in concentration of N_2 and O_2

(ii) unaffected by pressure change (as $\Delta n_g = 0$)

(iii) increase in temperature (as the reaction is endothermic).

(d) Melting of Ice

$$\underset{\substack{1\text{ g}\\1.09\text{ mL}}}{\text{Ice}} \rightleftharpoons \underset{\substack{1\text{ g}\\1.01\text{ mL}}}{\text{Water}} - x\text{ kcal}$$

In the above case, forward change is accompanied with absorption of heat and a decrease in volume.

Hence, on applying Le-Chatelier's principle, the favourable conditions for the melting of ice are high temperature (as forward reaction is endothermic) and high pressure (as forward reaction shows decrease in volume).

(e) Boiling of Water

$$\underset{\text{(low volume)}}{\text{Water}} \rightleftharpoons \underset{\text{(higher volume)}}{\text{Steam}} \quad -x\text{ kcal}$$

The forward change is accompanied with absorption of heat and increase in volume. Hence, according to Le-Chatelier principle, the favourable conditions for vaporisation of water are high temperature and low pressure.

(f) Solubility of Salts

If solubility of a salt is accompanied by absorption of heat. *e.g.*, Consider the solution of NaCl in water, following equilibrium exists

$$\text{NaCl}(s) + H_2O \rightleftharpoons \text{NaCl}(aq); \qquad \Delta H > 0$$

As the dissolution of NaCl proceeds with absorption of heat, it is favoured by high temperature.

If solubility of a salt is accompanied by evolution of heat, *e.g.*, KOH dissolves in water with evolution of heat, the solubility of KOH, thus decreases with increase in temperature.

$$\text{KOH}(s) + H_2O \rightleftharpoons \text{KOH}(aq) \qquad \Delta H < 0$$

Sample **Problem 11** *The exothermic formation of* ClF_3 *is represented by the equation,* $Cl_2(g) + 3F_2(g) \rightleftharpoons 2ClF_3(g)$, $\Delta H_r = -329\,kJ$. *Which of the following will increase the quantity of* ClF_3 *in an equilibrium mixture of* Cl_2, F_2 *and* ClF_3?

(a) *Removing* Cl_2
(b) *Adding* F_2
(c) *Increasing the temperature*
(d) *Increasing the volume of the container*

Interpret (*b*) For the reaction,

$$\Delta n_g = -\text{ve}$$
$$\Delta H = -\text{ve}$$

∴ The reaction will shift in the forward direction on decreasing the volume, decreasing temperature, removing ClF_3 and adding either Cl_2 or F_2.

Check Point 2

1. Explain why high pressure is applied in the synthesis of ammonia?
2. In the presence of Cl_2, dissociation of PCl_5 decreases, why?
3. What is the effect of halving the pressure by doubling the volume of the following system at 500°C?
$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
4. What is the effect on this equilibrium of halving the volume and doubling the total pressure?
$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 22\text{kcal}$$
5. When ice (solid) melts into water liquid, volume decreases explain, why?

6.8 Electrolytes and Non-Electrolytes

Electrolytes

The solutes which dissociate into ions when dissolved in water, are called **electrolytes.** These form a solution, which conducts electricity, however, not all the electrolytes ionise to the same extent in solution. Depending upon the extent of ionisation, the electrolytes are divided into two classes

(a) Strong Electrolytes

These are dissociated largely or almost completely in solution and the solution consequently becomes very good conductor of electricity. For example, HCl, H_2SO_4, HNO_3, NaOH, KOH, NaCl, KCl, KNO_3, NH_4Cl etc.

(b) Weak Electrolytes

These get never completely dissociated. In ordinary conditions, weak electrolytes dissociate in solution to a small extent and the solution consequently is poor conductor of electricity. For example, CH_3COOH, H_3PO_4, H_3BO_3, NH_4OH, $(NH_4)_2CO_3$, HCN etc.

Non-Electrolytes

A solution of solute like urea, glucose, etc., does not contain any ion, hence the solution is bad conductor of electricity. Such solutes are termed as **non-electrolytes.**

6.9 Arrhenius Theory of Electrolytic Ionisation

This theory explains the mechanism of electrolysis and abnormal behaviour of electrolytes in dilute solutions.

The main postulates of this theory are

1. In aqueous solution, the molecules of an electrolyte undergo spontaneous dissociation into positive and negative ions. The positively charged ions are called **cations** and the negatively charged ions are called **anions.**
2. When a current of electricity is passed through a solution of an electrolyte, the positively charged ions move towards cathode and negatively charged ions move towards anode and lose their charges and convert into products. This movement of ions constitutes the electric current in the solution.
3. A dynamic equilibrium, called the **ionic equilibrium,** is established between the ions and undissociated molecules.

$$AB \rightleftharpoons A^+ + B^-$$

4. The properties of solutions of electrolytes are essentially the properties of individual ions.
5. The fraction of the total number of molecules undergoing dissociation is called the **"degree of dissociation** (α)". Alternatively, the fraction of the amount of the electrolyte in solution present as free ions is called the degree of dissociation.

$$\alpha = \frac{\text{number of molecules of electrolyte dissociated as ions}}{\text{total number of molecules of electrolyte dissolved}}$$

or $$\alpha = \frac{\text{amount of electrolyte dissociated}}{\text{initial amount}}$$

Degree of dissociation (α) increases with dilution and reaches to maximum limit (unity) at infinite dilution for weak electrolytes.

Factors Affecting Degree of Dissociation

Various factors by which the degree of dissociation gets affected are as follows

(a) Nature of Solute

Strong electrolytes have high value of degree of dissociation while weak electrolytes have lower values.

(b) Nature of Solvent

Degree of dissociation of an electrolyte increases with the polarity of the solvent.

(c) Concentration

The degree of dissociation of an electrolyte decreases with rise in concentration of the electrolyte.

(d) Temperature

In general, the degree of dissociation rises with raise in temperature of the solution.

(e) Addition of Other Species

Addition of another species (solute) having an ion common to that of weak electrolyte shows a decrease in degree of dissociation of weak electrolyte (common ion effect).

Hot Spot 3

OSTWALD'S Dilution Law

It is one of the important topic of the chapter for JEE Main examination. The question is generally numerical type and its level varies from easy to moderate.

Ostwald proposed that the **law of mass action could be applied to the ionic equilibrium** as in the case of chemical equilibrium. This application of law of mass action to dilute solutions is called **Ostwald's dilution law.** Consider a binary electrolyte AB dissociating in solution according to the following equation

$$\begin{array}{lccc} & AB & \rightleftharpoons & A^+ & + & B^- \\ \text{Initially} & C & & 0 & & 0 \\ \text{At equilibrium} & C(1-\alpha) & & C\alpha & & C\alpha \end{array}$$

where, C (mol/L) be the initial concentration of the electrolyte and α be the degree of dissociation. So, dissociation constant may be given as

$$K = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} \qquad \text{...(i)}$$

For very weak electrolytes,

$$\alpha <<< 1 \Rightarrow (1-\alpha) \approx 1$$

$$\therefore \qquad K = C\alpha^2$$

$$\text{or} \qquad \alpha = \sqrt{\frac{K}{C}}$$

$$\text{or} \qquad \alpha \propto \frac{1}{\sqrt{C}} \propto \sqrt{V} \qquad \left(\because C \propto \frac{1}{V}\right)$$

$$V = \text{dilution of solution}$$

Thus, *"the degree of dissociation is proportional to the square root of dilution for weak electrolytes." This is the statement of Ostwald Law.* Degree of dissociation increases as dilution increases.

Applications of Ostwald's Dilution Law

This law is used

1. To calculate the value of dissociation constant (K) of the weak acids and weak bases, by determining the degree of dissociation (α) from conductance measurement $\left(\frac{\lambda_V}{\lambda_\infty}\right)$ at any concentration C.
2. To calculate the degree of dissociation, α of weak acids and bases by knowing the value of K.

   For weak acid, put $[A^+] = [H^+]$ and $K = K_a$

   Similarly for weak bases,

   $$[B^-] = [OH^-] \text{ and } K = K_b$$

Limitations of Ostwald's Law

1. This law holds good only in case of weak electrolytes. Even weak electrolytes do not obey this law in concentrated solutions.
2. The value of K can be calculated only in dilute solutions of weak electrolytes.

Caution Point *The approximation* $(1-\alpha) \approx 1$ *can be applied only if* $\alpha < 5\%$. *If on solving a problem by applying the approximate formula;* α *comes out to be* $>5\%$, *the problems may be solved by applying the exact formula and* α *may be calculated applying the solution of the quadratic equation*

$$\alpha = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \qquad (\text{for, } a\alpha^2 + b\alpha + c = 0)$$

Sample **Problem 12** *The ionisation constant of* 0.05 M *solution of phenol is* 1.0×10^{-10}. *What will be its degree of ionisation if the solution is also* 0.01 M *in sodium phenolate?*

[NCERT]

(a) 1×10^{-10} (b) 1×10^{-8}

(c) 1×10^{-4} (d) 1×10^{-6}

Interpret (b) Write equation of dissociation as

$$C_6H_5OH \longrightarrow C_6H_5O^- + H^+(H_3O^+)$$

When mixture contains 0.05 M phenol and 0.01 M phenolate ion (from sodium phenolate) then

$$K_a = \frac{[C_6H_5O^-][H_3O^+]}{[C_6H_5OH]}$$

$$1.0 \times 10^{-10} = \frac{[0.01] \times [H_3O^+]}{[0.05]}$$

$$[H_3O^+] = \frac{0.05 \times 1.0 \times 10^{-10}}{0.01}$$

$$= 5 \times 10^{-10} \text{ M}$$

$$[H_3O^+] = C \cdot \alpha = 5 \times 10^{-10}$$

$$\text{or} \qquad \alpha = \frac{5 \times 10^{-10}}{C}$$

$$\alpha = \frac{5 \times 10^{-10}}{0.05} = 1 \times 10^{-8}$$

Sample **Problem 13** *0.16 g N_2H_4 is dissolved in water and the total volume is made upto 500 mL. Calculate the percentage of N_2H_4 that has reacted with water in this solution. K_b for N_2H_4 is 4.0×10^{-6} M.*

(a) 12% (b) 8%
(c) 2% (d) 20%

Interpret (c)

$$\begin{array}{lcccl} N_2H_4 + H_2O & \rightleftharpoons & N_2H_5^+ & + OH^- & \\ 1 & & 0 & 0 & \text{initially} \\ 1-\alpha & & \alpha & \alpha & \text{after dissociation} \end{array}$$

$$K_b = \frac{C\alpha^2}{(1-\alpha)}$$

$$K_b = C\alpha^2 \quad [\text{if } (1-\alpha) \approx 1]$$

$$C = [N_2H_4] = \frac{0.16 \times 1000}{32 \times 500} = 0.01$$

$$K_b = 4 \times 10^{-6}\ M$$

$$\alpha = \sqrt{\frac{4 \times 10^{-6}}{0.01}} = 0.02 \quad \text{or} \quad 2\%$$

6.10 Various Concepts of Acids and Bases

The earlier criteria for acids and bases were the experimentally observed properties of aqueous solutions. An **acid** is that whose aqueous solution tastes sour, turns blue litmus red, neutralises bases and so on. On the other hand, the aqueous solution of a **base** tastes bitter, turns red litmus blue, neutralises acid and so on. Later on some concepts are given to signify acids and bases. These are

Arrhenius Concept

According to this concept, all substances, which give H^+ ions in their aqueous solutions are called **acids,** while those, which furnish OH^- ions in water are called **bases.**

$$HA \rightleftharpoons H^+ + A^- \text{ (acid)}$$

$$BOH \rightleftharpoons B^+ + OH^- \text{ (base)}$$

The strength of the acid or base depends upon its tendency to furnish H^+ or OH^- ions in solution.

Water is amphoteric because it furnish both H^+ *and* OH^- *ions in solution.*

$$H_2O \rightleftharpoons H^+ + OH^-$$

Number of H^+ ions delivered by an acid in its aqueous solution is called **basicity** or **protocity** of the acid. *The acids are referred as monobasic, dibasic, tribasic* etc., according as the number of protons given in aqueous solution are one, two or three.

Similarly, the number of OH^- furnished by the base in its aqueous solution is called its **acidity.**

Limitations of Arrhenius Theory

1. Free H^+ and OH^- ions do not exist in water.
2. The concept is limited to aqueous solutions only.
3. It cannot explain the acidic character of certain salts like, $AlCl_3$, BF_3 and basic character of NH_3, PH_3.
4. It cannot be applied to compounds which do not contain free H^+ or OH^- ions.

Caution Point *$H^{\oplus}$ ion is a bare proton (~10^{-15} m radius) with intense electric field, binds itself with the water molecules at one of the two available lone pairs on it, giving $H_3O^{\oplus}$.*

In aqueous solution, the $H_3O^{\oplus}$ is further hydrated to give species such as $H_5O_2^{\oplus}$, $H_7O_3^{\oplus}$ and $H_9O_4^{\oplus}$, e.g.,

$$H_3O^{\oplus} + H_2O \longrightarrow H_5O_2^{\oplus}$$

$$H_5O_2^{\oplus} + H_2O \longrightarrow H_7O_3^{\oplus}$$

Similarly, the $\overset{\ominus}{O}H$ ion is hydrated to give several ionic species such as $H_3O_2^{\ominus}$, $H_5O_3^{\ominus}$, and $H_7O_4^{\ominus}$.

$$\overset{\ominus}{O}H + H_2O \longrightarrow H_3O_2^{\oplus}$$

Bronsted-Lowry Concept

According to this concept, an **acid** is a substance (molecule or ion) that can donate H^+ to some other substance and a **base** is a substance that can accept a proton from an acid. Thus, an acid is a proton donor **(protogenic)** and a base is proton acceptor **(protophilic).**

Consider the following equilibrium

$$B + H^+ \rightleftharpoons BH^+$$

In the above reaction B is acting as **base.** The compound BH^+ has a tendency to release H^+.

The acid and base, which differ by a proton, are said to form a conjugate acid-base pair.

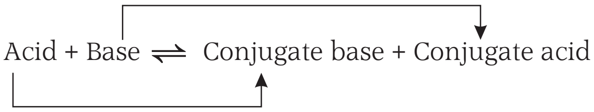
Consider the following reaction

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

It involves two conjugate pairs,

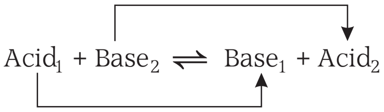
$$CH_3COOH \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} CH_3COO^- \text{ and } H_2O \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} H_3O^+$$

Such pairs of substances are known as conjugate acid-base pairs. In symbol, we can write



Acid + Base $\rightleftharpoons$ Conjugate base + Conjugate acid

Or



$Acid_1 + Base_2 \rightleftharpoons Base_1 + Acid_2$

Examples

$$H_2SO_4 + H_2O \rightleftharpoons HSO_4^- + H_3O^+$$

$$H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^-$$

$$HCl + OH^- \rightleftharpoons H_2O + Cl^-$$

$$H_3O^+ + OH^- \rightleftharpoons H_2O + H_2O$$

The strength of the acids/bases depend upon their tendency to donate/accept the proton.

Generally, a strong base has a weak conjugate acid and a weak base has strong conjugate acid. The above reactions, which involve the transfer of proton are called **neutralisation reactions.**

Always remember a substance behaves as an acid only if there is an acceptor of proton furnished by it.

The compounds which have dual character, *i.e.,* they may act as acid as well as base are called **amphoteric** or **amphiprotic**, *e.g.*, NH_3, H_2O, CH_3COOH, etc.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

$$CH_3COOH + CH_3COOH \rightleftharpoons CH_3CO\overset{+}{O}H_2 + CH_3COO^-$$

All strong acids or bases appear to be equally strong in water, hence water levels the strength of all acids and bases. This is called **levelling effect.** We, therefore, cannot compare the strength of acids or bases in aqueous medium. The strength of an acid depends on the solvent. *e.g.,* The acids $HClO_4$, H_2SO_4, HCl, HNO_3 all appear to have nearly same strength in aqueous solution, but their strength is in order $HClO_4 > H_2SO_4 > HCl > HNO_3$ in acetic acid.

HCl acts as an acid in H_2O, stronger acid in NH_3, weak acid in CH_3COOH, neutral in C_6H_6 and a weak base in HI.

Generalised variation of acidic and basic strengths can be seen as :

1. The acidic strength of hydracids in the same period increases across the period, *e.g.*, in II period,

   $$CH_4 < NH_3 < H_2O < HF$$

   This is due to the stability order of their conjugate base.

   $$CH_3^- < NH_2^- < H^- < F^-$$

2. The hydracids show a regular increase in strength down a group, because *E*—H (where *E* = any element except H) bond length increases which facilitate the removal of proton. *e.g.,*

   $$NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$$
   $$H_2O < H_2S < H_2Se < H_2Te$$
   $$HF < HCl < HBr < HI$$

3. The acidic character of oxyacids of same element increases with increase in number of oxygen atoms, *e.g.,*

   $$HClO < HClO_2 < HClO_3 < HClO_4$$
   $$H_2SO_3 < H_2SO_4$$
   $$HNO_2 < HNO_3$$

   However, the rule fails in oxyacids of phosphorus

   $$H_3PO_2 > H_3PO_3 > H_3PO_4$$

4. The acidic character of oxyacids of different elements which are in same oxidation state decreases with increase in atomic number (due to increase in size and decrease in electronegativity).

   $$HClO_4 > HBrO_4 > HIO_4$$
   $$H_2SO_3 > H_2SeO_3$$

Limitations of Bronsted-Lowry Concept

1. The protonic definition cannot be used to explain the reactions occurring in the non-protonic solvents such as $COCl_2$, SO_2, N_2O_4 etc.
2. This concept cannot explain the reactions between some acidic oxides (such as CO_2, SO_2, SO_3) and basic oxides (such as CaO, BaO, MgO) which take place even in the absence of the solvent, *e.g.,*

   $$CaO + SO_3 \longrightarrow CaSO_4$$

3. BF_3, $AlCl_3$ etc., do not have any hydrogen and hence, cannot give a proton but are known to behave as acids.

Caution Points *Solvents can be classified into following four types on the basis of proton interaction.*

(*i*) **Protophilic solvents** *These solvents have a high tendency to accept protons, e.g., water, alcohol, liquid ammonia etc.*

(*ii*) **Protogenic solvents** *These solvents have tendency to produce protons, e.g., water, liquid hydrogen chloride, glacial acetic acid etc.*

(*iii*) **Amphiprotic solvents** *They have tendency to accept as well as donate proton, e.g.,* NH_3 *etc.*

(*iv*) **Aprotic solvents** *These are the solvents which neither donate nor accept protons. These solvents do not influence the acid-base characteristic of solute. e.g., benzene, carbon tetrachloride, carbon disulphide etc.*

Lewis Concept

According to this concept, a **base** is defined as a substance, which can give a pair of electrons to form a co-ordinate bond and the **acid** is the substance which can accept the pair. Thus, *an acid is an electrophile, while a base is a nucleophile.*

According to Lewis, a general acid-base reaction can be expressed as below

$$A + {:}B \longrightarrow A \leftarrow B$$
$$\text{acid} + \text{base} \longrightarrow \text{complex}$$

Example

$$H^+ + {:}OH^- \longrightarrow H \leftarrow OH$$

$$BF_3 + \ddot{N}H_3 \longrightarrow H_3N \rightarrow BF_3$$

Types of Lewis acids include

1. Compounds in which the central atom has incomplete octet, *e.g.,* BF_3, $AlCl_3$, $GaCl_3$, $MgCl_2$, $BeCl_2$ etc.
2. Compounds in which the central atom has available *d*-orbital, *e.g.,* PF_3, PF_5, SF_4, SeF_4, $TeCl_4$, GeX_4, $SnCl_4$ etc.
3. All simple cations like Na^+, Cu^{2+}, Ag^+, Al^{3+}, Fe^{3+}, Ca^{2+}, H^+, etc. *However,* Na^+, K^+, Ca^{2+} *etc., have very little tendency to accept electrons.*
4. Molecules with multiple bonds between dissimilar atoms, *e.g.,* $O{=}C{=}O$, $O{=}S{=}O$, SO_3, etc.
5. Elements with an electron sextet, *e.g.,* O, S, etc.

Types of Lewis bases include

1. All simple anions, like Cl^-, F^-, OH^-, CN^-, etc.
2. Molecules with one or two unshared (lone) pairs, *e.g.,* $H_2\underset{\cdot\cdot}{\ddot{O}}$, $\ddot{N}H_3$, $R\underset{\cdot\cdot}{\ddot{O}}H$, $R_2\underset{\cdot\cdot}{\ddot{O}}$, $R_2\underset{\cdot\cdot}{\ddot{S}}$, pyridine, etc.
3. Multiple bonded compounds which form co-ordination compounds with transition metals, *e.g.,* CO, NO, ethylene, acetylene etc.

Limitations of Lewis Concept

1. The strength of Lewis acids and bases is found to depend on the type of reaction, *it is not possible to arrange them in any order of their relative strength.*
2. It does not explain the behaviour of protonic acids such as HNO_3, HCl, H_2SO_4 etc.
3. Catalytic activity of Lewis acid can't be explained because the catalytic activity of many acids is due to their tendency to furnish H^+. Lewis acid does not do so.

Hard and Soft Acids and Bases (HSAB) Principle

"Hardness" is the property of retaining valence electrons very strongly. It is the basis of this principle.

Hard Acids

These are characterised by small size of electron accepting atom. They have high charge and have no electron which are easily polarised or removed. Examples of hard acids are H^+, Li^+, Na^+, Be^{2+}, Mg^{2+}, Mn^{2+}, Al^{3+}, Cr^{3+}, Co^{3+}, Fe^{3+}, La^{3+}, Ce^{3+}, As^{3+}, BF_3, $AlCl_3$, SO_3 etc.

Soft Acids

In these acceptor atom is large, carries low charge, has electrons which can be easily distorted. Examples of soft acids are Pb^{2+}, Cd^{2+}, Pt^{3+}, Hg^{2+}, Cu^+, Ag^+, Tl^+, Hg^{2+}, $GaCl_3$, B_2H_6, RO^+, I_2, Br_2, metal atoms etc.

Hard Bases

These are the Lewis base that hold electrons strongly, *e.g.,* H_2O, NH_3, OH^-, F^-, Cl^-, CO_3^{2-}, ClO_4^-, NO_3^-, ROH· RO^-, R_2O, RNH_2 etc.

Soft Bases

These are the Lewis base from which electrons can be easily removed, *e.g.,* R_2S, RHS, RS^-, I^-, SCN^-, R_3P, R_3As, CN^-, RNC, CO, C_2H_4, H^-, R^-, etc.

Caution Point *Hard acid prefers hard base, for binding.*

Some rememberable facts are as

1. All organic acids (except those having $—SO_3H$) are weak acids.
2. Oxides of metals are normally basic while oxides of non-metals are normally acidic.
3. The oxides of alkali and alkaline earth metals are strong base and rest all oxides are weak base.

Relative Strengths of Acids and Bases

The extent to which the acidic property is shown by an acid is a measure of its strength. The strength of an acidic solution does not depend upon its concentration but depend upon the number of H^+ ions present. Thus, to measure the relative strength of the two acids, the measurements of their H^+ ions concentration, *i.e.,* the degree of dissociation of their equinormal solutions is used.

$$\frac{\text{Strength of acid I}}{\text{Strength of acid II}}=\frac{\alpha_1}{\alpha_2}=\sqrt{\frac{K_1/C}{K_2/C}}=\sqrt{\frac{K_1}{K_2}}$$

where, K_1 and K_2 are the dissociation constants of two acids at the same concentration, C.

α_1 and α_2 are their degree of dissociation.

Di- and Polybasic Acids and Di- and Polyacidic Bases

Acids which have more than one ionisable proton per molecule of acids are known as polybasic or polyprotic acids, *e.g.,* oxalic acid (HOOC — COOH), H_2SO_4, and H_3PO_4.

The ionisation reactions for a dibasic acid, H_2X are represented as

$$H_2X(aq) \rightleftharpoons H^{\oplus}(aq) + HX^{\ominus}(aq)$$

$$HX^{\ominus}(aq) \rightleftharpoons H^{\oplus}(aq) + X^{2-}(aq)$$

The corresponding equilibrium constants are as

$$K_{a_1}=\frac{[H^{\oplus}][HX^{\ominus}]}{[H_2X]} \text{ and } K_{a_2}=\frac{[H^{\oplus}][X^{2-}]}{[HX^{\ominus}]}$$

(K_{a_1} and K_{a_2} are called first and second ionisation constants, respectively, of the acid H_2X).

Similarly, for tribasic acids such as H_3PO_4, there are three ionisation constants.

It is found that K_{a_1} of polyprotic acid is greater than K_{a_2} or K_{a_3} (*i.e.*, $K_{a_1} > K_{a_2} > K_{a_3}$), because it is more difficult to remove a positively charged proton from a negative ion due to electrostatic forces. Similarly, it is more difficult to remove a proton from a doubly charged anion as compared to single charged anion.

The primary reaction involves the dissociation of H_2X and $H_3O^{\oplus}$ in the solution comes mainly from the first dissociation step.

Sample Problem 14 *K_1 and K_2 for dissociation of H_2S are 4×10^{-3} and 1×10^{-5}. Calculate sulphide ion concentration in 0.1 M H_2S solution.*

(a) 10^{-4} (b) 10^{-8}

(c) 10^{-5} (d) 10^{-6}

Interpret (c) $H_2S \rightleftharpoons H^{\oplus} + HS^{\ominus}$

$$K_1 = \frac{[H^{\oplus}][HS^{\ominus}]}{[H_2S]} = 4\times10^{-3}$$

$$[H^{\oplus}] = C\alpha, [HS^{\ominus}] = C\alpha, \quad [H_2S] = C(1-\alpha)$$

or $$4\times10^{-3} = \frac{C\alpha\cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

$$4\times10^{-3} = \frac{0.1\times\alpha^2}{(1-\alpha)} \quad (1-\alpha \text{ should not be neglected})$$

or $$\alpha = 0.18,$$

$\therefore$ $$[H^{\oplus}] = C\alpha = 0.1\times0.18 = 0.018\text{ M}$$

$$[HS^{\ominus}] = C\alpha = 0.1\times0.18 = 0.018\text{ M}$$

$$[H_2S] = C(1-\alpha) = 0.1(1-0.18)$$
$$= 0.082\text{ M}$$

Now, $HS^{\ominus}$ further dissociates to $H^{\oplus}$ and S^{2-};

$$C_1 = [HS^{\ominus}] = 0.018\text{ M}$$

$$\begin{array}{ccccc} HS^{\ominus} & \rightleftharpoons & H^{\oplus} & + & S^{2-} \\ 1 & & 0 & & 0 \\ (1-\alpha_1) & & \alpha_1 & & \alpha_1 \end{array}$$

$\therefore$ $$K_2 = 1\times10^{-5} = \frac{[H^{\oplus}][S^{2-}]}{[HS^{\ominus}]}$$

Because $[H^{\oplus}]$ already in solution $= 0.018$ and thus, dissociation of $HS^{\ominus}$ further suppresses due to common ion effect and $1-\alpha \approx 1$.

$\therefore$ $$1\times10^{-5} = \frac{0.018\times C_1\alpha_1}{C_1(1-\alpha_1)}$$
$$= 0.018\times\alpha_1$$

$\therefore$ $$\alpha_1 = \frac{1\times10^{-5}}{0.018} = 5.55\times10^{-4}$$

$\therefore$ $$[S^{2-}] = C_1\alpha_1 = 0.018\times5.55\times10^{-4}$$
$$= 10^{-5}$$

Check Point 3

1. Write the formulae for the conjugate bases of the following acids : HCN, HCO_3^-, C_2H_5OH.
2. Account for the acidic properties of nitrous acid in terms of Bronsted-Lowry theory.
3. Br^- ion is a Lewis as well as Bronsted base. Justify it.
4. Water acts both as an acid and as a base. Explain it.
5. Why K_{a_1} for H_2S is higher than K_{a_2} ?

6.11 Ionisation of Water

Pure water is a weak electrolyte and is ionised according to following equation

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

Applying law of mass action,

$$K = [H_3O^+][OH^-] / [H_2O]^2$$

Since concentration of water is very high, hence $[H_2O]$ may be taken as constant and we may write a new constant (K_w) in place of $K[H_2O]^2$.

Thus,
$$K_w = [H_3O^+][OH^-]$$

Since, $[H_3O^+] = [H^+]$, we get
$$K_w = [H^+][OH^-]$$

The constant K_w is termed as **ionic product of water.** Its value at 298 K is found to be 1.00×10^{-14} mol^2 L^{-2}.

Since, pure water is neutral.

Therefore, $[H^+] = [OH^-]$, clearly

$$[H^+] = [OH^-] = \sqrt{K_w} = C_\alpha$$
$$= \sqrt{(1.00\times10^{-14})} \text{ at 298 K}$$
$$= 1.00\times10^{-7}\text{ mol L}^{-1}$$

The molarity (*M*) of pure H_2O $$= \frac{\text{Density}}{M}$$
$$= \left(\frac{1000\text{ gL}^{-1}}{18.0\text{ g mol}^{-1}}\right)$$
$$= 55.55\text{ M}$$

$$\alpha = \frac{10^{-7}}{C} = \frac{10^{-7}}{55.6} = 1.8\times10^{-9}$$

or $$\%\text{ dissociation} = 1.8\times10^{-7}$$

Some facts related to ionic product of water are

1. With increase in temperature, the dissociation of water increases, increasing $[H^+]$ and $[OH^-]$ and consequently K_w increases.

2. If some acid or base is added to water then $[H^+] \neq [OH^-]$, however, K_w remains constant at the constant temperature.
3. If an acid is added to water, the concentration of H^+ increases. Consequently, the equilibrium shifts to reverse direction in order to maintain constant K_w, in any case, $[H^+][OH^-] = K_w$

   Therefore, in this case as $[H^+] > [OH^-]$
   $$[H^+] > 1 \times 10^{-7} \text{ mol L}^{-1}$$
   $$[OH^-] < 1 \times 10^{-7} \text{ mol L}^{-1}$$
   Similarly, if a base is added, concentration of OH^- increases and in this case,
   $$[H^+] < [OH^-]$$
   $$\therefore \quad [H^+] < 1 \times 10^{-7} \text{ mol L}^{-1}$$
   $$\text{and} \quad [OH^-] > 1 \times 10^{-7} \text{ mol L}^{-1}$$

Sample **Problem 15** *At 363 K, pure water has* $[H_3O^+] = 10^{-6}$ *M. The value of* K_w *at this temperature will be*

(a) 10^{-6} (b) 10^{-12}
(c) 10^{-13} (d) 10^{-14}

Interpret (b) $[H_3O^+] = [OH^-] = 10^{-6}$ M

From $$K_w = [H_3O^+][OH^-]$$
$$= 10^{-6} \times 10^{-6}$$
$$= 10^{-12} \text{ M}$$

6.12 Relation Between K_a and K_b

K_a and K_b represent the strength of an acid and a base, respectively. The conjugate acid-base pair are related in a manner so that if one is known, the other can be deducted.

For example in case of $\overset{\oplus}{N}H_4$ and NH_3,

$$\overset{\oplus}{N}H_4(aq) + H_2O(l) \rightleftharpoons H_3O^{\oplus}(aq) + NH_3(aq) \quad \text{...(i)}$$

$$K_a = \frac{[H_3O^{\oplus}][NH_3]}{[\overset{\oplus}{N}H_4]} = 5.6 \times 10^{-10}$$

(*K_a represents the strength of* $\overset{\oplus}{N}H_4$ *as an acid*)

$$NH_3(aq) + H_2O(l) \rightleftharpoons \overset{+}{N}H_4(aq) + \overset{\ominus}{O}H(aq) \quad \text{...(ii)}$$

$$K_b = \frac{[\overset{\oplus}{N}H_4][\overset{\ominus}{O}H]}{[NH_3]} = 1.8 \times 10^{-5}$$

(*K_b represents the strength of* NH_3 *as a base*)

Adding Eqs. (i) and (ii), the net equation is

$$2H_2O(l) \rightleftharpoons H_3O^{\oplus}(aq) + \overset{\ominus}{O}H(aq) \quad \text{...(iii)}$$

$$K_w = [H_3O^{\oplus}][\overset{\ominus}{O}H] = 10^{-14} \text{ M}$$

Multiplying K_a and K_b, we get

$$K_a \times K_b = \frac{[H_3O^{\oplus}][NH_3]}{[\overset{\oplus}{N}H_4]} \times \frac{[\overset{\oplus}{N}H_4][\overset{\ominus}{O}H]}{[NH_3]}$$
$$= [H_3O^{\oplus}][\overset{\ominus}{O}H]$$
$$= K_w = 10^{-14}$$

Thus, $$K_a \times K_b = K_w$$
$$(5.6 \times 10^{-10})(1.8 \times 10^{-5}) = 10^{-14} \text{ M}$$

Therefore, it can be generalised that the equilibrium constant for a net reaction obtained after adding two or more reactions equals to the product of the equilibrium constants for individual reactions :

$$\therefore \quad K_{\text{Net}} = K_1 \times K_2 \times \ldots \quad \text{...(iv)}$$

Similarly, in case of a conjugate acid-base pair,

$$K_a \times K_b = K_w \quad \text{...(v)}$$

Taking negative logarithm both side of Eq. (v)

$$-\log(K_a) - \log K_b = -\log K_w$$
$$\therefore \quad pK_a + pK_b = pK_w \quad \text{(at 298 K)} \quad \text{...(vi)}$$

Therefore, from Eqs. (v) and (vi), in case of conjugate acid-base pair, knowing one, the other can be obtained.

$$\therefore \quad K_b = \frac{K_w}{K_a} \quad \text{...(vii)}$$

$$\text{and} \quad K_a = \frac{K_w}{K_b} \quad \text{...(viii)}$$

6.13 pH Scale

The idea of pH scale and the scale was given by **Sorensen**. The pH of a solution is defined as *"the negative logarithm of the concentration* (in mol L^{-1}) *of hydrogen ions which it contains* (or logarithm of the reciprocal of H^+ ion concentration).

Thus, $$pH = -\log[H^+] = \log \frac{1}{[H^+]}$$

Concentration of hydrogen ions can be written as

$$[H^+] = 1 \times 10^{-pH}$$

Caution Point *A decrease of a single pH unit corresponds to ten folds increase in acidic nature.*

pOH Value

Just as pH indicates H^+ ion concentration, pOH represents the OH^- ion concentration,

i.e., $$pOH = -\log[OH^-]$$

Relation between pH and pOH

We know that at 298 K in aqueous solution,

$$[H^+][OH^-] = K_w = 1 \times 10^{-14}$$

$$\therefore \qquad pH + pOH = 14$$

1. In case of pure water as $[H^+] = [OH^-] = 1 \times 10^{-7}$, thus $pH = pOH = 7$ represents neutrality.
2. In case of acidic solution, $[H^+] > [OH^-]$, thus $pH < 7$ and $pOH > 7$.
3. Also, in case of alkaline solution, $[H^+] < [OH^-]$, thus, $pH > 7$ and $pOH < 7$.

The solutions having pH between 0 and 2 are strongly acidic, those with pH between 2 to 4 are moderately acidic, while others having pH between 4 to 7 are weakly acidic.

Similarly, the solutions having pH value between 7 to 10 are weakly basic, those having pH between 10 to 12 are moderately basic whereas others which have pH between 12 to 14 are strongly basic.

pH *range of some common substances are* :

Gastric juice	1.0–3.0	Rain water	6.0
Soft drinks	2.0–4.0	Tears	7.4
Lemon	2.2–2.4	Sea water	8.5
Vinegar	2.4–3.4	Milk of magnesia	10.5
Urine (human)	4.8–8.4	Milk (Cow)	6.3–6.6
Saliva (human)	6.5–7.5	Blood plasma (human)	7.36 –7.42

Caution Point *A change in blood* pH *by* 0.2 *units results in death.*

pH of a Weak Monobasic Acid

pH of such solutions can be calculated as

$$pH = -\log [H_3O^+] = -\log \sqrt{K_a \cdot C}$$

$$= -\frac{1}{2}\log K_a - \frac{1}{2}\log C$$

$$= \frac{1}{2}[pK_a - \log C]$$

pOH of a Weak Monoacidic Base

pH of such solutions can be calculated as

$$pOH = -\log [OH^-] = -\log\sqrt{K_b \cdot C}$$

$$= \frac{1}{2}[pK_b - \log C]$$

$$pH = 14 - pOH = 14 - \frac{1}{2}[pK_b - \log C]$$

Total $[OH^-]$ in a mixture of two weak bases,

$$[OH^-] = \sqrt{K_1C_1 + K_2C_2}$$

Sample Problem 16 *Calculate* pH *of* 0.10 *N acetic acid having* $K_a = 1.8 \times 10^{-5}$.

(*a*) 2.8 (*b*) 5.6
(*c*) 6.8 (*d*) 3.4

Interpret (a) $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ (weak acid)

$$\begin{array}{cccl} 1 & 0 & 0 & \text{initially} \\ (1-\alpha) & \alpha & \alpha & \text{at equilibrium} \end{array}$$

$$[H^+] = C\alpha \text{ or } C \cdot \sqrt{\frac{K_a}{C}} = \sqrt{K_a \cdot C}$$

$$= \sqrt{1.8 \times 10^{-5} \times 0.1} = 1.34 \times 10^{-3}\ M$$

Thus, $pH = -\log [H^+]$

$$= -\log (1.34 \times 10^{-3})$$

$$= 2.87$$

Sample Problem 17 2 *g of* NaOH *is dissolved in water to make* 1 *L solution. What is the* pH *of solution?*

(*a*) 10.25 (*b*) 8.56
(*c*) 12.69 (*d*) 10.89

Interpret (*c*) Weight of NaOH dissolved = 2 g

$\therefore$ Equivalent of NaOH dissolved $= \frac{2}{40}$

$$\therefore \qquad N_{NaOH} = \frac{2}{40} = 0.05$$

$$\therefore \qquad [OH^-] = 0.05 = 5 \times 10^{-2}$$

or

$$pOH = -\log [OH^-] = -\log (5 \times 10^{-2})$$

$$= 1.3010$$

$$pH + pOH = 14$$

$$\therefore \qquad pH = 14 - pOH$$

$$= 14 - 1.3010 = 12.699$$

pH of Mixtures of Acids and Bases

The rules for determining the pH *of mixtures of acids and bases are as follows*

1. If strong acid or strong base remains unused, calculate the concentration or molarity of $H^{\oplus}$ ions and $\overset{\ominus}{O}H$ ions left in the solution and then calculate the pH or pOH accordingly.
2. If weak acid or weak base is left behind or remains unused, a buffer (acidic or basic) is formed. Calculate the concentration of salt formed (mmoles of salt formed/volume of solution) and the concentration of weak acid or weak base left behind. Use the buffer equation to calculate the pH of the solution.
3. If acids or bases are completely neutralised, then salt is formed. Calculate the concentration of the salt formed and use the hydrolysis equation to calcualte the pH of the solution.

Sample **Problem 18** *What will be the resultant* pH *when* 200 *mL of an aqueous solution of* HCl (pH = 2) *is mixed with* 300 *mL of an aqueous solution of* NaOH (pH = 12)?

(*a*) 2 (*b*) 12
(*c*) 11.3 (*d*) 7

Interpret (*c*) pH of HCl = 2 $\therefore$ $[\text{HCl}] = 10^{-2}$ M

$$\text{pH of NaOH} = 12 \quad \therefore \ [\text{NaOH}] = 10^{-2}\ \text{M}$$

$$\text{HCl} + \text{NaOH} \rightleftharpoons \text{NaCl} + H_2O$$

$$\text{meq after reaction} \quad 0 \qquad 100 \times 10^{-2} = 1$$

$$[\text{OH}^-] \text{ after reaction} = \frac{1}{500} = 2 \times 10^{-3}\ \text{M}$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(2 \times 10^{-3}) = 2.7$$

$$\therefore \quad \text{pH} = 14 - 2.7 = 11.3$$

Limitations of pH Scale

1. pH values of the solutions do not give us immediate idea of the relative strengths of the solutions.
2. pH value of 1 N solution of strong acid is obtained zero. But in case the concentration is 2 N, 3 N, 10 N etc., the respective pH values are negative.
3. A solution of an acid having very low concentration say 10^{-8} N show pH value less than 7 inspite of 8, as shown by pH formula.

Sample **Problem 19** pH *of* 10^{-8} *M* HCl *is*

(*a*) 8 (*b*) 6.958
(*c*) 6 (*d*) *Cannot be calculated*

Interpret (*b*) $\because$ $\text{pH} = -\log[\text{H}^+]$

$$= -\log 10^{-8} = 8$$

But this is not true because an acidic solution cannot have pH greater than 7. In this condition, $[\text{H}^+]$ of water cannot be neglected.

Therefore, $$[\text{H}^+]_{\text{total}} = [\text{H}^+]_{\text{HCl}} + [\text{H}^+]_{H_2O}$$

$$= 10^{-8} + 10^{-7}$$

$$= 10^{-8}(1 + 10) = 11 \times 10^{-8}$$

Now from, $$\text{pH} = -\log[\text{H}^+]$$

$$= -\log(11 \times 10^{-8})$$

$$= -\log 11 - \log 10^{-8}$$

$$= 6.958$$

6.14 p*K* Value

p stands for negative logarithm. Thus, p*K* is the negative logarithm of dissociation constant.

$$\therefore \quad pK_a = -\log K_a \quad \text{and} \quad pK_b = -\log K_b$$

Weak acids have higher pK_a *values. Similarly weak bases have higher* pK_b *values.*

For any conjugate acid-base pair in aqueous solution, we know that,

$$K_a \times K_b = K_w = 1 \times 10^{-14} \qquad \text{(at 298 K)}$$

Taking logarithm on both sides, we have

$$\log(K_a \times K_b) = \log(1 \times 10^{-14})$$

$$\text{or} \qquad \log K_a + \log K_b = -14$$

$$\text{or} \qquad (-\log K_a) + (-\log K_b) = 14$$

$$\text{or} \qquad pK_a + pK_b = 14 \qquad \text{(at 298 K)}$$

Sample **Problem 20** *The* pH *of* 0.005 *M codeine* ($C_{18}H_{21}NO_3$) *solution is* 9.95. *Its* pK_b *value is* **[NCERT]**

(*a*) 8.92 (*b*) 5.81 (*c*) 3.76 (*d*) 4.29

Interpret (*b*)

$$\text{Codeine} \quad (C_{18}H_{21}NO_3) + H_2O \rightleftharpoons \text{Codeine H}^+ + \text{OH}^-$$

$$\text{pH} = 9.95 \quad \text{or} \quad \text{pOH} = 14 - 9.95 = 4.05$$

$$\text{pOH} = -\log[\text{OH}^-]$$

$$\log[\text{OH}^-] = -4.05 = \bar{5}.95$$

$$[\text{OH}^-] = \text{antilog } \bar{5}.95 = 8.913 \times 10^{-5}$$

$$K_b = \frac{[\text{codeine H}^+][\text{OH}^-]}{[\text{codeine}]} = \frac{[\text{OH}^-]^2}{[\text{codeine}]}$$

(because $[\text{codeine H}^+] = [\text{OH}^-]$)

$$K_b = \frac{(8.913 \times 10^{-5})^2}{0.005} = 1.588 \times 10^{-6}$$

$$pK_b = -\log[K_b] = -\log[1.588 \times 10^{-6}]$$

$$pK_b = 6 + (-0.2009) = 5.7791 \approx 5.80$$

6.15 Common Ion Effect

Let *AB* is a weak electrolyte dissociating as follows

$$AB \rightleftharpoons A^+ + B^-$$

Applying law of mass action,

$$K = [A^+][B^-]/[AB]$$

Now, if another electrolyte furnishing either A^+ or B^- ion be added to the above solution, it will increase the concentration of either A^+ or B^- ions accordingly. In order to keep *K* constant, the concentration of *AB* must increase, *i.e.,* the equilibrium shifts to left side. Thus, *the degree of dissociation of an electrolyte is suppressed here by the addition of another electrolyte containing a common ion. This phenomenon is termed as common ion effect. e.g.,* Consider a saturated solution of AgCl, following equilibrium is established.

$$\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$$

When NaCl is added to the solution, the concentration of Cl^- ions will increase and the equilibrium will shift towards left. Hence, the dissociation of AgCl will decrease.

When a partially soluble ionic solid, for example, AgCl, is dissolved in water, after a certain time, a dynamic equilibrium is established between the solid phase and the cations and anions in solutions.

$$AgCl(s) \rightleftharpoons Ag^+ + Cl^-$$

At equilibrium, the solute dissolves at the same rate at which the ions recombine to crystallise the salt. Such a solution is said to be saturated.

As a result of common ion effect, the concentration of the ions other than the common ion is decreased.
This phenomenon is used in qualitative analysis to adjust concentration of S^{2-} ions in second group and OH^- ion concentration in third group of analysis.

6.16 Salt Hydrolysis

The reaction between an acid and a base to from salt and water is known as **neutralisation.** *e.g.*,

$$HCl(aq) + NaOH\,(aq) \rightleftharpoons NaCl(aq) + H_2O\,(l)$$

Thus, salts are ionic compounds made by a reaction between an acid and a base. The positive part of a salt comes properties of salts in aqueous solutions are the propeerties of ions.

Consider BA is a salt of acid HA and base BOH and gets dissociated in aqueous solution as shown below

$$BA \rightleftharpoons B^+ + A^-$$

The ions A^- and B^+ may break O—H bond of water given by following reactions

$$A^- + H—O—H \rightleftharpoons HA + \bar{O}—H \qquad \text{...(i)}$$

$$B^+ + H—O—H \rightleftharpoons BOH + H^+ \qquad \text{...(ii)}$$

The process of salt hydrolysis is actually the reverse process of neutralisation.

The reaction of an anion or cation with water accompanied by cleavage of O—H *bond, is called hydrolysis*.

In above cases of reactions : (i) is called **anionic hydrolysis,** and the solution becomes slightly basic (pH > 7) and (ii) is called **cationic hydrolysis** and the solution becomes slightly acidic (pH < 7).

The hydrolysis depends on the type of salt being used for the purpose.

Depending upon the nature of acid and base, the salts are classified into following four classes

Salts of Weak Acids and Strong Bases

Salts of sodium and potassium other than halides, sulphates and nitrates fall in this category. Such a salt, BA in aqueous medium exhibits following equilibrium

$$BA \longrightarrow B^+ + A^-$$

$$B^+ + A^- + H_2O \rightleftharpoons HA + OH^- + B^+$$

(BOH being a strong base remains dissociated completely). Thus, for this reaction,

$$\text{Equilibrium constant, } K = \frac{[HA][OH^-]}{[A^-][H_2O]}$$

As K, $[H_2O]$ is regarded as constant, hence we may write a new constant K_h

$$\therefore \qquad K_h = \frac{[HA][OH^-]}{[A^-]}$$

K_h is called **hydrolysis constant.**

(a) Degree of Hydrolysis

It is defined as the fraction of total salt that has undergone hydrolysis on attainment of equilibrum. It is denoted by h. Let C be the concentration of salt and h be its degree of hydrolysis.

$$\underset{C-Ch}{A^{\ominus}} + H_2O \rightleftharpoons \underset{Ch}{\overset{\ominus}{O}H} + \underset{Ch}{HA} \qquad \text{(equation of hydrolysis)}$$

$$K_h = \frac{[\overset{\ominus}{O}H][HA]}{[A^{\ominus}]} = \frac{(Ch)(Ch)}{C-Ch} = \frac{Ch^2}{1-h}$$

$$\Rightarrow \qquad K_h = Ch^2 \;\text{[assuming } h << 1] \Rightarrow h = \sqrt{\frac{K_h}{C}}$$

Now, considering the dissociations of weak acid HA and H_2O.

$$HA \rightleftharpoons H^{\oplus} + A^{\ominus};\; K_a = \frac{[H^{\oplus}]}{[HA]} \qquad \text{...(i)}$$

$$H_2O \rightleftharpoons H^{\oplus} + \overset{\ominus}{O}H:\; K_w = [H^{\oplus}][\overset{\ominus}{O}H] \qquad \text{...(ii)}$$

$\Rightarrow K_h = \dfrac{K_w}{K_a}$ (Subtracting Eqs. (i) from Eqs. (ii), we get the equation of hydrolysis)

Now substituting the value of K_h in expression of h.

$$\Rightarrow \qquad h = \sqrt{\frac{K_w}{K_a C}}$$

Caution Point *Weaker is the acid, greatest is the hydrolysis constant. The degree of hydrolysis increases when C decreases, i.e., with dilution.*

(b) pH of Solution

pH of a basic solution is given as

$$pH = 14 + \log[\overset{\ominus}{O}H] \text{ and } [\overset{\ominus}{O}H] = Ch = \sqrt{K_h C}$$

Substituting for K_h, we get

$$[\overset{\ominus}{O}H] = \sqrt{\frac{K_w C}{K_a}}$$

$$\Rightarrow \qquad \text{pH} = 14 + \log\sqrt{\frac{K_w C}{K_a}}$$

$$\Rightarrow \qquad \text{pH} = \frac{1}{2}(\text{p}K_w + \text{p}K_a + \log C)$$

$$= 7 + \frac{1}{2}(\text{p}K_a + \log C) \text{ at } 25^\circ\text{C}$$

Clearly, pH > 7

Salts of Strong Acids and Weak Bases

Halides, sulphates and nitrates of metals other than sodium, potassium fall in this category. The aqueous solution of such a salt BA, exhibits following equilibrium :

$$BA \longrightarrow B^+ + A^-$$

$$B^+ + A^- + H_2O \rightleftharpoons BOH + H^+ + A^-$$

[As the acid HA is strong].

The hydrolysis constant is given by,

$$K_h = \frac{[H^+][BOH]}{[B^+]}$$

(a) Degree of Hydrolysis

The net reaction of hydrolysis is

$$\underset{C-Ch}{B^{\ominus}} + H_2O \rightleftharpoons \underset{Ch}{BOH(aq)} + \underset{Ch}{H^{\oplus}(aq)}$$

[It is also called cationic hydrolysis.]

$$K_h = \frac{[BOH][H^{\oplus}]}{[B^{\oplus}]} = \frac{(Ch)(Ch)}{C-Ch} = \frac{Ch^2}{1-h} = Ch^2$$

$$(h << 1) \Rightarrow h = \sqrt{\frac{K_h}{C}}$$

Considering ionisation of weak base BOH and H_2O

$$BOH \rightleftharpoons B^{\oplus} + \overset{\ominus}{O}H: \; K_b = \frac{[B^{\oplus}][\overset{\ominus}{O}H]}{[BOH]} \qquad \text{...(ii)}$$

$$H_2O \rightleftharpoons H^{\oplus} + \overset{\ominus}{O}H; \; K_w = [H^{\oplus}][\overset{\ominus}{O}H] \qquad \text{...(i)}$$

Relation between K_w, K_b and K_h can be written as

$$\frac{K_w}{K_b} = K_h$$

Thus, the hydrolysis constant K_h, varies inversely with the dissociation constant, K_b of the weak base.

As in the above case, the degree of dissociation,

$$h = \sqrt{\frac{K_w}{K_b}V} = \sqrt{\frac{K_w}{K_b C}}$$

(b) pH of Solution

Now, $\quad \text{pH} = -\log[H^{\oplus}]$ and $[H^{\oplus}] = Ch = C\sqrt{\frac{K_h}{C}} = \sqrt{K_h C}$

$$\Rightarrow \qquad [H^{\oplus}] = \sqrt{\frac{K_w C}{K_b}} \Rightarrow \text{pH} = -\log\sqrt{\frac{K_w C}{K_b}}$$

$$\Rightarrow \qquad \text{pH} = \frac{1}{2}(\text{p}K_w - \text{p}K_b - \log C)$$

$$= 7 - \frac{1}{2}(\text{p}K_b + \log C) \text{ at } 25^\circ\text{C}$$

Clearly, pH < 7

Salts of Weak Acids and Weak Bases

The salts other than halides, sulphates, nitrates of metals (other than sodium, potassium) fall in this category. In aqueous solution such a salt BA exhibits following equilibrium

$$B^+ + A^- + H_2O \rightleftharpoons BOH + HA$$

The hydrolysis constant is given by, $K_h = \dfrac{[BOH][HA]}{[B^+][A^-]}$

(a) Degree of Hydrolysis

$$\begin{array}{lccccc}
 & B^+ + & A^{\ominus} + H_2O & \rightleftharpoons & \underset{\text{(weak base)}}{BOH(aq)} & + \; \underset{\text{(weak acid)}}{HA(aq)} \\
\text{Initially} & C & C & & 0 & 0 \\
\text{At equilibrium} & C-Ch & C-Ch & & Ch & Ch
\end{array}$$

$$\Rightarrow \qquad K_b = \frac{[BOH][HA]}{[B^{\oplus}][A^{\ominus}]} = \frac{(Ch)(Ch)}{(C-Ch)^2}$$

$\Rightarrow \quad K_b = \dfrac{h^2}{(1-h)^2}$; taking square root on both sides to get

$$h = \frac{\sqrt{K_h}}{1+\sqrt{K_h}} \qquad (\text{Here, } 1-h \neq 1)$$

(Remember that the degree of hydrolysis of such salts is independent of the concentration of salt solution.)

Now considering the dissociation of both weak base and acid.

$$HA \rightleftharpoons H^{\oplus} + A^{\ominus}: \qquad K_a = \frac{[H^{\oplus}][A^{\ominus}]}{[HA]}$$

$$BOH \rightleftharpoons B^{\oplus} + \overset{\ominus}{O}H: \qquad K_b = \frac{[B^{\oplus}][\overset{\ominus}{O}H]}{[BOH]}$$

$$H_2O \rightleftharpoons H^{\oplus} + \overset{\ominus}{O}H; \qquad K_w = [H^{\oplus}][\overset{\ominus}{O}H]$$

Combining K_h, K_b, K_a, and K_w, we have

$$K_b = \frac{K_w}{K_a K_b} \text{ and } h = \frac{\sqrt{K_h}}{1+\sqrt{K_h}}$$

[It is also called cationic-anionic hydrolysis.]

(Observe that $1-h \neq 1$) (if K_h is small, then $h = \sqrt{K_h}$)

(b) pH of Solution

Consider, $K_a = \dfrac{[\mathrm{H}^{\oplus}][A^{\ominus}]}{[\mathrm{H}A]} \Rightarrow [\mathrm{H}^{\oplus}] = K_a \dfrac{[\mathrm{H}A]}{[A^{\ominus}]}$

Since, bases and acids are weaker, hence

$$[B\mathrm{OH}] = [\mathrm{H}A] \Rightarrow [B^{\oplus}] = [A^{\ominus}]$$

$$\Rightarrow \quad K_h = \frac{[B\mathrm{OH}][\mathrm{H}A]}{[B^{\oplus}][A^{\ominus}]} = \frac{[\mathrm{H}A]^2}{[A^{\ominus}]}$$

$$\Rightarrow \quad [\mathrm{H}^{\oplus}] = K_a\sqrt{K_h} = \sqrt{\frac{K_w K_a}{K_b}}$$

$$\mathrm{pH} = -\log[\mathrm{H}^{\oplus}] = -\log\sqrt{\frac{K_w K_a}{K_b}}$$

$$\Rightarrow \quad \mathrm{pH} = \frac{1}{2}(\mathrm{p}K_w + \mathrm{p}K_a - \mathrm{p}K_b) \text{ at } 25°\mathrm{C}$$

$$= 7 + \frac{1}{2}(\mathrm{p}K_a - \mathrm{p}K_b)$$

If $\mathrm{p}K_a = \mathrm{p}K_b$, *i.e.,* the dissociation constants of acid and base are equal, then $\mathrm{pH} = 7$. Thus, the solution will be neutral, despite the fact that hydrolysis has taken place.

***Case* I** If $\mathrm{p}K_a > \mathrm{p}K_b$, or $K_a < K_b$, *i.e.,* **base** is relatively stronger, then $\mathrm{pH} > 7$

***Case* II** If $\mathrm{p}K_a < \mathrm{p}K_b$ or $K_a > K_b$, *i.e.,* **acid** is relatively stronger, then $\mathrm{pH} < 7$.

Salts of Strong Acids and Strong Bases

Halides, sulphates, nitrates of sodium and potassium fall in this category. Following equilibrium will be observed in aqueous solution of such a salt BA

$$B^+ + A^- + \mathrm{H_2O} \rightleftharpoons B^+ + A^- + \mathrm{H_2O}$$

[As the acid as well as base is strong.]

Hence, no hydrolysis takes place in this case and the solution remains neutral.

Hydrolysis of Amphiprotic Anion

(a) Cation is not Hydrolysed

e.g., $\mathrm{NaHCO_3}$, NaHS, etc., can undergo ionisation to form $\mathrm{H^+}$ ion and can undergo hydrolysis to form $\mathrm{OH^-}$ ($\mathrm{Na^+}$ ion is not hydrolysed).

(i) $$\mathrm{HCO_3^- + H_2O \xrightleftharpoons{\text{Ionisation}} \underset{\text{acid}}{CO_3^{2-} + H_3O^+}}$$

$$\mathrm{HCO_3^- + H_2O \xrightleftharpoons{\text{Hydrolysis}} H_2CO_3 + \underset{\text{base}}{OH^-}}$$

Thus, $\mathrm{HCO_3^-}$ is an amphiprotic anion.

$$\mathrm{H_2CO_3 \rightleftharpoons H^+ + HCO_3^-}$$

K_{a_1} = first ionisation constant

$$\mathrm{HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}}$$

K_{a_2} = second ionisation constant

$$\mathrm{pH(HCO_3^-)} = \left(\frac{\mathrm{p}K_{a_1} + \mathrm{p}K_{a_2}}{2}\right)$$

(ii) $$\mathrm{H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+}$$

K_{a_1} = first ionisation constant

$$\mathrm{H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+}$$

K_{a_2} = second ionisation constant

$$\mathrm{HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+}$$

K_{a_3} = third ionisation constant

$\mathrm{H_2PO_4^-}$ and $\mathrm{HPO_4^{2-}}$ are amphiprotic anions.

$$\mathrm{pH}_{(\mathrm{H_2PO_4^-})} = \frac{\mathrm{p}K_{a_1} + \mathrm{p}K_{a_2}}{2}$$

$$\mathrm{pH}_{(\mathrm{HPO_4^{2-}})} = \left(\frac{\mathrm{p}K_{a_2} + \mathrm{p}K_{a_3}}{2}\right)$$

Since, $\mathrm{H_2PO_4^-}$ is involved between $\mathrm{HPO_4^{2-}}$ (conjugate base) and $\mathrm{H_3PO_4}$ (conjugate acid), hence we use $\mathrm{p}K_{a_1}$ and $\mathrm{p}K_{a_2}$ values in hydrolysis of $\mathrm{H_2PO_4^-}$. In $\mathrm{HPO_4^{2-}}$, we use $\mathrm{p}K_{a_2}$ and $\mathrm{p}K_{a_3}$ values since it is involved between $\mathrm{PO_4^{3-}}$(conjugate base) and $\mathrm{HPO_4^{2-}}$ (conjugate acid).

(b) Cation is also Hydrolysed

$[\mathrm{H_3O^+}]$ in salts like $\mathrm{NH_4^+}$, $\mathrm{HCO_3^-}$, $\mathrm{NH_4^+HS^-}$ (in which $\mathrm{HCO_3^-}$, $\mathrm{HS^-}$ are amphiprotic and $\mathrm{NH_4^+}$ ion is also hydrolysed) is

$$[\mathrm{H_3O^+}] = \sqrt{K_{a_1}\left(\frac{K_w}{K_b} + K_{a_2}\right)}$$

Table 6.2 **Hydrolysis at a Glance**

S. No.	Salt	Nature	Degree of Hydrolysis	pH
1.	NaCl (strong acid + strong base)	Neutral	No hydrolysis	—
2.	$\mathrm{CH_3COONa}$ (weak acid + strong base)	Basic	$h = \sqrt{\dfrac{K_w}{CK_a}}$	$\mathrm{pH} = \dfrac{1}{2}[\mathrm{p}K_w + \mathrm{p}K_a + \log C]$
3.	$\mathrm{NH_4Cl}$ (strong acid + weak base)	Acidic	$h = \sqrt{\dfrac{K_w}{CK_b}}$	$\mathrm{pH} = \dfrac{1}{2}[\mathrm{p}K_w - \mathrm{p}K_b - \log C]$
4.	$\mathrm{CH_3COONH_4}$ (weak acid + weak base)	*	$h = \sqrt{\dfrac{K_w}{K_a \times K_b}}$	$\mathrm{pH} = \dfrac{1}{2}[\mathrm{p}K_w + \mathrm{p}K_a - \mathrm{p}K_b]$

Sample **Problem 21** *A 0.02 M solution of pyridinium hydrochloride has* pH = 3.44. *The ionisation constant of pyridine is* [**NCERT**]

(*a*) 1.84×10^{-7}
(*b*) 2.63×10^{-9}
(*c*) 1.5×10^{-9}
(*d*) 3.62×10^{-7}

Interpret (*c*) Pyridinium hydrochloride is a salt of weak base (pyridine) and strong acid (hydrochloric acid), hence, its pH is given as

$$\mathrm{pH} = 7 - \frac{\mathrm{p}K_b}{2} - \frac{\log C}{2}$$

$$3.44 = 7 - \frac{\mathrm{p}K_b}{2} - \frac{\log 0.02}{2}$$

$$\mathrm{p}K_b = 8.82$$

$$\mathrm{p}K_b = 8.82 = -\log K_b$$

$$\log K_b = -8.82 = \bar{9}.18$$

$$K_b = \text{antilog } \bar{9}.18 = 1.5 \times 10^{-9}$$

Alternatively,

$$C_6H_5N \cdot HCl + H_2O \rightleftharpoons C_6H_5N^+Cl^- + H_3O^+$$

$$K_a = \frac{[C_6H_5N^+Cl^-][H_3O^+]}{[C_6H_5N \cdot HCl]}$$

$$\mathrm{pH} = 3.44 = -\log [H_3O^+]$$

$$\log [H_3O^+] = -3.44 = \bar{4}.56$$

$$[H_3O^+] = \text{ antilog } \bar{4}.56 = 3.63 \times 10^{-4} \text{ M}$$

$$[H_3O^+] = [C_6H_5N^+Cl^-] = 3.63 \times 10^{-4}$$

Hence,
$$K_a = \frac{3.63 \times 10^{-4} \times 3.63 \times 10^{-4}}{0.02} = 6.588 \times 10^{-6}$$

$$\mathrm{p}K_a = -\log K_a = -\log (6.588 \times 10^{-6})$$

$$\mathrm{p}K_a = 6 + (-0.8187) = 5.18$$

$$\mathrm{p}K_a + \mathrm{p}K_b = 14$$

$$\mathrm{p}K_b = 14 - 5.18 = 8.82$$

$$-\log K_b = -8.82$$

$$\log K_b = -8.82 = \bar{9}.18$$

$$K_b = \text{antilog } \bar{9}.18 = 1.5 \times 10^{-9}$$

Sample **Problem 22** *The ionisation constant of nitrous acid is* 4.5×10^{-4}. *The pH of 0.04 M* $NaNO_2$ *solution and its degree of hydrolysis are respectively.*

(*a*) $8.23, 2.36 \times 10^{-4}$
(*b*) $7.98, 2.36 \times 10^{-4}$
(*c*) $7.98, 2.36 \times 10^{-5}$
(*d*) $8.23, 2.36 \times 10^{-5}$

Interpret (*c*) Sodium nitrite is a salt of weak acid and strong base. Hence, to calculate pH of its aqueous solution use the formula

$$\mathrm{pH} = 7 + \frac{\mathrm{p}K_a + \log C}{2},$$

$$\therefore \quad \mathrm{pH} = 7 + \frac{3.35 + \log 0.04}{2} = 7.98$$

$$[\mathrm{p}K_a = -\log K_a = -\log (4.5 \times 10^{-4}) = 3.35]$$

$$\mathrm{pH} = 7.98$$

Degree of hydrolysis,
$$h = \sqrt{\frac{K_w}{K_a C}} = \sqrt{\frac{10^{-14}}{4.5 \times 10^{-4} \times 0.04}}$$

$$h = 2.36 \times 10^{-5}$$

Alternatively, $NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$

	NO_2^-	HNO_2	OH^-
Initial conc.	C	0	0
After hydrolysis conc.	$(C - Ch)$	Ch	Ch

$$[OH^-] = Ch = 0.04 \times 2.36 \times 10^{-5}$$

$$[OH^-] = 9.44 \times 10^{-7}$$

$$\mathrm{pOH} = -\log [9.44 \times 10^{-7}]$$

$$\mathrm{pOH} = 7 - 0.9750 = 6.03$$

$$\mathrm{pH} + \mathrm{pOH} = 14 \quad \text{or} \quad \mathrm{pH} = 14 - 6.03 = 7.97$$

Check Point 4

1. pH of an aqueous 10^{-2} M acetic acid solution is not 2.0, why?
2. Explain why pH of 10^{-8} M HCl is not 8?
3. AgCl is more soluble in pure water as compared to salty water. Explain why?
4. The aqueous solution of $FeCl_3$ is acidic while that of sodium acetate is basic. Explain, why?

Hot Spot 4 SOLUBILITY and Solubility Product

It is the most important topic of the chapter for JEE Main examination. The level of question may vary from easy to typical. The question may be numerical based or expression based. A small practice can help you to solve the question and score higher.

The concentration of substance in a saturated solution is defined as its **solubility** (S). It is generally represented as gram of solute in 100 mL of solution or as moles per litre (*i.e.,* molarity). The value of solubility depends on the solvent and the temperature.

Consider saturated solution of sparingly soluble electrolyte, AB.

$$\underset{\text{solid}}{AB} \rightleftharpoons \underset{\substack{\text{unionised}\\ \text{(dissolved)}}}{AB} \rightleftharpoons \underbrace{A^+ + B^-}_{\text{ions}}$$

Applying the law of mass action,

$$K = \frac{[A^+][B^-]}{[AB]}$$

Since, the solution is saturated, the concentration of unionised molecules of the electrolyte will be constant at a particular temperature. *i.e.,*

$$[AB] = \text{constant} = K' \text{ (say)}$$

Hence, $$[A^+][B^-] = KK'$$
$$= K_{sp} \text{ (constant)}$$

This new constant K_{sp} is called **solubility product** and is defined as the product of the concentration of ions in a saturated solution of an electrolyte at a given temperature.

Consider, in general, the electrolyte of the type A_xB_y, which is dissociated as

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$$
$$K_{sp} = [A^{y+}]^x[B^{x-}]^y$$

Thus, *solubility product may be defined as the product of concentrations of the ions raised to a power equal to the number of times the ions occur in the equation representing the dissociation of the electrolyte at a given temperature when the solution is saturated.*

Caution Point *$K_{sp} = x^x y^y S^{x+y}$ is the general expression for relation between S and K_{sp}. By putting the values of x and y, you can directly obtain it (Here x and y = no. of cation and anion respectively.)*

e.g., For $$As_2S_3 \rightleftharpoons 2As^{3+} + 3S^{2-}$$
$$x = 2$$
and $$y = 3$$
$$K_{sp} = (2)^2 \times (3)^3 \times S^{2+3} = 108S^5$$

Finding Relationship Between S and K_{sp}

In order to find the relation between solubility (S) and solubility product (K_{sp}) follow the following steps

Steps	Example
Step I Dissociate electrolyte into ion as $A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$	$Ag_2CO_3 \rightleftharpoons 2Ag^+ + CO_3^{2-}$
Step II Write solubility of each ion. (Remember, if solubility of one ion is S, then for x ions, it is xS.) $\underset{S}{A_xB_y} \rightleftharpoons \underset{xS}{xA^{y+}} + \underset{yS}{yB^{x-}}$	$\underset{S}{Ag_2CO_3} \rightleftharpoons \underset{2\times S}{2Ag^+} + \underset{1\times S}{CO_3^{2-}}$
Step III Write the expression of K_{sp} and put the values of solubilities of ions. $K_{sp} = [A^{y+}]^x[B^{x-}]^y$ $= (xS)^x(yS)^y$	$K_{sp} = [Ag^+]^2[CO_3^{2-}]$ $= (2S)^2(S)$
Step IV Solve the equation obtained to get the relation $K_{sp} = x^x y^y S^{x+y}$	$K_{sp} = 4S^2 \cdot S = 4S^3$

Predicting Precipitate Formation From K_{sp}

When two reacting solutions are mixed, we calculate the concentration of each ion in the solution in which precipitate is produced. The ionic product (Q), *i.e.,* the product of concentration of ions is then calculated.

If $Q > K_{sp}$, then precipitation will take place.

If $Q < K_{sp}$, then no precipitation will occur.

If $Q = K_{sp}$, the reaction is at equilibrium.

Sample Problem 23 *The solubility product of* $BaSO_4$ *at* 25°C *is* 1.0×10^{-9}. *What would be the concentration of* H_2SO_4 *necessary to precipitate* $BaSO_4$ *from a solution of* 0.01 *M* Ba^{2+} *ions?*

(a) 10^{-10} (b) 10^{-9}

(c) 10^{-8} (d) 10^{-7}

Interpret (*d*) Precipitation will take place when, ionic product > solubility product

$$\underset{}{BaSO_4} \rightleftharpoons \underset{0.01}{Ba^{2+}} + \underset{s}{SO_4^{2-}}$$

$$\because \quad K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

$$\therefore \quad S = \frac{1.0 \times 10^{-9}}{0.01} = 10^{-7} \text{ mol/L}$$

Sample **Problem 24** *What is the maximum concentration of equimolar solutions of ferrous sulphate and sodium sulphide so that when mixed in equal volumes, there is no precipitation of iron sulphide? (For iron sulphide,* $K_{sp} = 6.3 \times 10^{-18}$*)* **[NCERT]**

(*a*) 2.51×10^{-18}

(*b*) 2.51×10^{-9}

(*c*) 5.02×10^{-18}

(*d*) 5.02×10^{-9}

Interpret (*d*) FeS is at the point of precipitation when

$$[Fe^{2+}][S^{2-}] = K_{sp}$$

$$[Fe^{2+}] = [S^{2-}] = \sqrt{K_{sp}} = \sqrt{6.3 \times 10^{-10}}$$

$$[Fe^{2+}] = [S^{2-}] = 2.51 \times 10^{-9} \text{ M}$$

Since, equimolar solutions are to be mixed, hence on mixing concentration is halved. Thus, in original solution

$$[FeSO_4] = [Na_2S] = 2 \times 2.51 \times 10^{-9} \text{ M}$$
$$= 5.02 \times 10^{-9} \text{ M}$$

Relation between S and K_{sp} in the Presence of Common Ion

Let S is the solubility of silver chromate,

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$$

The solubility product of Ag_2CrO_4 is

$$K_{sp} = (2s)^2 \times s = 4s^3 \qquad \text{... (i)}$$

Now suppose that x mol/ L of $AgNO_3$ is added and in this solution, the solubility of Ag_2CrO_4 is s' then

$$[Ag^+] = 2s' + x \text{ and } [CrO_4^{2-}] = s'$$

so
$$K_{sp} = (2s' + x)(s') \qquad \text{...(ii)}$$

Eqs. (i) and (ii) can be used to find s'.

If K_{sp} is very small, we may neglect $2s'$ against x in (ii) and it becomes

$$K_{sp} = xs' \qquad \text{...(iii)}$$

Difference between Ionic Product and Solubility Product

Both ionic product and solubility product represent the product of the concentrations of the ions in the solution. Ionic product is applicable to all types of solutions, either unsaturated or saturated and varies accordingly. On the other hand, solubility product is applied only to a saturated solution in which there exists a dynamic equilibrium between the undissolved salt and the ions present in the solution.

Caution Point *When the ionic product is less than the solubility product, the solution is unsaturated and the solution contain only ions and no undissociated salt.*

Applications of Solubility Product

Solubility product found its applications in following respects.

(a) Calculation of Remaining Concentration After Precipitation

Remaining concentration of an ion after precipitation may be calculated as

$$[A^+]_{\text{left}} = \frac{K_{sp}[AB]}{[B^-]}$$

Percentage precipitation of an ion

$$= \left[\frac{\text{initial conc.} - \text{left conc.}}{\text{initial conc.}}\right] \times 100$$

(b) Salting out Action of Soap

Soaps are sodium salts of higher fatty acids. A saturated solution of soap ($RCOONa$) show precipitation of soap on addition of sodium chloride. This is because of the fact that an increase in Na^+ ion concentration helps in crossing over $[Na^+][RCOO^-]$ to their K_{sp} value.

$$\begin{array}{r} RCOONa \rightleftharpoons \boxed{Na^+} + RCOO^- \\ NaCl \rightleftharpoons \boxed{Na^+} + Cl^- \\ \text{common ion} \end{array}$$

(c) Purification of Common Salt

HCl gas is circulated through the saturated solution of common salt (NaCl). Thus, the concentration of Cl^- ions increases considerably in the solution due to ionisation of HCl. Hence, the ionic product $[Na^+][Cl^-]$ exceeds to their K_{sp} value and therefore, pure NaCl precipitates out from the solution.

(d) In Qualitative Analysis

Principle of selective precipitation is used in qualitative analysis of a mixture containing all the common cations. In selective precipitation, the precipitation of only cation is brought about at a time. The cations are divided into different groups for this purpose.

(i) **Group I** contains Ag^+, Pb^{2+} and Hg_2^{2+} which are precipitated as chlorides by adding excess of dil HCl.

K_{sp} of their chlorides is very low and is easily exceeded. The K_{sp} of other chlorides is comparatively high.

(ii) **Group II** contains Hg^{2+}, Cd^{2+}, Bi^{3+}, Cu^{2+} and Sn^{4+}, which are precipitated as sulphides by passing H_2S. K_{sp} of their sulphides is low, thus very small concentration of S^{2-} is needed. *The passage of* H_2S *in acidic medium, due to common ion effect results in low concentration of* S^{2-}, *just sufficient for precipitation of these sulphides.*

$$HCl \rightleftharpoons \boxed{H^+} + Cl^-$$
$$H_2S \rightleftharpoons \boxed{2H^+} + S^{2-}$$

common ion

The ions $Mn^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}$ (which belong to IV group) may also precipitate as sulphide, but their sulphides have high K_{sp}, hence, not precipitated in this step.

(iii) **Group III** contains Al^{3+}, Fe^{3+}, Cr^{3+} which are precipitated as hydroxide. The K_{sp} values of their hydroxides are extremely low, thus a very small quantity of OH^- ions is needed. **This is obtained by adding NH_4Cl followed by NH_4OH** (common ion effect).

$$NH_4Cl \rightleftharpoons \boxed{NH_4^+} + Cl^-$$
$$NH_4OH \rightleftharpoons \boxed{NH_4^+} + OH^-$$

common ion

The ions like Zn^{2+}, Mn^{2+} (of IV group) and Mg^{2+} (of VI group) have high K_{sp} of their hydroxide hence, these are not precipitated in this step.

(iv) **Group IV** contains Mn^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+} which are precipitated as sulphides. The K_{sp} of these sulphides are high. *The required amount of* S^{2-} *ions are provided by passing* H_2S *in the presence of* NH_4OH. *Here,* H_2S *is dissociated to a larger extent due to alkaline nature of testing solution*

(v) **Group V** contains $Mg^{2+}, Ba^{2+}, Sr^{2+}$ and Ca^{2+} which are precipitated as carbonates by adding an excess of sodium carbonate solution.

(vi) **Group VI** contains Mg^{2+}, Na^+ and K^+, Mg^{2+} is precipitated as its phosphate while remaining ions, if present in the mixture, are identified through individual testing by the flame test.

Simultaneous Solubility

Solubility of two eletrolytes having common ion, when they are dissolved in the same solution, is called **simultaneous solubility.** *e.g.,*

(i) Solubility of AgBr and AgSCN, when dissolved together.

(ii) Solubility of CaF_2 and SrF_2, when dissolved together.

(iii) Solubility of MgF_2 and CaF_2, when dissolved together.

Sample Problem 25 *If* K_{sp} $AgCNS = 1 \times 10^{-12}$ *and* K_{sp} $AgBr = 5 \times 10^{-13}$ *then the value of simultanoeus solubility of* AgCNS *and* AgBr *in a solution of water will be*

(a) $8.16 \times 10^{-7}, 4.08 \times 10^{-7}$ (b) $4.08 \times 10^{-7}, 8.16 \times 10^{-7}$

(c) 8.16, 4.08 (d) $1 \times 10^{-12}, 5 \times 10^{-13}$

Interpret (a) Let the solubility of AgCNS and AgBr in water are x and y respectively.

$$AgCNS \rightleftharpoons \underset{x}{Ag^+} + \underset{x}{CNS^-}$$
$$AgBr \rightleftharpoons \underset{y}{Ag^+} + \underset{y}{Br^-}$$

$\therefore$ $[Ag^+] = (x + y), [CNS^-] = x, [Br^-] = y$

$K_{sp}[AgCNS] = [Ag^+][CNS^-] = x(x + y)$

$\Rightarrow$ $1 \times 10^{-12} = x(x + y)$ ...(i)

and, $K_{sp}[AgBr] = [Ag^+][Br^-] = y(x + y)$

$\Rightarrow$ $5 \times 10^{-13} = y(x + y)$ ...(ii)

On solving Eq. (i) and (ii), we get

$$x = 8.16 \times 10^{-7} \text{ mol/L}$$
$$y = 4.08 \times 10^{-7} \text{ mol/L}$$

6.17 Buffer Solution

The solution, which maintains its pH constant or reserve acidic or basic nature even upon addition of small amounts of acid or base, is called **buffer solution.** The ability of buffer solution to resist changes in pH on addition of acid or base is called **buffer action.**

Characteristics of a Buffer Solution

A buffer solution should exhibit following characteristics

1. Buffer solutions posses a definite pH value.
2. Their pH value remains constant on keeping long or dilution.
3. The pH value is not changed on the addition of a strong acid in acidic buffer and a strong base in basic buffer.

Preparation of Buffer

A buffer solution can be obtained.

1. By mixing an acid salt with a normal salt of a polybasic acid, *e.g.,* $Na_2HPO_4 + Na_3PO_4$ or a salt of weak acid and a weak base, such as CH_3COONH_4 (*natural buffer*).
2. By a solution of ampholyte. The ampholytes or amphoteric electrolytes are the substances which show properties of both an acid and a base. Proteins and amino acids are the examples of such electrolytes.

3. By mixing a weak acid with its salt of strong base. These are called *acidic buffer. e.g.,*
   - (i) $CH_3COOH + CH_3COONa$
   - (ii) Boric acid + Borax
   - (iii) Phthalic acid + Potassium acid phthalate
4. By mixing a weak base with its salt of strong acid. These are called *basic buffer. e.g.,*
   - (i) $NH_4OH + NH_4Cl$
   - (ii) Glycine + Glycine hydrochloride

Acidic Buffer

A buffer solution pH of which is less than 7 is called **acidic buffer.** It contains equimolal quantities of weak acid and its salt with a strong base, *e.g.,* $CH_3COOH + CH_3COONa$; boric acid + borax; phthalic acid + potassium phthalate.

Mechanism of Buffer Action

Consider a solution containing CH_3COOH and CH_3COONa, which dissociate as follows

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \quad \text{(feebly ionised)}$$

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+ \text{(completely ionised)}$$

$$H_2O \rightleftharpoons H^+ + OH^- \quad \text{(very weakly ionised)}$$

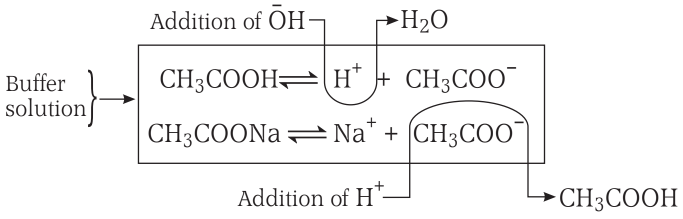
***Case* I** Now suppose we add a drop of conc HCl (a strong electrolyte) to the above solution. HCl immediately ionises as $HCl \rightleftharpoons H^+ + Cl^-$. These H^+ ions combine with CH_3COO^- ions present in the solution to form CH_3COOH, which ionises to a slight extent. This means that CH_3COO^- and H^+ ions cannot exist together in solution to a large extent. Hence, even addition of HCl, a strong electrolyte does not produce any appreciable change in H^+ ion concentration or pH of the solution.

***Case* II** When a drop of NaOH is added to it, the OH^- ions react with undissociated acid to form H_2O molecules.

$$CH_3COOH + OH^- \longrightarrow CH_3COO^- + H_2O$$

Again, pH remains unchanged.

The mechanism of acidic buffer can be summarized as



It is clear from the above mechanism that the reserve acidity is due to the presence of CH_3COOH and reserve alkalinity is due to the presence of CH_3COO^-.

pH of Acidic Buffer

pH of an acidic buffer is given by **Henderson-Hesselbalch equation** or **Henderson equation** which is as

$$pH = pK_a + \log\frac{[salt]}{[acid]}$$

where, K_a is dissociation constant of the acid.

Basic Buffer

A buffer solution having pH more than 7 is called **basic buffer.** It is obtained by mixing equimolal amounts of a weak base and its salt with strong acid, *e.g.,* $NH_4OH + NH_4Cl$, glycine + glycine hydrochloride.

Mechanism of Buffer Action

The buffer action of a basic buffer can be similarly explained by taking a solution of weak base (NH_4OH) and one of its salt (NH_4Cl). The solution contains a very small concentration of OH^- ions in the solution because NH_4OH is slightly ionised. Morever, common NH_4^+ ions from highly ionised NH_4Cl further suppress the ionisation of NH_4OH, a weak electrolyte.

$$NH_4OH \rightleftharpoons NH_4^+ + OH^- \quad \text{(feebly ionised)}$$

$$NH_4Cl \longrightarrow NH_4^+ + Cl^- \text{(completely ionised)}$$

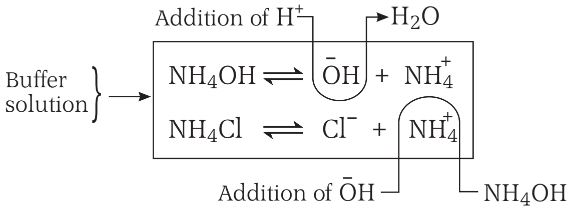
***Case* I** When a drop of NaOH is added to it, the OH^- ions from it, combined with NH_4^+ ions present in the solution to form NH_4OH which ionises to slight extent. Thus, the addition of NaOH, a strong electrolyte, does not produce a marked change in the pH of the solution.

***Case* II** Now suppose we add a drop of conc HCl, a strong electrolyte to the above solution. HCl immediately ionises as $HCl \rightleftharpoons H^+ + Cl^-$. The H^+ ions react with undissociated base to form H_2O molecules.

$$NH_4OH + H^+ \longrightarrow NH_4^+ + H_2O$$

Again, pH remains unchanged.

The mechanism of basic buffer can be summarised as



It is clear from the above mechanism that the reserve acidity is due to the presence of NH_4^+ and reserve alkalinity is due to the presence of NH_4OH.

pH of a Basic Buffer

It is calculated through **Henderson-Hesselbalch equation** or **Henderson equation** and can be given as

$$\text{pOH} = \text{p}K_b + \log\frac{[\text{salt}]}{[\text{base}]} \quad \text{and} \quad \text{pH} = 14 - \text{pOH}$$

Sample Problem 26 *A weak acid* HA *after treatment with* 1.2 *mL of* 0.1*M strong base has a pH of* 5. *At the end point, the volume of same base required is* 26.6 *mL. The value of* K_a *is*

(a) 8.2×10^{-6} (b) 6.4×10^{-6}

(c) 5.3×10^{-5} (d) 2.4×10^{-6}

Interpret (a) For complete neutralisation,

Total millieq. of acid = millieq. of base = $26.6 \times 0.1 = 2.66$

For partial neutralisation

$$\begin{array}{llcll} HA & + \ BOH & \longrightarrow & BA & + \ H_2O \\ 2.66 & 1.2 & & 0 & 0 \quad \text{before reaction} \\ 1.46 & 0 & & 1.2 & 1.2 \quad \text{after reaction} \end{array}$$

The resultant mixture has HA and BA and thus acts as buffer.

$$\because \quad \text{pH} = -\log K_a + \log\frac{[\text{salt}]}{[\text{acid}]}$$

$$5 = -\log K_a + \log\frac{1.2}{1.46} \quad \text{or} \quad K_a = 8.21 \times 10^{-6}$$

Buffer Capacity

Buffer capacity is quantitatively defined as the number of moles of acid or base added in 1 L of solution to change the pH by unity.

Buffer capacity (ϕ)

$$= \frac{\text{no. of moles of acid or base added to 1 L of buffer}}{\text{change in pH}}$$

The ability of buffer mixtures to maintain almost constant pH value is based on the fact that individual components combine with the H^+ or OH^- ions of acids or bases added to the solution (or formed as a result of reactions). This ability however depends on the concentrations of the components in the buffer mixture. For example, if more than 0.1 mole of HCl or NaOH is added to 1 L of 0.1 N ammonium buffer mixture ($NH_4OH + NH_4Cl$ at 0.1 N concentrations), a very large change of pH is obtained in either case.

This is due to the fact that the amount of NH_4OH or NH_4Cl available are not sufficient to combine with the H^+ or OH^- ions. Thus, excess of added strong acid or strong base remains in the solution and hence, causes a sharp change in pH value. Thus, *every buffer mixture maintains a practically constant pH value only up to a certain limiting amount of added acid or alkali, i.e., it has a definite buffer capacity.*

The higher the concentrations of the components of a buffer mixture, the greater will be the buffer capacity.

Buffer capacity is maximum

(i) When [salt] = [acid], *i.e.,* pH = pK_a for acidic buffer.

(ii) When [salt] = [base], *i.e.,* pH = 14 − pK_b or pK_w − pK_b for basic buffer.

Under above conditions the buffer is called **efficient.**

Sample Problem 27 *When* 0.01 *moles of sodium hydroxide are added to a buffer solution, its pH changes from* 4.745 *to* 4.815. *The buffer capacity of the buffer solution is*

(a) 0.14 (b) 0.36 (c) 0.27 (d) 0.04

Interpret (a) Buffer capacity

$$= \frac{\text{no. of moles of acid or base added to 1 L of buffer}}{\text{change in pH}}$$

$$= \frac{0.01}{4.815 - 4.745} = \frac{0.01}{0.07} = 0.14$$

Applications of Buffer Solution

1. Normal blood has pH of 7.4. This pH is maintained by buffer action of following two buffers
   (i) buffer of carbonic acid (H_2CO_3 and $NaHCO_3$)
   (ii) buffer of phosphoric acid ($H_2PO_4^-$, HPO_4^{2-})
2. Buffers are used to determine pH with the help of indicators.
3. Buffers are used for the removal of phosphate ion in the qualitative inorganic analysis after second group. For this purpose $CH_3COOH + CH_3COONa$ buffer is used.
4. $CH_3COOH + CH_3COONa$ is used for the precipitation of lead chromate quantitatively in gravimetric analysis.
5. $NH_4Cl + NH_4OH$ buffer is used for the precipitation of hydroxides of third group of qualitative analysis.
6. Buffers find numerous applications in industrial processes, like manufacture of paper, drugs, dyes, inks, paints etc.
7. Buffer solutions are applied for digestion process of food.
8. These are used as preservatives of foods and fruits.
9. Buffer can be used for preservation of many dairy and agricultural products.

Check Point 5

1. Explain why solubility of AgCl is more in water than in a solution of common salt?
2. Explain why Zn^{2+} is precipitated by passing H_2S in ammoniacal solution but it is not precipitated from acidic solution.
3. Degree of dissociation is more in the presence of polar solvents. Explain, why?
4. A mixture of sodium acetate and acetic acid resists change in its pH value on adding acids or bases. Explain, why?
5. Explain why a solution containing a strong base and its salt does not act as a buffer solution?

WORKED **OUT**
Examples

Example 1 *Following equilibrium is studied by taking 1 mole of* N_2 *and 3 moles of* H_2 *in 1 L flask at a given temperature*

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$NH_3(g)$ *formed at equilibrium is neutralised by* 100 *mL of* 1 *M* HCl. *The value of equilibrium constant,* K_c *will be*

(a) 3.7×10^{-2} (b) 1.22×10^{-2}
(c) 2.25×10^{-3} (d) 4.55×10^{-4}

Solution (d) $NH_3(g) + HCl(aq) \rightleftharpoons NH_4Cl(aq)$

$$\Rightarrow \quad 1 \text{ mole of } NH_3 = 1 \text{ mole of HCl}$$

$$100 \text{ mL of } 1 \text{ M HCl} \equiv 100 \text{ millimole of HCl}$$
$$= 0.1 \text{ mole of HCl}$$
$$= 0.1 \text{ mole of } NH_3$$

$$\begin{array}{cccl} N_2(g) & + \; 3H_2(g) & \rightleftharpoons \; 2NH_3(g) & \\ 1 & 3 & 0 & \text{Initially} \\ 1-x & 3-3x & 2x & \text{At equilibrium} \end{array}$$

$$\Rightarrow \quad 2x = 0.1 \quad i.e., \quad x = \frac{0.1}{2} = 0.05 \text{ mol}$$

and $\quad V = 1 \text{ L}$

Therefore,

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$= \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{1-x}{V}\right)\left(\frac{3-3x}{V}\right)^3}$$

$$= \frac{4x^2V^2}{27(1-x)^4}$$

$$= \frac{4 \times (0.05)^2 \times (1)^2}{27(1-0.05)^4}$$

$$= 4.55 \times 10^{-4}$$

Example 2 *What is the value of* K_c *for the equilibrium,*

$$HA + OH^- \rightleftharpoons H_2O + A^- \, ?$$

Given,

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-, \qquad K_1 = 2 \times 10^{-5}$$

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- \qquad K_2 = 1 \times 10^{-14}$$

(a) 2×10^{-9} (b) 4×10^{-8}
(c) 2×10^{-8} (d) 6×10^{-9}

Solution (a) $HA + H_2O \rightleftharpoons H_3O^+ + A^-; \quad K_1 = 2 \times 10^{-5}$ ...(i)

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-; K_2 = 1 \times 10^{-14} \text{ ...(ii)}$$

$$H_3O^+ + OH^- \rightleftharpoons H_2O + H_2O; \; K_2' = 1 \times 10^{14} \text{ ...(iii)}$$

$$\left(\because \; K_2' = \frac{1}{K_2}\right)$$

On adding Eqs. (i) and (iii), we get

$$HA + OH^- \rightleftharpoons H_2O + A^- \qquad K = K_1K_2' = 2 \times 10^{+9}$$

Example 3 *The degree of dissociation of* I_2 *molecule at* $1000°C$ *and under atmospheric pressure is* 40% *by volume. The total pressure on the gas at equilibrium so that the dissociation is reduced to* 20% *at the same temperature, will be*

(a) 4.57 *atm* (b) 2.83 *atm*
(c) 5.33 *atm* (d) 7.57 *atm*

Solution (c) $I_2(g) \rightleftharpoons 2I(g)$

$$\begin{array}{llll} \text{At } t = 0 & 1 & 0 & \\ \text{At equilibrium} & 1-x & 2x & x = 0.40, p_1 = 1 \text{ atm in case I} \\ & 1-y & 2y & y = 0.20, p_2 = \text{? in case II} \end{array}$$

$$K_p = \frac{p_1^2}{p_{1_2}} = \frac{4x^2p_1}{(1-x)} = \frac{4y^2p_2}{(1-y)}$$

$$\therefore \quad \frac{4 \times 0.16 \times 1}{(1-0.4)} = \frac{4 \times 0.04 \times p_2}{(1-0.2)}$$

$$\Rightarrow \quad p_2 = 5.33 \text{ atm}$$

Example 4 *If* 2.0 *mole each of A and B were allowed to come to equilibrium at* 300 *K for the reaction*

$$A + B \rightleftharpoons C + D, \qquad \Delta G° = 460 \text{ cal}$$

the equilibrium concentration ratio of C to A will be

(a) 1 (b) $\frac{1}{2}$
(c) 0.68 (d) 0.46

Solution (c) We know, $-\Delta G° = 2.303 \, RT \log K$

$$\therefore \quad \log K = \frac{-\Delta G°}{2.303 \, RT}$$

$$= \frac{-460}{2.303 \times 2 \times 300}$$

$$= -0.333$$

$$\therefore \qquad K = 0.464$$

Also, at equilibrium

$$[A] = [B] \quad \text{and} \quad [C] = [D]$$

$$\therefore \qquad K = \frac{[C][D]}{[A][B]} = \frac{[C]^2}{[A]^2} = 0.464$$

$$\Rightarrow \qquad \frac{[C]}{[A]} = 0.681$$

Example 5 *In what manner will increase of pressure affect the equation,* $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$ *?*

(a) *Shift in the reverse direction*
(b) *Increase in the yield of* H_2
(c) *Shift in the forward reaction*
(d) *No effect*

Solution (a) Since for the given reaction,

$$n_R = 1$$

$$n_p = 2$$

$$\therefore \qquad \Delta n_g = n_p - n_R = 1$$

Positive value of Δn_g shows shifting of equilibrium in reverse direction on applying pressure.

Example 6 *A solution which is* 10^{-3} *M each in* Mn^{2+}, Fe^{2+}, Zn^{2+} *and* Hg^{2+} *is treated with* 10^{-16} *M sulphide ion. If* K_{sp} *of* MnS, FeS, ZnS *and* HgS *are* 10^{-15}, 10^{-23}, 10^{-20} *and* 10^{-54} *respectively, which one will precipitate first?*

(a) FeS (b) HgS
(c) ZnS (d) MgS

Solution (b) Precipitation will occur only when

$$Q_{ip} > K_{sp}$$

Salt	Q_{ip}	K_{sp}
MnS	$10^{-3} \times 10^{-16} = 10^{-19}$	10^{-15}
FeS	$10^{-3} \times 10^{-16} = 10^{-19}$	10^{-23}
ZnS	$10^{-3} \times 10^{-16} = 10^{-19}$	10^{-20}
HgS	$10^{-3} \times 10^{-16} = 10^{-19}$	10^{-54}

Therefore, HgS will be precipitated first.

Example 7 *The solubility product of* $Ag_2C_2O_4$ *at* 25°C *is* 1.29×10^{-11} *mol*^{3} *L*$^{-3}$. *A solution of* $K_2C_2O_4$ *containing* 0.1520 *mole in* 500 *mL of water is shaken with excess of* Ag_2CO_3 *till the following equilibrium is reached.*

$$Ag_2CO_3 + K_2C_2O_4 \rightleftharpoons Ag_2C_2O_4 + K_2CO_3$$

At equilibrium, the solution contains 0.0358 *mole of* K_2CO_3. *Assuming the degree of dissociation of* $K_2C_2O_4$ *and* K_2CO_3 *to be equal, the solubility product of* Ag_2CO_3 *will be*

(a) 1.96×10^{-12} (b) 8.48×10^{-11}
(c) 1.29×10^{-11} (d) 3.97×10^{-12}

Solution (d) $Ag_2CO_3 + K_2C_2O_4 \rightleftharpoons Ag_2C_2O_4 + K_2CO_3$

	$K_2C_2O_4$	K_2CO_3
At $t = 0$	0.1520 mol	0
At equilibrium	0.1520 – 0.0358 = 0.1162 mol	0.0358 mol
Concentration	2×0.1162 = 0.2324 M	2×0.0358 = 0.0716 M

$$K_{sp}(Ag_2C_2O_4) = [Ag^+]^2[C_2O_4^{2-}]$$

$$\text{or,} \qquad [Ag^+] = \left[\frac{K_{sp}\,(Ag_2C_2O_4)}{[C_2O_4^{2-}]}\right]^{1/2} \qquad \ldots\text{(i)}$$

$$\text{and,} \qquad K_{sp}(Ag_2CO_3) = [Ag^+]^2[CO_3^{2-}]$$

$$\text{or} \qquad [Ag^+] = \left[\frac{K_{sp}\,(Ag_2CO_3)}{[CO_3^{2-}]}\right]^{1/2} \qquad \ldots\text{(ii)}$$

From Eqs. (i) and (ii),

$$\left[\frac{K_{sp}\,(Ag_2C_2O_4)}{[C_2O_4^{2-}]}\right]^{1/2} = \left[\frac{K_{sp}(Ag_2CO_3)}{[CO_3^{2-}]}\right]^{1/2}$$

$$\text{or,} \qquad K_{sp}(Ag_2CO_3) = \frac{K_{sp}\,(Ag_2C_2O_4) \times [CO_3^{2-}]}{[C_2O_4^{2-}]}$$

$$= \frac{K_{sp}\,(Ag_2C_2O_4) \times [K_2CO_3]}{[K_2C_2O_4]}$$

$$= \frac{1.29 \times 10^{-11} \times 0.0716}{0.2324}$$

$$= 3.97 \times 10^{-12}\ \text{mol}^3\ \text{L}^{-3}$$

Example 8 *A solution has* 0.05 *M* Mg^{2+} *ions and* 0.05 *M* NH_3. *Calculate the concentration of* NH_4Cl *required to prevent the formation of* $Mg(OH)_2$ *in this solution.* K_{sp} *of* $Mg(OH)_2 = 9.0 \times 10^{-12}$ *and ionisation constant of* $NH_3 = 1.8 \times 10^{-5}$.

(a) 0.05 *M* (b) 0.067 *M*
(c) 2.0×10^{6} *M* (d) 1.8×10^{-10} *M*

Solution (b) The maximum concentration of OH^- ions that will precipitate $Mg(OH)_2$ is given by

$$K_{sp} = [Mg^{2+}][OH^-]^2$$

$$[OH^-]^2 = \frac{K_{sp}}{[Mg^{2+}]} = \frac{9.0 \times 10^{-12}}{0.05}$$

$$= 1.8 \times 10^{-10}$$

$$\text{or} \qquad [OH^-] = 1.34 \times 10^{-5}\ \text{M}$$

NH_3 is present in solution in the form of NH_4OH

$$\underset{0.05}{NH_3} + H_2O \rightleftharpoons \underset{0.05}{NH_4OH} \rightleftharpoons NH_4^+ + OH^-$$

The ionisation of NH_4OH is suppressed by the addition of strong electrolyte, NH_4Cl.

$$K_{NH_3} = K_{NH_4OH} = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

$$[NH_4^+] = \frac{K_{NH_4OH} \times [NH_4OH]}{[OH^-]}$$

$$= \frac{1.8 \times 10^{-5} \times 0.05}{1.34 \times 10^{-5}} = 0.067 \text{ M}$$

i.e., $[NH_4Cl] = 0.067$ M

Example 9 *What volume of 0.10 M sodium formate solution should be added to 50 mL of 0.05 M formic acid to produce a buffer solution of pH 4.0? (pK_a for formic acid is 3.80).*

(*a*) 3.96 *mL* (*b*) 25 *mL*
(*c*) 39.6 *mL* (*d*) 100 *mL*

Solution (*c*) Let *x* mL of 0.10 M sodium formate is added.

Number of moles in *x* mL of 0.10 M sodium formate $= \frac{0.10}{1000} \times x$

Number of moles in 50 mL of 0.05 M formic acid $= \frac{0.05}{1000} \times 50$

$$\therefore \quad \frac{[\text{Sodium formate}]}{[\text{Formic acid}]} = \frac{\frac{0.10 \times x}{1000}}{\frac{0.05 \times 50}{1000}} = 0.04\,x$$

From Henderson's equation,

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$4.0 = 3.80 + \log 0.04x$$

$$\log 0.04x = 0.2$$

$$\therefore \quad x = 39.6 \text{ mL}$$

Example 10 *An aqueous solution contains 10% ammonia by mass and has a density 0.99 g cm^{-3}. If K_a for NH_4^+ is 5.0×10^{-10} M, the value of hydroxyl ion concentration will be*

(*a*) 9.27×10^{-13} (*b*) 9.27×10^{-11}
(*c*) 9.27×10^{-10} (*d*) 9.27×10^{-6}

Solution (*a*) Mass of 1 L solution $= 1000 \times 0.99$ g $= 990$ g

NH_3 present in 990 g solution $= 10\%$ of $990 = 99$ g

1 L solution contains $= \frac{99}{17} = 5.8$ mol NH_3

$$\begin{array}{lccccccc} & NH_3 & + H_2O & \rightleftharpoons & NH_4OH & \rightleftharpoons & NH_4^+ & + OH^- \\ \text{At } t = 0 & 5.8 & & & & & 0 & 0 \\ \text{At equilibrium} & (5.8 - x) & & & & & x & x \end{array}$$

$$\therefore \quad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x \cdot x}{(5.8 - x)} \approx \frac{x^2}{5.8} \quad \text{...(i)}$$

$$\text{Again,} \quad K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{5.0 \times 10^{-10}} = 2 \times 10^{-5} \quad \text{...(ii)}$$

From Eqs. (i) and (ii), we get

$$\frac{x^2}{5.8} = 2 \times 10^{-5}$$

$$x^2 = 5.8 \times 2 \times 10^{-5}$$

i.e., $[OH^-] = x = 1.078 \times 10^{-2}$ M

$\because$ $[H^+][OH^-] = 10^{-14}$

$$\therefore \quad [H^+] = \frac{10^{-14}}{1.078 \times 10^{-2}} = 9.27 \times 10^{-13} \text{ M}$$

Example 11 *How much must be a 0.02 M solution of sodium acetate be diluted at 25°C in order to double the degree of hydrolysis?*

(*a*) 0.25 *times* (*b*) 2 *times*
(*c*) 4 *times* (*d*) 8 *times*

Solution (*c*) Let *h* be the initial degree of hydrolysis.

$$K_h = Ch^2 = 0.2 \times h^2 \quad \text{...(i)}$$

Let the concentration becomes C_1 when degree of hydrolysis is 2*h*.

$$K_h = C_1(2h)^2 = 4C_1h^2 \quad \text{...(ii)}$$

Dividing Eqs. (i) by (ii),

$$\frac{K_h}{K_h} = \frac{0.2\,h^2}{4C_1h^2}, \quad 1 = \frac{0.2}{4C_1}, \quad C_1 = \frac{0.2}{4} = 0.05 \text{ M}$$

Now, from, $M_1V_1 = M_2V_2$, $0.2\,V_1 = 0.05\,V_2$

$$V_2 = \frac{0.2}{0.05} V_1 = 4V_1$$

Therefore, the solution must be diluted four times

Start **Practice** *for* JEE Main

Round I (Topically Divided Problems)

Equilibria in Physical and Chemical Processes

1. In the thermal decomposition of potassium chlorate given as

$2KClO_3 \longrightarrow 2KCl + 3O_2$, law of mass action

(a) can be applied
(b) cannot be applied
(c) can be applied at low temperature
(d) can be applied at high temperature and pressure

2. Which of the following is a characteristic of a reversible reaction?

(a) It can never proceed to completion
(b) It can be influenced by a catalyst
(c) Number of moles of reactants and products are equal
(d) None of the above

3. Which of the following is not a general characteristic of equilibria involving physical processes? **[NCERT Exemplar]**

(a) Equilibrium is possible only in a closed system at a given temperature
(b) All measurable properties of the system remain constant
(c) All the physical processes stop at equilibrium
(d) The opposing processes occur at the same rate and there is dynamic but stable condition

4. In chemical reaction, $A \rightleftharpoons B$, the system will be known in equilibrium when

(a) 50% of A changes to B
(b) A completely changes to B
(c) only 10% of A changes to B
(d) the rate of change of A to B and B to A on both the sides are same

Law of Mass Action, *K* (K_p and K_c) and their Significance

5. The active mass of 45 g of KCl in a 3 L flask would be

(a) 0.20
(b) 2.0
(c) 3
(d) 4

6. According to the law of mass action, rate of a chemical reaction is proportional to

(a) molar concentration of reactants
(b) concentration of reactants
(c) concentration of products
(d) molar concentration of products

7. In the equilibrium, $AB \rightleftharpoons A + B$, if the equilibrium concentration of A is doubled, the equilibrium concentration of B would become

(a) half
(b) twice
(c) $\frac{1}{4}$th
(d) $\frac{1}{8}$th

8. What is the equilibrium expression for the reaction,

$$P_4(s) + 5O_2(g) \rightleftharpoons P_4O_{10}(s) ?$$

(a) $K_c = \frac{1}{[O_2]^5}$
(b) $K_c = [O_2]^5$
(c) $K_c = \frac{[P_4O_{10}]}{5[P_4][O_2]}$
(d) $K_c = \frac{[P_4O_{10}]}{[P_4][O_2]^5}$

9. The equilibrium constant in a reversible reaction at a given temperature

(a) does not depend on the initial concentrations
(b) depends on the initial concentrations of the reactants
(c) depends on the concentration of the products at equilibrium
(d) it is not a characteristic of the reaction

10. $A + B \rightleftharpoons C + D$. If finally the concentration of A and B are equal but at equilibrium, concentration of D will be twice of that of A then what will be the equilibrium constant of reaction?

(a) 2 (b) 4
(c) $\frac{2}{3}$ (d) $\frac{4}{5}$

11. In the reaction, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, the equilibrium concentration of PCl_5 and PCl_3 are 0.4 and 0.2 mol/L respectively. If the value of K_c is 0.5 what is the concentration of Cl_2 in mol/L?

(a) 0.5 (b) 1.0 (c) 1.5 (d) 2.0

12. The rate constant for forward reaction and backward reaction of hydrolysis of ester are 1.1×10^{-2} and 1.5×10^{-3} per minute respectively. Equilibrium constant for the reaction is

$$CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$$

(a) 33.7 (b) 7.33
(c) 5.33 (d) 33.3

13. The value of K_c for the reaction,

$$3O_2(g) \rightleftharpoons 2O_3(g)$$

is 2.0×10^{-50} at 25°C. If the equilibrium concentration of O_2 in air at 25°C is 1.6×10^{-2}, what is the concentration of O_3? **[NCERT]**

(a) $2.0 \times 10^{-50} \times (1.6 \times 10^{-2})^3$
(b) 2.86×10^{-28}
(c) $(1.6 \times 10^{-2})^4$
(d) Both (a) and (b)

14. A sample of $HI(g)$ is placed in a flask at a pressure of 0.2 atm. At equilibrium, the partial pressure of $HI(g)$ is 0.04 atm. What is K_p for the given equilibrium? **[NCERT]**

(a) 3 (b) 4 (c) 6 (d) 8

15. A sample of pure PCl_5 was introduced into an evacuated vessel at 473 K. After equilibrium was attained, concentration of PCl_5 was found to be 0.5×10^{-1} mol L^{-1}. If value of K_c is 8.3×10^{-3}, what is the concentration of PCl_3 at equilibrium?

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$ **[NCERT]**

(a) 4.15×10^{-5} (b) 1.85×10^{-4}
(c) 2×10^{-4} (d) 2×10^{-2}

16. The equilibrium concentration of ICl in the equilibrium when the initial concentration of ICl was 0.78 M is

$$2ICl(g) \rightleftharpoons I_2(g) + Cl_2(g);$$ **[NCERT]**

(a) 0.28 (b) 0.25
(c) 0.38 (d) 0.45

17. For the reaction, $H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g)$ if the initial concentration of $[H_2] = [CO_2]$ and x mol/L of hydrogen is consumed at equilibrium, the correct expression of K_p is

(a) $\frac{x^2}{(1-x)^2}$ (b) $\frac{x^2}{(2+x)^2}$
(c) $\frac{x^2}{1-x^3}$ (d) $\frac{(1+x)^2}{(1-x)^2}$

18. The reaction,

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

is at equilibrium at 1300 K in a 1 L flask. It also contains 0.30 mole of CO, 0.10 mole of H_2 and 0.02 mole of H_2O and an unknown amount of CH_4 in the flask. Determine the concentration of CH_4 in the mixture. The equilibrium constant, K_c for the reaction at the given temperature is 3.90. **[NCERT]**

(a) 5.85×10^{-2} (b) 4.23×10^{-2}
(c) 5.02×10^{-3} (d) 5.22×10^{-4}

19. In which of the following reactions, the equilibrium remains unaffected on addition of small amount of argon at constant volume? **[NCERT Exemplar]**

(a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
(b) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
(c) $N_2(g) + 3H_2 \rightleftharpoons 2NH_3$
(d) The equilibrium will remain unaffected in all the three cases

20. Equilibrium constants K_1 and K_2 for the following equilibria

$$NO(g) + \frac{1}{2}O_2 \overset{K_1}{\rightleftharpoons} NO_2(g)$$

and, $2NO_2(g) \overset{K_2}{\rightleftharpoons} 2NO(g) + O_2(g)$ are related as

(a) $K_1 = \frac{1}{K_2}$ (b) $K_2 = \frac{1}{K_1}$
(c) $K_2 = \frac{1}{K_1^2}$ (d) $K_1 = \frac{1}{K_2^2}$

21. At 500 K, equilibrium constant, K_c, for the following reaction is 5.

$$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \rightleftharpoons HI(g)$$

What would be the equilibrium constant K_c for the reaction?

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$ **[NCERT Exemplar]**

(a) 0.04 (b) 0.4
(c) 25 (d) 2.5

22. At 450 K, $K_p = 2.0 \times 10^{10}$/bar for the given reaction at equilibrium,

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

The value of K_c at this temperature is **[NCERT]**

(a) 7.38×10^{11} (b) 5.24×10^{10}
(c) 5.41×10^{8} (d) 2.67×10^{7}

23. In which of the following reactions, the value of K_p will be equal to K_c?

(a) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ (b) $2NH_3 \rightleftharpoons N_2 + 3H_2$
(c) $H_2 + I_2 \rightleftharpoons 2HI$ (d) $2SO_2 + O_2 \rightleftharpoons 2SO_3$

24. We know that the relationship between K_c and K_p is $K_p = K_c(RT)^{\Delta n}$.

What would be the value of Δn for the reaction?

$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$ **[NCERT Exemplar]**

(a) 1 (b) 0.5
(c) 1.5 (d) 2

25. The unit of equilibrium constant, K for the reaction, $A + B \rightleftharpoons C$, would be

(a) mol L^{-1} (b) mol L
(c) L mol^{-1} (d) dimensionless

Gibbs Free Energy and Relation of α with Vapour Density

26. Ice and water are in equilibrium at 273 K, which of the following statements is correct?

(a) $G_{(ice)} > G_{(H_2O)}$ (b) $G_{(ice)} < G_{(H_2O)}$
(c) $G_{(ice)} = G_{(H_2O)} = 0$ (d) $G_{(ice)} = G_{(H_2O)} \neq 0$

27. Which of the following options will be correct for the stage of half completion of the reaction $A \rightleftharpoons B$? **[NCERT Exemplar]**

(a) $\Delta G^{\ominus} = 0$ (b) $\Delta G^{\ominus} > 0$
(c) $\Delta G^{\ominus} < 0$ (d) $\Delta G^{\ominus} = -RT \log 2$

28. For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, the standard free energy is $\Delta G^{\ominus} > 0$. The equilibrium constant (K) would be **[NCERT Exemplar]**

(a) $K = 0$ (b) $K > 1$
(c) $K = 1$ (d) $K < 1$

29. The vapour density of PCl_5 is 104.16, but when heated at 230°C, its vapour density is reduced to 62. The percentage of dissociation of PCl_5 at this temperature will be

(a) 6.8% (b) 68%
(c) 46% (d) 64%

30. The vapour density of N_2O_4 at a certain temperature is 30. What is the percentage dissociation of N_2O_4 at this temperature?

(a) 46.5% (b) 36.2%
(c) 53.3% (d) 64.2%

Le-Chatelier's Principle with Applications

31. According to Le-Chatelier's principle, if heat is given to solid-liquid system, then

(a) quantity of solid will reduce
(b) quantity of liquid will reduce
(c) temperature becomes constant
(d) temperature will decrease

32. What is the effect of pressure by doubling the volume on the following system at 500°C?

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

(a) Shift to product side (b) Shift to reactant side
(c) Liquifaction of HI (d) No effect

33. In the reaction, $A_2(g) + 4B_2(g) \rightleftharpoons 2AB_4(g), \Delta H < 0$, the formation of AB_4 will be favoured at

(a) low temperature, high pressure
(b) high temperature, low pressure
(c) low temperature, low pressure
(d) high temperature, high pressure

34. The equilibrium which remains unaffected by change in pressure of the reactants is

(a) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$
(b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
(c) $2O_3(g) \rightleftharpoons 3O_2(g)$
(d) $2NO_2 \rightleftharpoons N_2O_4(g)$

35. In the manufacture of NH_3 by Haber's process, the condition which would give maximum yield is

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + Q \text{ kcal}$$

(a) low temperature and high pressure
(b) low temperature, low pressure and low concentration of H_2
(c) high temperature, low pressure and low concentration
(d) high temperature, high pressure and high concentration

36. Under what conditions of temperature and pressure, the formation of atomic hydrogen from molecular hydrogen will be favoured most?

(a) High temperature and high pressure
(b) High temperature and low pressure
(c) Low temperature and low pressure
(d) Low temperature and high pressure

Electrolytes, Concepts of Acids and Bases (Including Ostwald's Dilution law)

37. The extent of ionisation increases
(a) with the increase in concentration
(b) on addition of excess water to the solution
(c) on decreasing the temperature of solution
(d) on stirring the solution vigorously

38. The degree of ionisation of a compound depends
(a) size of solute molecules
(b) nature of solute molecules
(c) nature of vessel used
(d) quantity of electricity passed

39. Which one is the strongest electrolyte in the following?
(a) NaCl (b) CH_3COOH
(c) NH_4OH (d) $C_6H_{12}O_6$

40. Theory of ionisation was given by
(a) Rutherford (b) Graham
(c) Faraday (d) Arrhenius

41. The conjugate base of NH_2^- is
(a) NH_3 (b) NH^{2-} (c) NH_4^+ (d) N_3^-

42. Diacidic base is
(a) $CH_2(OH)_2$ (b) $Ca(OH)_2$
(c) $CH_3CH(OH)_2$ (d) All of these

43. Which of the following behaves as both Lewis and Bronsted base?
(a) BF_3 (b) Cl^-
(c) CO (d) None of these

44. The species which acts as a Lewis but not a Bronsted acid is
(a) NH_2^- (b) O^{2-}
(c) BF_3 (d) OH^-

45. Which of the following is the strongest conjugate base?
(a) Cl^- (b) CH_3COO^-
(c) SO_4^{2-} (d) NO_2^-

46. Which of the following is a conjugated acid-base pair?
(a) HCl, NaOH (b) NH_4Cl, NH_4OH
(c) H_2SO_4, HSO_4^- (d) KCN, HCN

47. The ionisation constant of an acid, K_a, is the measure of strength of an acid. The K_a values of acetic acid, hypochlorous acid and formic acid are 1.74×10^{-5}, 3.0×10^{-8} and 1.8×10^{-4} respectively. Which of the following orders of pH of 0.1 mol dm^{-3} solutions of these acids is correct? **[NCERT** Exemplar]
(a) Acetic acid > hypochlorous acid > formic acid
(b) Hypochlorous acid > acetic acid > formic acid
(c) Formic acid > hypochlorous acid > acetic acid
(d) Formic acid > acetic acid > hypochlorous acid

48. Acidity of BF_3 can be explained on the basis of which of the following concepts? **[NCERT** Exemplar]
(a) Arrhenius concept
(b) Bronsted Lowry concept
(c) Lewis concept
(d) Bronsted Lowry as well as Lewis concept

49. The degree of dissociation of 0.1 M HCN solution is 0.01%. Its ionisation constant would be
(a) 10^{-3} (b) 10^{-5}
(c) 10^{-7} (d) 10^{-9}

50. The ionisation constant of acetic acid is 1.74×10^{-5}. The degree of dissociation of acetic acid in its 0.05 M solution and its pH are respectively **[NCERT]**
(a) 1.86×10^{-2}, 4 (b) 1.24×10^{-3}, 3
(c) 1.24×10^{-3}, 4 (d) 1.86×10^{-2}, 3

51. Ionisation constant of CH_3COOH is 1.7×10^{-5} and $[H^+]$ is 3.4×10^{-4}. Then, initial concentration of CH_3COOH molecules is
(a) 6.8×10^{-3} (b) 2.5×10^{-4}
(c) 3.5×10^{-3} (d) 4.5×10^{-3}

pH, Salt Hydrolysis, Buffer Solution

52. The pH of a sample of vinegar is 3.76. Calculate the concentration of hydrogen ion in it. **[NCERT]**
(a) 1.84×10^{-4} (b) 1.97×10^{-4}
(c) 1.738×10^{-4} (d) 1.283×10^{-4}

53. The pH of a 10^{-10} M NaOH solution is nearest to
(a) 10 (b) 7 (c) 4 (d) −10

54. 0.01 mole of lime (CaO) was dissolved in 100 cm^3 of water. Assuming the base is completely ionised in the solution, the pH of the solution will be
(a) 13.3 (b) 8.5 (c) 6 (d) 8

55. NaOH(*aq*), HCl(*aq*) and NaCl(*aq*) concentration of each is 10^{-3} M. Their pH will be respectively
(a) 10, 6, 2 (b) 11, 3, 7
(c) 10, 2, 6 (d) 3, 4, 7

56. pH of a solution of a strong acid is 5.0. What will be the pH of the solution obtained after diluting the given solution 100 times? **[NCERT** Exemplar]
(a) 5.8 (b) 6.7
(c) 9.3 (d) 13

57. To a 10 mL of 10^{-3} N H_2SO_4 solution water has been added to make the total volume 1 L. Its pOH would be

(a) 9
(b) 3
(c) 12
(d) 4

58. The pH of a solution formed by mixing equal volumes of two solutions, A and B of a strong acid having $pH = 6$ and $pH = 4$ respectively is **[NCERT Exemplar]**

(a) 5
(b) 4.3
(c) 6
(d) 5.5

59. pH of 0.08 mol dm^{-3} HOCl solution is 2.85. Calculate its ionisation constant. **[NCERT Exemplar]**

(a) 24.9×10^{-6}
(b) 28.6×10^{-5}
(c) 2.5×10^{-6}
(d) 24.9×10^{-5}

60. What will be the value of pH of 0.01 mol dm^{-3} $CH_3COOH\,(K_a = 1.74 \times 10^{-5})$? **[NCERT Exemplar]**

(a) 3.4
(b) 3.9
(c) 3.6
(d) 3.0

61. The pH of neutral water at 25°C is 7.0. As the temperature increases, ionisation of water increases, however, the concentration of H^+ ions and OH^- ions are equal. What will be the pH of pure water at 60°C? **[NCERT Exemplar]**

(a) Equal to 7.0
(b) Greater than 7.0
(c) Less than 7.0
(d) Equal to zero

62. What will be the pH and % α respectively for the salt BA of 0.1 M concentration? Given, K_a for $HA = 10^{-6}$ and K_b for $BOH = 10^{-6}$.

(a) 7, 10%
(b) 5, 10%
(c) 5, 0.1%
(d) 7, 1%

63. K_a for CH_3COOH is 1.8×10^{-5} and K_b for NH_4OH is 1.8×10^{-5}. The pH of ammonium acetate will be **[NCERT Exemplar]**

(a) 7.005
(b) 4.75
(c) 7.0
(d) between 6 and 7

64. An aqueous solution of sodium carbonate is alkaline because sodium carbonate is a salt of

(a) weak acid and weak base
(b) strong acid and weak base
(c) weak acid and strong base
(d) strong acid and strong base

65. The aqueous solution of $AlCl_3$ is acidic due to the hydrolysis of

(a) aluminium ion
(b) chloride ion
(c) Both aluminium and chloride ion
(d) None of the above

66. 0.5 M ammonium benzoate is hydrolysed to 0.25 per cent. Hence, its hydrolysis constant is

(a) 2.5×10^{-5}
(b) 1.25×10^{-5}
(c) 3.125×10^{-6}
(d) 6.25×10^{-6}

67. A weak acid HX has the dissociation constant 1×10^{-5} M. It forms a salt NaX on reaction with alkali. The degree of hydrolysis of 0.1 M solution of NaX is

(a) 0.0001%
(b) 0.01%
(c) 0.1%
(d) 0.15%

68. A buffer solution can be prepared from a mixture of

(i) sodium acetate and acetic acid in water
(ii) sodium acetate and hydrochloric acid in water
(iii) ammonia and ammonium chloride in water
(iv) ammonia and sodium hydroxide in water

(a) (i), (ii)
(b) (ii), (iii)
(c) (iii), (iv)
(d) (i), (iii)

69. How much sodium acetate should be added to 0.1 M solution of CH_3COOH to give a solution of $pH = 5.5$ (pK_a of $CH_3COOH = 4.5$)?

(a) 0.1 M
(b) 0.01 M
(c) 1.0 M
(d) 10.0 M

70. The pK_a of HCN is 9.30. The pH of a solution prepared by mixing 2.5 moles of KCN and 2.5 moles of HCN in water and making up the total volume of 500 mL, is

(a) 9.30
(b) 7.30
(c) 10.30
(d) 8.30

71. Which of the following will produce a buffer solution when mixed in equal volumes? **[NCERT Exemplar]**

(a) 0.1 mol dm^{-3} NH_4OH and 0.1 mol dm^{-3} HCl
(b) 0.05 mol dm^{-3} NH_4OH and 0.1 mol dm^{-3} HCl
(c) 0.1 mol dm^{-3} NH_4OH and 0.05 mol dm^{-3} HCl
(d) 0.1 mol dm^{-3} CH_3COONa and 0.1 mol dm^{-3} NaOH

Common Ion Effect and Solubility Product

72. Which pair will show common ion effect?

(a) $BaCl_2 + Ba(NO_3)_2$
(b) $NaCl + HCl$
(c) $NH_4OH + NH_4Cl$
(d) $AgCN + KCN$

73. If acetic acid is mixed with sodium acetate then H^+ ion concentration will

(a) increase
(b) decrease
(c) remain unchanged
(d) pH decreases

74. When ammonium chloride is added to a solution of ammonium hydroxide,
(a) dissociation of NH_4OH increases
(b) concentration of OH^- decreases
(c) concentration of NH_4^+ and OH^- increases
(d) concentration of NH_4^+ decreases

75. If the solubility product of $BaSO_4$ is 15×10^{-10} in water, its solubility, in moles per litre, is
(a) 1.5×10^{-9} (b) 3.9×10^{-5}
(c) 7.5×10^{-5} (d) 1.5×10^{-5}

76. Solubility of BaF_2 in a solution of $Ba(NO_3)_2$ will be represented by the concentration term
(a) $[Ba^{2+}]$ (b) $[F^-]$
(c) $\frac{1}{2}[F^-]$ (d) $2[NO_3^-]$

77. For a concentrated solution of a weak electrolyte A_xB_y of concentration 'C', the degree of dissociation 'α' is given as
(a) $\alpha = \sqrt{K_{eq}/C(x+y)}$
(b) $\alpha = \sqrt{K_{eq}C/(xy)}$
(c) $\alpha = (K_{eq}/C^{x+y-1}x^x y^y)^{1/(x+y)}$
(d) $\alpha = (K_{eq}/Cxy)$

78. In which of the following solvents is silver chloride most soluble? **[NCERT Exemplar]**
(a) 0.1 mol dm^{-3} $AgNO_3$ solution
(b) 0.1 mol dm^{-3} HCl solution
(c) H_2O
(d) Aqueous ammonia

79. The solubility product of Ag_2CrO_4 is 32×10^{-12}. What is the concentration of CrO_4^- ions in that solution?
(a) 2×10^{-4} M (b) 16×10^{-4} M
(c) 8×10^{-4} M (d) 8×10^{-8} M

80. A sparingly soluble salt gets precipitated only when the product of concentration of its ions in the solution (K_{sp}) becomes greater than its solubility product. If the solubility of $BaSO_4$ in water is 8×10^{-4} mol dm^{-3}, calculate its solubility in 0.01 mol dm^{-3} of H_2SO_4. **[NCERT]**
(a) 6.4×10^{-5} (b) 6.4×10^{-12}
(c) 6.3×10^{-6} (d) 6.4×10^{-10}

81. The solubility product of $Al(OH)_3$ is 2.7×10^{-11}. Its solubility in gL^{-1} and pH of this solution are respectively (Atomic mass of Al = 27 u) **[NCERT Exemplar]**
(a) 7.8×10^{-2}, 11.5 (b) 7.8×10^{-3}, 9.5
(c) 7.8×10^{-2}, 9.5 (d) 7.8×10^{-3}, 11.5

82. Calculate the volume of water required to dissolve 0.1 g lead (II) chloride to get a saturated solution. (K_{sp} of $PbCl_2 = 3.2 \times 10^{-8}$, atomic mass of Pb = 207 u) **[NCERT]**
(a) 100 mL (b) 180 mL
(c) 120 mL (d) 150 mL

Round II (Mixed Bag)

Only One Correct Option

1. In Haber's process, 30 L of dihydrogen and 30 L of dinitrogen were taken for reaction which yielded only 50% of the expected product. What will be the composition of gaseous mixture under the aforesaid condition at the end?
(a) 10 L NH_3, 25 L N_2, 15 L H_2
(b) 20 L NH_3, 20 L N_2, 20 L H_2
(c) 20 L NH_3, 25 L N_2, 15 L H_2
(d) 20 L NH_3, 10 L N_2, 30 L H_2

2. When $NaNO_3$ is heated in a closed vessel, O_2 is liberated and $NaNO_2$ is left behind. At equilibrium,
(i) addition of $NaNO_3$ favours forward reaction
(ii) addition of $NaNO_2$ favours backward reaction
(iii) increasing pressure favours reverse reaction
(iv) increasing temperature favours forward reaction

Correct options are
(a) (i), (ii), (iii) (b) (ii), (iii), (iv)
(c) (i), (iii), (iv) (d) (i), (ii), (iii), (iv)

3. The pK_a of acetylsalicylic acid (aspirin) is 3.5. The pH of gastric juice in human stomach is about 2–3 and the pH in the small intestine is about 8. Aspirin will be
(a) unionised in the small intestine and in the stomach
(b) completely ionised in the small intestine and in the stomach
(c) ionised in the stomach and almost unionised in the small intestine
(d) ionised in the small intestine and almost unionised in the stomach

4. A precipitate of AgCl is formed when equal volumes of the following are mixed [K_{sp} for $AgCl = 10^{-10}$]

(a) 10^{-4} M $AgNO_3$ and 10^{-7} M HCl

(b) 10^{-5} M $AgNO_3$ and 10^{-6} M HCl

(c) 10^{-5} M $AgNO_3$ and 10^{-4} M HCl

(d) 10^{-6} M $AgNO_3$ and 10^{-6} M HCl

5. A decimolar solution of ammonium hydroxide is ionised to the extent of 1.3%. If $\log 1.3 = 0.11$, what is the pH of the solution?

(a) 11.11
(b) 9.11
(c) 8.11
(d) Unpredictable

6. $K_p = 0.04$ atm at 899 K for the equilibrium shown below. The equilibrium concentration of C_2H_6 when it is placed in a flask at 4.0 atm pressure and allowed to come to equilibrium is **[NCERT]**

$$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$$

(a) 0.30
(b) 3.6
(c) 4.0
(d) 2.8

7. If first dissociation of $X(OH)_3$ is 100%, second dissociation is 50% and third dissociation is negligible then the pH of 4×10^{-3} M $X(OH)_3$ is

(a) 7.5
(b) 9.54
(c) 11.78
(d) 13.25

8. Conjugate acid of a weak base is always stronger. The decreasing order of basic strength of the following conjugate bases is

$OH^-, RO^-, CH_3COO^-, Cl^-$ **[NCERT Exemplar]**

(a) $RO^- > OH^- > CH_3COO^- > Cl^-$

(b) $OH^- > RO^- > CH_3COO^- > Cl^-$

(c) $Cl^- > RO^- > OH^- > CH_3COO^-$

(d) $CH_3COO^- > RO^- > OH^- > Cl^-$

9. Arrange the following in increasing order of pH. $KNO_3(aq)$, $CH_3COONa(aq)$, $NH_4Cl(aq)$, $C_6H_5COONH_4(aq)$ **[NCERT Exemplar]**

(a) $CH_3COONa < C_6H_5COONH_4 < NH_4Cl < KNO_3$

(b) $KNO_3 < NH_4Cl < CH_3COONa < C_6H_5COONa$

(c) $NH_4Cl < KNO_3 < CH_3COONa < C_6H_5COONH_4$

(d) $NH_4Cl < KNO_3 < C_6H_5COONH_4 < CH_3COONa$

10. The ionisation constant of benzoic acid is 6.46×10^{-5} and K_{sp} for silver benzoate is 2.5×10^{-13}. How many times is silver benzoate more soluble in a buffer of pH 3.19 as compared to its solubility in pure water? **[NCERT]**

(a) 1.5
(b) 2.8
(c) 3.2
(d) 2.3

11. The ionisation constant of chloroacetic acid is 1.35×10^{-3}. The pH of 0.1 M acid and its 0.1 M sodium salt solution are respectively **[NCERT]**

(a) 1.94, 1.85
(b) 1.94, 7.94
(c) 7.94, 1.85
(d) 1.94, 8.25

12. The solubility product constant of Ag_2CrO_4 and AgBr are 1.1×10^{-12} and 5.0×10^{-13} respectively. Calculate the ratio of the molarities of their saturated solutions. **[NCERT]**

(a) 85
(b) 23
(c) 15
(d) 92

13. pH of which of the following solutions is highest? **[NCERT]**

(a) 2g of TlOH dissolved in water to give 2 L of solution

(b) 0.3 g of $Ca(OH)_2$ dissolved in water to give 500 mL of solution

(c) 0.3 g of NaOH dissolved in water to give 200 mL of solution

(d) 1 mL of 13.6 M HCl is diluted with water to give 1 L of solution

14. At 1127 K and 1 atm pressure, a gaseous mixture of CO and CO_2 in equilibrium with solid carbon has 90.55% CO by mass.

$$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$$

K_c for this reaction at the above temperature is **[NCERT]**

(a) 0.153
(b) 0.513
(c) 0.283
(d) 0.365

15. Bromine monochloride, BrCl decomposes into bromine and chlorine and reaches the equilibrium,

$$2BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g)$$

for which $K_c = 32$ at 500 K. If initially pure BrCl is present at a concentration of 3.3×10^{-3} mol L^{-1}, what is its molar concentration in the mixture at equilibrium? **[NCERT]**

(a) 2.68×10^{-5}
(b) 0.268×10^{-4}
(c) 26.8×10^{-5}
(d) 0.223×10^{-6}

16. What mole of $Ca(OH)_2$ is dissolved in 250 mL aqueous solution to give a solution of pH 10.65, assuming full dissociation?

(a) 0.47×10^{-4}
(b) 0.48×10^{-4}
(c) 0.56×10^{-4}
(d) 0.68×10^{-4}

17. K_a for HCN is 5×10^{-10} at 25°C. For maintaining a constant pH = 9, the volume of 5 M KCN solution required to be added to 10 mL of 2 M HCN solution is

(a) 2 mL
(b) 4 mL
(c) 8.2 mL
(d) 6.4 mL

18. 2.5 mL of $\frac{2}{5}$ M weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25°C) is titrated with $\frac{2}{15}$ M HCl in water at 25°C. The concentration of H^+ at equivalence point is ($K_w = 1 \times 10^{-14}$ at 25°C)

(a) 3.7×10^{-13} M
(b) 3.2×10^{-7} M
(c) 3.2×10^{-2} M
(d) 2.7×10^{-2} M

19. Solubility product constant (K_{sp}) of salts of types MX, MX_2 and M_3X at temperature T are 4.0×10^{-8}, 3.2×10^{-14} and 2.7×10^{-15}, respectively. Solubilities (mol dm^{-3}) of the salts at temperature T are in the order

(a) $MX > MX_2 > M_3X$
(b) $M_3X > MX_2 > MX$
(c) $MX_2 > M_3X > MX$
(d) $MX > M_3X > MX_2$

20. Ammonia under a pressure of 15 atm at 27°C is heated to 347°C in a closed vessel in the presence of catalyst. Under the conditions, NH_3 is partially decomposed according to the equation, $2NH_3 \rightleftharpoons N_2 + 3H_2$. The vessel is such that the volume remains effectively constant whereas pressure increases to 50 atm. Calculate the percentage of NH_3 actually decomposed.

(a) 61.3%
(b) 63.5%
(c) 65.3%
(d) 66.6%

21. One of the reaction that takes place in producing steel from iron ore is the reduction of iron(II) oxide by carbon monoxide to give iron metal and CO_2.

$$FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g);$$
$$K_p = 0.265 \text{ atm at } 1050 \text{ K}$$

The equilibrium partial pressures of CO and CO_2 at 1050 K, if the initial partial pressures are; $p_{CO} = 1.4$ atm and $p_{CO_2} = 0.80$ atm, are respectively **[NCERT]**

(a) 1.739, 0.461
(b) 0.461, 0.461
(c) 0.461, 1.739
(d) None of these

22. The concentration of sulphide ion in 0.1 M HCl solution saturated with hydrogen sulphide is 1.0×10^{-19} M. If 10 mL of this is added to 5 mL of 0.04 M solution of the following : $FeSO_4$, $MnCl_2$, $ZnCl_2$ and $CdCl_2$, in which of these solutions precipitation will take place?

(Given, K_{sp} of FeS $= 6.3 \times 10^{-18}$, K_{sp} of MnS $= 2.5 \times 10^{-13}$ K_{sp} of ZnS $= 1.6 \times 10^{-24}$, K_{sp} of CdS $= 8.0 \times 10^{-27}$) **[NCERT]**

(a) $FeSO_4$ only
(b) $CdCl_2$ and $ZnCl_2$
(c) Both $MnCl_2$ and $ZnCl_2$
(d) Both $CdCl_2$ and $FeSO_4$

More than One Correct Option

23. For the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, the value of K is 50 at 400 K and 1700 at 500 K. Which of the following options is correct? **[NCERT Exemplar]**

(a) The reaction is endothermic
(b) The reaction is exothermic
(c) If $NO_2(g)$ and $N_2O_4(g)$ are mixed at 400 K at partial pressures 20 bar and 2 bar respectively, more $N_2O_4(g)$ will be formed.
(d) The entropy of the system increases

24. 138 g of $N_2O_4(g)$ is placed in 8.2 L container at 300 K. The equilibrium vapour density of mixture was found to be 30.67. Then ($R = 0.082$ L atm mol^{-1} K^{-1})

(a) total pressure at equilibrium = 6.75 atm
(b) degree of dissociation of N_2O_5 = 0.25
(c) the density of equilibrium mixture = 16.83 g/L
(d) K_p of $N_2O_4 \rightleftharpoons 2NO_2(g)$ will be 9 atm

25. A reaction mixture containing 0.050 atm N_2, 3.0 atm H_2 and 0.050 atm NH_3 is heated to 450°C. The value of K_p is 4.28×10^{-5} atm^{-2}.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

The correct statement(s) is/are

(a) reaction goes towards the left
(b) reaction goes towards the right
(c) N_2 and H_2 combine to form ammonia
(d) ammonia gas decomposes into H_2 and N_2

26. pH of following solution is not affected by dilution

(a) 0.01 M CH_3COONH_4
(b) 0.01 M NaH_2PO_4
(c) 0.01 M NaCl
(d) 0.01 M $NaHCO_3$

27. The solubility of a sparingly soluble salt A_xB_y in water at 25°C is 1.4×10^{-4} M. The solubility product is 1.1×10^{-11}. The possibilities are

(a) $x = 1, y = 2$
(b) $x = 2, y = 1$
(c) $x = 3, y = 1$
(d) $x = 1, y = 3$

Assertion and Reason

Directions (Q. Nos. 28 to 32) *Each of these questions contains two statements : Statement* I *(Assertion) and Statement* II *(Reason). Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c), (d) given below*

(a) Statement I is true; Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true; Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

28. **Statement I** The reaction,

$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$ is favoured in the forward direction with increase of pressure.

Statement II The reaction is exothermic.

29. **Statement I** Buffer system of carbonic acid and sodium bicarbonate is used for the precipitation of hydroxides of third group elements.

Statement II It maintains the pH to a constant value, about 7.4.

30. **Statement I** The ionisation of hydrogen sulphide in water is low in the presence of hydrochloric acid.

Statement II Hydrogen sulphide is a weak acid.

[NCERT Exemplar]

31. **Statement I** Aqueous solution of ammonium carbonate is basic.

Statement II Acidic/ basic nature of a salt solution of a salt of weak acid and weak base depends on K_a and K_b value of the acid and the base forming it.

[NCERT Exemplar]

32. **Statement I** In the dissociation of PCl_5 at constant pressure and temperature addition of helium at equilibrium increases the dissociation PCl_5.

Statement II Helium removes Cl_2 from the field of action. [NCERT Exemplar]

Comprehension Based Questions

Directions (Q. Nos. 33 to 35) The rate of the reaction is directly proportional to the product of the active masses of the reactants raised to the suitable powers, at a given temperature.

$$aA + bB + cC \longrightarrow \text{Product}$$
$$\text{Rate} = k[a]^a\,[B]^b[C]^c$$

If the reaction is written in reversed direction

$$k_b = \frac{1}{k_f}$$

For gaseous reaction, equilibrium constant, can also be expressed in terms of partial pressure.

Equilibrium constant, K_c for

$$aA + bB \rightleftharpoons cC + dD \text{ is}$$
$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \text{ and } K_p = \frac{p_C{}^c\, p_D{}^d}{p_A{}^a\, p_B{}^b}$$

K_p and K_c are related with each other as $K_p = K_c\,(RT)^{\Delta n_g}$.

33. Calculate the partial pressure of carbon monoxide from the following data

$$CaCO_3(s) \overset{\Delta}{\rightleftharpoons} CaO(s) + CO_2\uparrow; \qquad K_p = 8\times 10^{-2}$$
$$CO_2(g) + C(s) \rightleftharpoons 2CO(g); \qquad K_p = 2$$

(a) 0.2 atm (b) 0.6 atm
(c) 0.8 atm (d) 0.4 atm

34. A vessel at 1000 K contains CO_2 with a pressure of 0.5 atm. Some of CO_2 is converted into CO on addition of graphite. The value of K at equilibrium when total pressure is 0.8 atm will be [AIEEE 2011]

(a) 2.5 atm (b) 3.6 atm
(c) 1.8 atm (d) 0.9 atm

35. For the following equilibrium

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

K_p is found to be equal to K_c. This is attained when

(a) $T = 1$ K
(b) $T = 273$ K
(c) $T = 12.18$ K
(d) $T = 17.15$ K

Directions (Q. Nos. 36 to 38) Radiochemical methods can be used to determine solubility product estimation. The measurement of radioactivity can be used to find the concentration in a solubility equilibrium giving a fair idea about various equilibrium concentrations. In an experiment, 50.00 mL of a 0.010 M $AgNO_3$ solution containing a silver isotope with a radioactivity of 75000 counts per min per mL were mixed with 100 mL of a 0.03 M $NaIO_3$ solution. The mixed solution was diluted to 500 mL and filtered to remove all the $AgIO_3$ precipitate leaving behind a radioactive solution. Molar mass of $AgIO_3$ = 285 g/mol.

36. The percentage of unprecipitated silver ions is

(a) 0.25% (b) 0.66%
(c) 0.43% (d) 0.57%

37. The K_{sp} of $AgIO_3$ are

(a) 5.3×10^{-8}
(b) 6.9×10^{-12}
(c) 4.2×10^{-10}
(d) 2.8×10^{-8}

38. The remaining solution was found to have a radioactivity of 50 counts per min per mL. Then, find the mass of the ppt of $AgIO_3$ obtained separated.

(a) 242 (b) 283
(c) 332 (d) 285

Previous Years' Questions

39. The equilibrium constant (K_c) for the reaction, $N_2(g) + O_2(g) \longrightarrow 2NO(g)$ at temperature T is 4×10^{-4}. The value of K_c for the reaction $NO(g) \longrightarrow \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$ at the same temperature is **[AIEEE 2012]**

(a) 0.02
(b) 2.5×10^2
(c) 4×10^{-4}
(d) 50.0

40. The pH of a 0.1 molar solution of the acid HQ is 3. the value of the ionisation constant, K_a of the acid is **[AIEEE 2012]**

(a) 3×10^{-1}
(b) 1×10^{-3}
(c) 1×10^{-5}
(d) 1×10^{-7}

41. The K_{sp} for $Cr(OH)_3$ is 1.6×10^{-30}. The molar solubility of this compound in water is **[AIEEE 2011]**

(a) $\sqrt[2]{1.6 \times 10^{-30}}$
(b) $\sqrt[4]{1.6 \times 10^{-30}}$
(c) $\sqrt[4]{1.6 \times 10^{-30} / 27}$
(d) $1.6 \times 10^{-30} / 27$

42. Three reactions involving $H_2PO_4^-$ are given below

I. $H_3PO_4 + H_2O \longrightarrow H_3O^+ + H_2PO_4^-$
II. $H_2PO_4^- + H_2O \longrightarrow HPO_4^{2-} + H_3O^+$
III. $H_2PO_4^- + OH^- \longrightarrow H_3PO_4 + O^{2-}$

In which of the above does $H_2PO_4^-$ act as an acid? **[AIEEE 2010]**

(a) II only
(b) I and II
(c) III only
(d) I only

43. In aqueous solution, the ionisation constants for carbonic acid are **[AIEEE 2010]**

$$K_1 = 4.2 \times 10^{-7} \text{ and } K_2 = 4.8 \times 10^{-11}$$

Select the correct statement for a saturated 0.034 M solution of the carbonic acid.

(a) The concentration of CO_3^{2-} is 0.034 M
(b) The concentration of CO_3^{2-} is greater than that of HCO_3^{2-}
(c) The concentration of H^+ and HCO_3^{2-} are approximately equal
(d) The concentration of H^+ is double that of CO_3^{2-}

44. Solubility product of silver bromide is 5.0×10^{-13}. The quantity of potassium bromide (molar mass taken as 120 g mol^{-1}) to be added to 1 L of 0.05 M solution of silver nitrate to start the precipitation of AgBr is **[AIEEE 2010]**

(a) 1.2×10^{-10} g
(b) 1.2×10^{-9} g
(c) 6.2×10^{-5} g
(d) 5.0×10^{-8} g

45. At 25°C, the solubility product of $Mg(OH)_2$ is 1.0×10^{-11}. At which pH, will Mg^{2+} ions start precipitating in the form of $Mg(OH)_2$ from a solution of 0.001 M Mg^{2+} ions? **[AIEEE 2010]**

(a) 9
(b) 10
(c) 11
(d) 8

46. Solid $Ba(NO_3)_2$ is gradually dissolved in a 1.0×10^{-4} M Na_2CO_3 solution. At what concentration of Ba^{2+} will a precipitate begin to form? (K_{sp} for $BaCO_3 = 5.1 \times 10^{-9}$) **[AIEEE 2009]**

(a) 4.1×10^{-5} M
(b) 5.1×10^{-5} M
(c) 8.1×10^{-8} M
(d) 8.1×10^{-7} M

47. For the following three reactions I, II and III, equilibrium constants are given

I. $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g); K_1$
II. $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g); K_2$
III. $CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g); K_3$

Which of the following relations is correct? **[AIEEE 2003]**

(a) $K_1\sqrt{K_2} = K_3$
(b) $K_2K_3 = K_1$
(c) $K_3 = K_1K_2$
(d) $K_3K_2^3 = K_1^2$

48. Four species are listed below

I. HCO_3^-
II. H_3O^+
III. HSO_4^-
IV. HSO_3F

Which one of the following is the correct sequence of their acid strength? **[AIEEE 2008]**

(a) IV < II < III < I
(b) II < III < I < IV
(c) I < III < II < IV
(d) III < I < IV < II

49. The equilibrium constants K_{p_1} and K_{p_2} for the reactions $X \rightleftharpoons 2Y$ and $Z \rightleftharpoons P + Q$, respectively are in the ratio of 1 : 9. If the degree of dissociation of X and Z be equal, then the ratio of total pressure at these equilibria is **[AIEEE 2008]**

(a) 1 : 36
(b) 1 : 1
(c) 1 : 3
(d) 1 : 9

50. The pK_a of a weak acid, HA, is 4.80. The pK_b of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be **[AIEEE 2008]**

(a) 9.58
(b) 4.79
(c) 7.01
(d) 9.22

51. In a saturated solution of the sparingly soluble strong electrolyte $AgIO_3$ (molecular mass = 283) the equilibrium which sets in, is

$$AgIO_3(s) \rightleftharpoons Ag^+(aq) + IO_3^-(aq)$$

If the solubility product constant, K_{sp} of $AgIO_3$ at a given temperature is 1.0×10^{-8}, what is the mass of $AgIO_3$ contained in 100 mL of its saturated solution? **[AIEEE 2007]**

(a) 28.3×10^{-2} g (b) 2.83×10^{-3} g

(c) 1.0×10^{-7} g (d) 1.0×10^{-4} g

52. The equilibrium constant K_c for the reaction

$$SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2} O_2(g)$$

is 4.9×10^{-2}. The value of K_c for the reaction

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

will be **[AIEEE 2006]**

(a) 416 (b) 2.40×10^{-3}

(c) 9.8×10^{-2} (d) 4.9×10^{-2}

53. Phosphorus pentachloride dissociates as follows, in a closed reaction vessel,

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

If total pressure, at equilibrium, of the reaction mixture is p and degree of dissociation of PCl_5 is x, the partial pressure of PCl_3 will be **[AIEEE 2006]**

(a) $\left(\frac{x}{x+1}\right)p$ (b) $\left(\frac{2x}{1-x}\right)p$

(c) $\left(\frac{x}{x-1}\right)p$ (d) $\left(\frac{x}{1-x}\right)p$

54. An amount of solid NH_4HS is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm pressure. Ammonium hydrogen sulphide decomposes to yield NH_3 and H_2S gases in the flask. When the decomposition reaction reaches at equilibrium, the total pressure in the flask rises to 0.84 atm. The equilibrium constant for the decomposition of NH_4HS at this temperature is **[AIEEE 2005]**

(a) 0.11 (b) 0.17 (c) 0.18 (d) 0.30

55. For the reaction,

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$

[$K_c = 1.8 \times 10^{-6}$ at 184°C, $R = 0.00831$ kJ/(mol K)]

When K_p and K_c are compared at 184°C it is found that **[AIEEE 2005]**

(a) whether K_p is greater than, less than or equal to K_c depends upon the total gas pressure

(b) $K_p = K_c$

(c) K_p is less than K_c

(d) K_p is greater than K_c

56. What is the conjugate base of OH^-? **[AIEEE 2005]**

(a) O^{2-} (b) O^-

(c) H_2O (d) O_2

57. The solubility product of a salt having general formula MX_2, in water is 4×10^{-12}. The concentration of M^{2+} ions in the aqueous solution of the salt is **[AIEEE 2005]**

(a) 4.0×10^{-10} M

(b) 1.6×10^{-4} M

(c) 1.0×10^{-4} M

(d) 2.0×10^{-6} M

58. For the reaction,

$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$, the K_p / K_c is equal to **[AIEEE 2004]**

(a) $1/RT$ (b) RT

(c) $\sqrt{RT}$ (d) 1.0

59. Consider the reaction equilibrium

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g); \quad \Delta H° = -198 \text{ kJ}$$

On the basis of Le-Chatelier's principle, the condition favourable for the forward reaction is **[AIEEE 2003]**

(a) lowering of temperature as well as pressure

(b) increasing temperature as well as pressure

(c) lowering the temperature and increasing the pressure

(d) any value of temperature and pressure

60. Which one of the following species acts as both Bronsted acid and base ? **[AIEEE 2002]**

(a) $H_2PO_2^-$

(b) HPO_3^{2-}

(c) HPO_4^{2-}

(d) All of the above

Answers

Round I

1. (b)	**2.** (a)	**3.** (c)	**4.** (d)	**5.** (a)	**6.** (a)	**7.** (a)	**8.** (a)	**9.** (a)	**10.** (b)
11. (b)	**12.** (b)	**13.** (b)	**14.** (b)	**15.** (d)	**16.** (d)	**17.** (a)	**18.** (a)	**19.** (d)	**20.** (c)
21. (a)	**22.** (a)	**23.** (c)	**24.** (d)	**25.** (c)	**26.** (d)	**27.** (a)	**28.** (d)	**29.** (b)	**30.** (c)
31. (a)	**32.** (d)	**33.** (a)	**34.** (a)	**35.** (a)	**36.** (b)	**37.** (b)	**38.** (b)	**39.** (a)	**40.** (d)
41. (b)	**42.** (b)	**43.** (b)	**44.** (c)	**45.** (b)	**46.** (c)	**47.** (b)	**48.** (c)	**49.** (d)	**50.** (d)
51. (a)	**52.** (c)	**53.** (b)	**54.** (a)	**55.** (b)	**56.** (b)	**57.** (a)	**58.** (b)	**59.** (a)	**60.** (a)
61. (c)	**62.** (a)	**63.** (c)	**64.** (c)	**65.** (a)	**66.** (c)	**67.** (b)	**68.** (d)	**69.** (c)	**70.** (a)
71. (c)	**72.** (c)	**73.** (b)	**74.** (b)	**75.** (b)	**76.** (c)	**77.** (c)	**78.** (d)	**79.** (a)	**80.** (a)
81. (a)	**82.** (b)								

Round II

1. (a)	**2.** (d)	**3.** (d)	**4.** (c)	**5.** (a)	**6.** (b)	**7.** (c)	**8.** (a)	**9.** (d)	**10.** (c)
11. (b)	**12.** (d)	**13.** (c)	**14.** (a)	**15.** (c)	**16.** (c)	**17.** (a)	**18.** (d)	**19.** (d)	**20.** (a)
21. (a)	**22.** (b)	**23.** (a,c,d)	**24.** (a,c,d)	**25.** (a,d)	**26.** (a,b,d)	**27.** (a,b)	**28.** (b)	**29.** (d)	**30.** (b)
31. (a)	**32.** (c)	**33.** (d)	**34.** (c)	**35.** (c)	**36.** (b)	**37.** (a)	**38.** (b)	**39.** (d)	**40.** (c)
41. (c)	**42.** (a)	**43.** (c)	**44.** (b)	**45.** (b)	**46.** (b)	**47.** (c)	**48.** (c)	**49.** (a)	**50.** (c)
51. (b)	**52.** (a)	**53.** (a)	**54.** (a)	**55.** (d)	**56.** (a)	**57.** (c)	**58.** (a)	**59.** (c)	**60.** (c)

the Guidance

Round I

1. Thermal decomposition of potassium chlorate is irreversible. So, law of mass action cannot be applied on this reaction.

2. In a reversible reaction some amount of the reactants remains unconverted into products and it never go for completion.

3. At the stage of equilibrium, process does not stop but the opposite processes *i.e.*, forward and reverse process occur with the same rate.

5. Active mass $= \dfrac{\text{moles of KCl}}{\text{volume of solution in L}} = \dfrac{45}{74.5 \times 3} = 0.20$

7. $AB \rightleftharpoons A + B$

$$K = \frac{[A][B]}{[AB]}$$

If concentration of A is doubled, the equilibrium concentration of B becomes half to maintain K constant.

8. $P_4(s) + 5O_2(g) \rightleftharpoons P_4O_{10}(s)$

$$K_c = \frac{[P_4O_{10}(s)]}{[P_4(s)][O_2(g)]^5}$$

We know that concentration of a solid component is always taken as unity.

$$K_c = \frac{1}{[O_2]^5}$$

10. $A + B \rightleftharpoons C + D$

$x \quad x \qquad 0 \quad 0$

$2x \quad 2x$ At equilibrium

$$K_c = \frac{[C][D]}{[A][B]} = \frac{2x \cdot 2x}{x \cdot x} = 4$$

11. $K_c = \dfrac{[PCl_3][Cl_2]}{[PCl_5]} = \dfrac{0.2 \times x}{0.4} = 0.5$

$\therefore \qquad x = 1$

12. $k_f = 1.1 \times 10^{-2}, k_b = 1.5 \times 10^{-3}$

$$K_c = \frac{k_f}{k_b} = \frac{1.1 \times 10^{-2}}{1.5 \times 10^{-3}} = 7.33$$

13. $3O_2(g) \rightleftharpoons 2O_3(g)$

Equili. conc. $\quad 1.6 \times 10^{-2} \qquad ?$

$$K = \frac{[O_3]^2}{[O_2]^3}$$

$$2.0 \times 10^{-50} = \frac{[O_3]^2}{[1.6 \times 10^{-2}]^3}$$

$$[O_3]^2 = 2.0 \times 10^{-50} \times [1.6 \times 10^{-2}]^3$$

$$[O_3]^2 = 8.192 \times 10^{-56}$$

$$[O_3] = 2.86 \times 10^{-28} \text{ mol L}^{-1}$$

14.

$$\begin{array}{llll} & 2HI(g) & \rightleftharpoons H_2(g) & + \; I_2(g) \\ \text{Initial pressure} & 0.2 \text{ atm} & 0 & 0 \\ \text{Equili. pressure} & 0.04 \text{ atm} & 0.08 \text{ atm} & 0.08 \text{ atm} \end{array}$$

(Decrease in pressure of HI = 0.2 − 0.04 = 0.16 atm; so equilibrium pressure of H_2 is $\frac{0.16}{2} = 0.08$ atm and for I_2 is $\frac{0.16}{2} = 0.08$ atm as two moles of HI on dissociation gives 1 mol H_2 and 1 mol I_2)

$$K_p = \frac{p_{H_2} \cdot p_{I_2}}{p_{HI}^2} = \frac{0.08 \text{ atm} \times 0.08 \text{ atm}}{(0.04 \text{ atm})^2} = 4.0$$

15.

$$\begin{array}{llll} & PCl_5(g) & \rightleftharpoons PCl_3(g) & + \; Cl_2(g) \\ \text{At equili.} & 0.05 \text{ M} & x & x \end{array}$$

Given, $[PCl_5]_{\text{equili.}} = 0.5 \times 10^{-1}$ mol L^{-1} (= 0.05 mol L^{-1})

$$K_c = 8.3 \times 10^{-3}$$

$$K_c = 8.3 \times 10^{-3} = \frac{[PCl_3]\,[Cl_2]}{[PCl_5]}$$

$$8.3 \times 10^{-3} = \frac{x^2}{0.05} \qquad (\text{because } [PCl_3] = [Cl_2])$$

$$x^2 = 0.415 \times 10^{-3} = 4.15 \times 10^{-4}$$

$$x = 2.037 \times 10^{-2} \approx 2.04 \times 10^{-2} \text{ mol L}^{-1}$$

Hence, $[PCl_3] = [Cl_2] = 2.04 \times 10^{-2}$ mol L^{-1}

16.

$$\begin{array}{llll} & 2ICl(g) & \rightleftharpoons I_2(g) & + \; Cl_2(g) \\ \text{Initial conc.} & 0.78 \text{ M} & 0 & 0 \\ \text{Equili conc.} & 0.78 - 2x & x & x \end{array}$$

$$K_c = \frac{[I_2]\,[Cl_2]}{[ICl]^2} = \frac{x \,.\, x}{(0.78 - 2x)^2} = 0.14$$

or $$\frac{x}{(0.78 - 2x)} = \sqrt{0.14} = 0.374$$

or $$x = 0.29172 - 0.748x$$

or $$1.748x = 0.29172$$

or $$x = \frac{0.29172}{1.748} = 0.1668$$

$$[\,ICl]_{\text{equili}} = 0.78 - (2 \times 0.1668) = 0.45$$

17.

$$\begin{array}{lllll} & H_2(g) & + \; CO_2(g) & \rightleftharpoons CO(g) & + \; H_2O(l) \\ \text{Initial conc.} & 1 & 1 & 0 & 0 \\ \text{At equilibrium} & (1-x) & (1-x) & x & x \end{array}$$

$$K_p = \frac{p_{CO} \cdot p_{H_2O}}{p_{H_2} \cdot p_{CO_2}} = \frac{x \cdot x}{(1-x)(1-x)} = \frac{x^2}{(1-x)^2}$$

18. $CO(g) + 3\,H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$;

$K_c = 3.90$ at 1300 K.

$$K_c = \frac{[CH_4] \cdot [H_2O]}{[CO]\;[H_2]^3}$$

$$3.90 = \frac{[CH_4]\;[0.02]}{[0.30]\;[0.10]^3}$$

(Molar concentration means number of moles present in 1 L and volume of the flask is 1 L.)

$$[CH_4] = \frac{3.90 \times 0.30 \times (0.10)^3}{0.02} = 0.0585 \text{ M}$$

$$[CH_4]_{eq} = 5.85 \times 10^{-2} \text{M}$$

19. At constant volume, the equilibrium remain unaffected on addition of small amount of inert gas like argon.

20.

$$K_1 = \frac{[NO_2]}{[NO][O_2]^{1/2}} \qquad \text{...(i)}$$

$$K_2 = \frac{[NO]^2[O_2]}{[NO_2]^2} \qquad \text{...(ii)}$$

$$\therefore \quad \frac{1}{K_2} = \frac{[NO_2]^2}{[NO]^2[O_2]}$$

or, $$\frac{1}{\sqrt{K_2}} = \frac{[NO_2]}{[NO][O_2]^{1/2}} \qquad \text{...(iii)}$$

From Eqs. (i) and (iii),

$$K_1 = \frac{1}{\sqrt{K_2}}$$

$$\therefore \quad K_2 = \frac{1}{K_1^2}$$

21. For the reaction, $\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \rightleftharpoons HI(g)$

$$K_c = \frac{[HI]}{[H_2]^{1/2}[I_2]^{1/2}} = 5$$

Thus, for the reaction,

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

$$K_{c_1} = \frac{[H_2][I_2]}{[HI]^2} = \left(\frac{1}{K_c}\right)^2 = \left(\frac{1}{5}\right)^2 = \frac{1}{25} = 0.04$$

22. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$$K_p = K_c(RT)^{\Delta n_g}$$

$$\Delta n_g = 2 - 3 = -1$$

$$2.0 \times 10^{10} = K_c\,(0.0821 \times 450)^{-1}$$

$$K_c = 2.0 \times 10^{10} \times 0.082 \times 450$$

$$= 7.38 \times 10^{11}$$

23. If $n_P = n_R$, then $K_p = K_c$

[where, n_P = number of moles of products

n_R = number of moles of reactants]

24. Δ_{n_g} = Moles of gaseous products − moles of gaseous reactants

$$= 2 - 0 = 2$$

25. $A + B \rightleftharpoons C$

$$K = \frac{[C]}{[A][B]}$$

$$= \frac{\text{mol L}^{-1}}{\text{mol L}^{-1} \times \text{mol L}^{-1}}$$

$$= (\text{mol L}^{-1})^{-1} = \text{mol}^{-1}\text{ L}$$

27. $\Delta G^{\ominus} = -RT \ln K$

At the stage of half completion of reaction $[A] = [B]$. Therefore, $K = 1$. Thus, $\Delta G^{\ominus} = 0$

28. $\Delta G°$ and K are related as $\Delta G° = -2.303\, RT \log k_c$

When $\Delta G° > 0$, *i.e.*, + ve then $K_c < 1$

29. $\alpha = \dfrac{D - d}{d} = \dfrac{104.16 - 62}{62} = 0.68 = 68\%$

31. On increasing temperature, equilibrium will shift in forward direction due to decrease in intermolecular forces of solid.

32. We know that

$$pV = nRT$$

p become $\frac{1}{2}p$ and V becomes $2V$, so

$$\frac{1}{2}p \times 2V = pV = nRT$$

Hence, there is no effect in equation.

33. Since the reaction is exothermic (as $\Delta H < 0$), low temperature favours forward reaction. Moreover $n_p < n_R$, high pressure favours forward reaction.

34. In the reaction, $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, the number of moles of reactants and products are equal, thus it remains unaffected by change in pressure.

41. $NH_2^- \rightleftharpoons NH^{2-} + H^+$

42. $Ca(OH)_2$, being an ionic compound readily gives two hydroxyl ions when dissolved in water, hence it is a diacidic base.

$$\underset{\text{diacidic base}}{Ca(OH)_2} \longrightarrow Ca^{2+} + 2OH^-$$

44. BF_3 can accept a pair of electrons, but it cannot give H^+ ions in the aqueous solution, hence BF_3 acts as Lewis acid but not as a Bronsted acid.

45. CH_3COO^-, because it is the conjugate base of weak acid.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

46. $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$

47. As the acidity or K_a value increases, pH decreases, thus, the order of pH value of the acids is

$$\underset{(3.0 \times 10^{-8})}{\text{Hypochlorous acid}} > \underset{(1.74 \times 10^{-5})}{\text{acetic acid}} > \underset{(1.8 \times 10^{-4})}{\text{formic acid}}$$

$$\left[\textbf{Note}\ K_a \propto \frac{1}{\text{pH}}\right]$$

50. $$\underset{\substack{C \\ C - C\alpha}}{CH_3COOH} + H_2O \rightleftharpoons \underset{\substack{0 \\ C\alpha}}{CH_3COO^-} + \underset{\substack{0 \\ C\alpha}}{H_3O^+} \quad \begin{matrix}\text{Initially} \\ \text{At time } t\end{matrix}$$

$$K_a = \frac{[CH_3COO^-]\ [H_3O^+]}{[CH_3COOH]}$$

Given, $K_a = 1.74 \times 10^{-5}$, $[CH_3COOH] = 0.05$ M

$[CH_3COO^-] = [H_3O^+] = \sqrt{K_a \cdot [CH_3COOH]}$

$[CH_3COO^-] = [H_3O^+] = \sqrt{1.74 \times 10^{-5} \times 0.05}$

$[CH_3COO^-] = [H_3O^+] = \sqrt{17.4 \times 10^{-6} \times 5.0 \times 10^{-2}}$

$= 9.33 \times 10^{-4}$ M

$[CH_3COO^-] = [H_3O^+] = C \cdot \alpha$

Degree of dissociation, $\alpha = \dfrac{[H_3O^+]}{C}$

$= \dfrac{9.33 \times 10^{-4}}{0.05} = 1.86 \times 10^{-2}$

pH = $-\log [H_3O^+]$

pH = $-\log [9.33 \times 10^{-4}]$

pH = $4 - 0.9699 = 3.0301$

51. $[H^+] = \sqrt{K_a \cdot C}$

where, C = initial concentration of the weak acid

$$C = \frac{[H^+]^2}{K_a} = \frac{(3.4 \times 10^{-4})^2}{1.7 \times 10^{-5}}$$

$$C = 6.8 \times 10^{-3}\ \text{M}$$

Alternatively

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$1.7 \times 10^{-5} = \frac{[3.4 \times 10^{-4}]^2}{[CH_3COOH]}$$

$[\because\ [CH_3COO^-] = [H^+]]$

$[CH_3COOH] = 6.8 \times 10^{-3}$ M

52. pH = 3.76 = $-\log [H^+]$

$\log [H^+] = -3.76$

[Before taking antilog add -1 in characteristic (-3) and $+1$ in mantissa (0.76), *i.e.*, $-3.76 - 1 + 1 = \overline{4}.24$]

$\log [H^+] = \overline{4}.24$ or $[H^+] = \text{antilog } \overline{4}.24$

$[H^+] = 1.738 \times 10^{-4}$ M

54. $[Ca(OH)_2] = 0.01 \text{mol}/100 \text{ cc} = 0.1 \text{ mol L}^{-1}$

Assuming complete ionisation,

$[OH^-] = 0.2$ M, $[H^+] = \dfrac{10^{-14}}{0.2} = 5 \times 10^{-14}$

pH $= -\log [H^+]$

$= -\log (5 \times 10^{-14})$

$= 14 - 0.698 = 13.3$

55. NaOH $= [OH^-] = 10^{-3}$

$[H^+][OH^-] = 10^{-14}$

$[H^+] = 10^{-11}$

pH $= -\log [H^+]$

$= -\log [10^{-11}] = 11$

$$HCl(aq) = [H^+] = 10^{-3}$$

$$pH = -\log [10^{-3}] = 3$$

$NaCl(aq)$ = Neutral; $[H^+] = [OH^-] = 10^{-7}$

i.e., $pH = 7$

56. $pH = 5$

$$[H^+] = 10^{-5} \text{ mol L}^{-1}$$

On diluting the solution 100 times,

$$[H^+] = \frac{10^{-5}}{100} = 10^{-7} \text{ mol L}^{-1}$$

Total H^+ ion concentration = H^+ ions from acid + H^+ ions from water

$$[H^+] = 10^{-7} + 10^{-7} = 2 \times 10^{-7} \text{ M}$$

$$pH = -\log [2 \times 10^{-7}]$$

$$pH = 7 - 0.3010 = 6.699$$

57.

$$N_1V_1 = N_2V_2$$

$$10^{-3} \times 10 = N_2 \times 1000$$

$$N_2 = 10^{-5}$$

$$pH = 5$$

So, $pOH = 14 - 5 = 9$

58. pH of solution $A = 6$. Hence, $[H^+] = 10^{-6}$ mol L^{-1}

pH of solution $B = 4$. Hence, $[H^+] = 10^{-4}$ mol L^{-1}

On mixing 1 L of each solution, molar concentration of total H^+ is halved.

Total $$[H^+] = \frac{10^{-6} + 10^{-4}}{2} \text{ mol L}^{-1}$$

$$[H^+] = \frac{1.01 \times 10^{-4}}{2} = 5.05 \times 10^{-5} \text{ mol L}^{-1}$$

$$[H^+] = 5.0 \times 10^{-5} \text{ mol L}^{-1}$$

$$pH = -\log [H^+]$$

$$pH = -\log (5.0 \times 10^{-5})$$

$$pH = 5 - \log 5 = 5 - 0.6990$$

$$pH = 4.3010 \approx 4.3$$

59. pH of $HOCl = 2.85$

But, $-pH = \log [H^+]$

$\therefore$ $-2.85 = \log [H^+]$

$\Rightarrow$ $\bar{3}.15 = \log [H^+]$

$\Rightarrow$ $[H^+] = 1.413 \times 10^{-3}$

For weak monobasic acid, $[H^+] = \sqrt{K_a \times C}$

$\Rightarrow$ $$K_a = \frac{[H^+]^2}{C} = \frac{(1.413 \times 10^{-3})^2}{0.08}$$

$$= 24.957 \times 10^{-6} = 2.4957 \times 10^{-5}.$$

60. $[H^+] = \sqrt{K_a \cdot C} = \sqrt{1.74 \times 10^{-5} \times 0.01}$

$$= 4.17 \times 10^{-4}$$

$$pH = -\log[H^+] = -\log (4.17 \times 10^{-4}) = 3.4$$

61. With rise in temperature pH decreases, thus, for water becomes less than 7 at 60° C.

62. $\because$ $pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a - \frac{1}{2} pK_b$

$$= \frac{1}{2} \times 14 + \frac{1}{2} \times 6 - \frac{1}{2} \times 6$$

$pH = 7$

$$\alpha = \sqrt{\frac{K_w}{K_a \times K_b}} = \sqrt{\frac{10^{-14}}{10^{-6} \times 10^{-6}}} = \sqrt{10^{-2}}$$

$$= 10^{-1} = 0.1 \quad \text{or} \quad 10\%$$

63. Ammonium acetate is a salt of weak acid and weak base. For such salts,

$$pH = 7 + \frac{pK_a - pK_b}{2}$$

$$= 7 + \frac{[-\log 1.8 \times 10^{-5}] - [-\log 1.8 \times 10^{-5}]}{2}$$

$$= 7 + \frac{4.74 - 4.74}{2} = 7.00$$

64. $Na_2CO_3 + 2H_2O \rightleftharpoons 2NaOH + H_2CO_3$. It is a salt of strong base and weak acid, so it is basic.

65. Aqueous solution of $AlCl_3$ is acidic due to the hydrolysis of aluminium ion.

$$AlCl_3 \xrightarrow{\text{Hydrolysis}} Al(OH)_3 + H^+$$

66. $K_h = Ch^2 = 0.5 \times \left(\frac{0.25}{100}\right)^2 = 3.125 \times 10^{-6}$

67. $X^- + H_2O \rightleftharpoons HX + OH^-$

$$K_h = \frac{10^{-14}}{10^{-5}} \text{ so, } h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{10^{-9}}{10^{-1}}} = 10^{-4}$$

$$= 100 \times 10^{-4} = 10^{-2}$$

So, degree of hydrolysis is 0.01%.

69. We know that,

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$5.5 = 4.5 + \log \frac{[\text{salt}]}{[0.1]}$$

$$[\text{salt}] = 1.0 \text{ M}$$

70. $pH = pK_a + \log \frac{[KCN]}{[HCN]} = 9.3 + \log \frac{2.5}{2.5} = 9.30$

71. When the concentration of NH_4OH (weak base) is higher than the strong acid (HCl), a mixture of weak base and its conjugate acid is obtained, which acts as basic buffer.

	NH_4OH +	HCl $\longrightarrow$	NH_4Cl +	H_2O
Initially	0.1 M	0.05 M	0	0
After reaction	0.05 M	0	0.05 M	0

72. $NH_4OH \rightleftharpoons \boxed{NH_4^+} + OH^-$

$NH_4Cl \rightleftharpoons \boxed{NH_4^+} + Cl^-$

common ion

73. $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

On adding CH_3COONa, $[H^+]$ decreases.

75. $BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$

Solubility product $= s \times s$

$15 \times 10^{-10} = s^2 : s = \sqrt{15 \times 10^{-10}} : s = 3.9 \times 10^{-5}$

76. $Ba(NO_3)_2$ gives NO_3^- and Ba^{2+} ions, hence Ba^{2+} ion increases. To keep K_{sp} constant, $[F^-]$ decreases. Thus, it is represented as $\frac{1}{2}[F^-]$.

77. The weak electrolyte A_xB_y dissociates as follows

$$\begin{array}{llll} A_xB_y & \rightleftharpoons \; xA^{y+} & + \; yB^{x-} & \\ C & 0 & 0 & \text{Initially} \\ C(1-\alpha) & xC\alpha & yC\alpha & \text{At equilibrium} \end{array}$$

where, α = degree of dissociation, C = concentration

$$K_{eq} = \frac{[A^{y+}]^x [B^{x-}]^y}{[A_xB_y]} = \frac{[xC\alpha]^x [yC\alpha]^y}{C(1-\alpha)}$$

$$= \frac{x^x \cdot C^x \cdot \alpha^x \cdot y^y \cdot C^y \cdot \alpha^y}{C} \qquad [\because 1 - a \approx 1]$$

$$= x^x \cdot y^y \cdot \alpha^{x+y} \cdot C^{x+y-1}$$

$$\alpha^{x+y} = \frac{K_{eq}}{x^x \cdot y^y \cdot C^{x+y-1}}$$

$$\alpha = \left(\frac{K_{eq}}{x^x \cdot y^y \cdot C^{x+y-1}}\right)^{\left(\frac{1}{x+y}\right)}$$

78. Among the given, AgCl is most soluble in aqueous ammonia solution because it forms a soluble complex with it.

79. $\underset{s}{Ag_2CrO_4} \longrightarrow \underset{2s}{2Ag^+} + \underset{s}{CrO_4^{2-}}$

$$K_{sp} = (2s)^2 s = 4s^3$$

$$s = \left(\frac{K_{sp}}{4}\right)^{1/3} = \left(\frac{32 \times 10^{-12}}{4}\right)^{1/3} = 2 \times 10^{-4}\ \text{M}$$

80. $\underset{(1-s)}{BaSO_4(s)} \rightleftharpoons \underset{s}{Ba^{2+}(aq)} + \underset{s}{SO_4^{2-}(aq)}$

At equili.

K_{sp} for $\quad BaSO_4 = [Ba^{2+}][SO_4^{2-}] = s \times s = s^2$

But $\quad s = 8 \times 10^{-4}$ mol dm^{-3}

$\therefore \quad K_{sp} = (8 \times 10^{-4})^2 = 64 \times 10^{-8}$

In the presence of 0.01 M H_2SO_4, the expression for K_{sp} will be

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

$$K_{sp} = (s) \cdot (s + 0.01)$$

(0.01 M SO_4^{2-} ions from 0.01 M H_2SO_4)

$$64 \times 10^{-8} = s \cdot (s + 0.01)$$

$$s^2 + 0.01s - 64 \times 10^{-8} = 0$$

$$s = \frac{-0.01 \pm \sqrt{(0.01)^2 + (4 \times 64 \times 10^{-8})}}{2}$$

$$= 5 \times 10^{-3}(-1 + 1.012719)$$

$$= 6.4 \times 10^{-5}\ \text{mol dm}^{-3}$$

Note $s <<< 0.01$, so, $s + 0.01 \approx 0.01$ and $64 \times 10^{-8} = s \times 0.01$

$$s = \frac{64 \times 10^{-8}}{0.01} = 6.4 \times 10^{-5}$$

81. Let s be the solubility of $Al(OH)_3$.

	$Al(OH)_3$ $\rightleftharpoons$	$Al^{3+}(aq)$ +	$3OH^-(aq)$
Concentration at $t = 0$	1	0	0
Concentration at equilibrium	$1 - s$	s	$3s$

$$K_{sp} = [Al^{3+}][OH]^{-3} = (s)(3s)^3 = 27s^4$$

$$s^4 = \frac{K_{sp}}{27} = \frac{27 \times 10^{-11}}{27 \times 10} = 1 \times 10^{-12}$$

$$s^4 = 1 \times 10^{-3}\ \text{mol L}^{-1}$$

Molar mass of $Al(OH)_3$ is 78 g. Therefore, solubility of $Al(OH)_3$ in g L^{-1} $= 1 \times 10^{-3} \times 78$ g L^{-1}

$$= 78 \times 10^{-3}\ \text{g L}^{-1}$$

$$= 7.8 \times 10^{-2}\ \text{g L}^{-1}$$

pH of the solution

$$s = 1 \times 10^{-3}\ \text{mol L}^{-1}$$

$$[OH^-] = 3s = 3 \times 1 \times 10^{-3} = 3 \times 10^{-3}$$

$$\text{pOH} = 3 - \log 3$$

$$\text{pH} = 14 - \text{pOH} = 11 + \log 3 = 11.4771$$

82. Suppose solubility of $PbCl_2$ in water is s mol L^{-1}.

$$\underset{(1-s)}{PbCl_2(s)} \rightleftharpoons \underset{s}{Pb^{2+}(aq)} + \underset{2s}{2Cl^-(aq)}$$

$$K_{sp} = [Pb^{2+}] \cdot [Cl^-]^2$$

$$K_{sp} = [s][2s]^2 = 4s^3$$

$$3.2 \times 10^{-8} = 4s^3$$

$$s^3 = \frac{3.2 \times 10^{-8}}{4} = 0.8 \times 10^{-8}$$

$$s^3 = 8.0 \times 10^{-9}$$

Solubility of $PbCl_2$, $s = 2 \times 10^{-3}$ mol L^{-1}

Solubility of $PbCl_2$ in g L^{-1} $= 278 \times 2 \times 10^{-3} = 0.556$ g L^{-1}

($\because$ Molar mass of $PbCl_2 = 207 + (2 \times 35.5) = 278$)

0.556 g of $PbCl_2$ dissolve in 1 L of water.

$\therefore$ 0.1 g of $PbCl_2$ will dissolve in $\frac{1 \times 0.1}{0.556}$ L of water

$$= 0.1798\ \text{L} = 179.8\ \text{mL} \approx 180\ \text{mL}$$

Round II

1.

$$\begin{array}{llll} N_2 & + \; 3H_2 & \rightleftharpoons \; 2NH_3 & \\ 30 & 30 & 0 & \text{Initially} \\ (30-x) & (30-x) & 2x & \text{At equilibrium} \end{array}$$

$$2x = 10, \quad \therefore \; x = \frac{10}{2} = 5 \quad [\because \text{ yield is } 50\%]$$

$$N_2 = 30 - 5 = 25 \text{ L}$$

$$H_2 = 30 - 3 \times 5 = 15 \text{ L}$$

$$NH_3 = 2 \times 5 = 10 \text{ L}$$

2. $2NaNO_3 \rightleftharpoons 2NaNO_2 + O_2$

According to Le-Chatelier principle, low pressure, high temperature and addition of $NaNO_3$ favour forward reaction.

3. Aspirin is a weak acid. Due to common ion effect, it is unionised in acid medium but completely ionised in alkaline medium.

4. For the precipitation of an electrolyte, it is necessary that the ionic product must exceed its solubility product.

5.

$$\begin{array}{llll} & NH_4OH & \rightleftharpoons \; NH_4^+ & + \; OH^- \\ \text{At } t = 0 & 0.1 \text{ M} & 0 & 0 \\ \text{At equilibrium} & \left(0.1 - \frac{1.3 \times 0.1}{100} \text{ M}\right) & 0.0013 \text{ M} & (0.0013 \text{ M}) \\ & = 0.1 \text{ M} & & \end{array}$$

$$[OH^-] = 0.0013 \text{ M} = 13 \times 10^{-4} \text{ M}$$

$$pOH = -\log [OH^-] = -\log (13 \times 10^{-4}) = 2.89$$

$$pH = 14 - 2.89 = 11.11$$

6.

$$\begin{array}{llll} & C_2H_6(g) & \rightleftharpoons \; C_2H_4(g) & + \; H_2(g) \\ \text{Initial pressure} & 4.0 \text{ atm} & 0 & 0 \\ \text{Equili. pressure} & (4.0 - p) \text{ atm} & p & p \end{array}$$

$$K_p = \frac{p_{C_2H_4} \cdot p_{H_2}}{p_{C_2H_6}} = \frac{p.p}{4.0 - p}$$

$$0.04 = \frac{p^2}{4.0 - p} \quad \text{or} \quad 0.16 - 0.04p = p^2$$

$$p = \frac{-0.04 \pm \sqrt{0.0016 - 4(-0.16)}}{2}$$

$$p = \frac{-0.04 \pm 0.80}{2}$$

$$p = 0.38 \qquad \text{(by taking positive value)}$$

Hence, $p_{C_2H_6} = 4.0 - 0.38 = 3.62$ atm

7. First dissociation

$$X(OH)_3 \longrightarrow X(OH)_2^+ + OH^-$$

Second dissociation

$$X(OH)_2^+ \longrightarrow X(OH)^{2+} + OH^-$$

$$\text{Total } [OH^-] = 4 \times 10^{-3} + 2 \times 10^{-3} = 6 \times 10^{-3}$$

$$pOH = 3 - \log 6 = 3 - 0.78 = 2.22$$

$$pH = 14 - 2.22 = 11.78$$

8. Conjugate acids of the given bases are, H_2O, ROH, CH_3COOH and HCl. Order of acidic strength is

$$HCl > CH_3COOH > H_2O > ROH$$

Hence, order of basic strength of their conjugate bases is

$$R\bar{O} > \bar{O}H > CH_3CO\bar{O} > Cl^-$$

9.
(i) KNO_3 is a salt of strong acid and strong base, hence its aqueous solution is neutral; pH = 7

(ii) CH_3COONa is a salt of weak acid and strong base, hence, its aqueous solution is basic; pH > 7.

(iii) NH_4Cl is a salt of strong acid and weak base, hence its aqueous solution is acidic; pH < 7.

(iv) $C_6H_5COONH_4$ is a salt of weak acid, C_6H_5COOH and weak base, NH_4OH. But NH_4OH is slightly stronger than C_6H_5COOH. Hence, pH is slightly > 7.

Therefore, increasing order of pH of the given salts is

$$NH_4Cl < KNO_3 < C_6H_5COONH_4 < CH_3COONa$$

10.

$$C_6H_5COOAg(s) \rightleftharpoons C_6H_5COO^- + Ag^+; \quad K_1 = K_{sp}$$

$$C_6H_5COO^- + H^+ \rightleftharpoons C_6H_5COOH; \quad K_2 = \frac{1}{K_a}$$

$$C_6H_5COOAg(s) + H^+ \rightleftharpoons C_6H_5COOH + Ag^+; \quad K_3 = \frac{K_{sp}}{K_a}$$

$$K_3 = \frac{[C_6H_5COOH][Ag^+]}{[H^+]} = \frac{s \cdot s}{[H^+]} = \frac{s^2}{[H^+]} = \frac{K_{sp}}{K_a}$$

where, s is the solubility of C_6H_5COOAg.

In a buffer of pH = 3.19

$$\log [H^+] = -3.19 = \bar{4}.81$$

$$[H^+] = \text{antilog } \bar{4}.81 = 6.46 \times 10^{-4}$$

$$\frac{s^2}{[H^+]} = \frac{K_{sp}}{K_a} \text{ or } s^2 = \frac{K_{sp} \times [H^+]}{K_a}$$

$$s = \sqrt{\frac{2.5 \times 10^{-13} \times 6.46 \times 10^{-4}}{6.46 \times 10^{-5}}}$$

$$s = \sqrt{2.5 \times 10^{-13} \times 10}$$

$$s = 1.6 \times 10^{-6} \text{ M (in buffer)}$$

In aqueous solution, solubility of C_6H_5COOAg :

$$K_{sp} = [C_6H_5COO^-][Ag^+] = s \cdot s = s^2$$

$$s = \sqrt{K_{sp}} = \sqrt{2.5 \times 10^{-13}} = 5 \times 10^{-7} \text{ M}$$

$$\frac{s_{(C_6H_5COOAg)} \text{ in buffer}}{s_{(C_6H_5COOAg)} \text{ in aqueous solution}} = \frac{1.6 \times 10^{-6}}{5.0 \times 10^{-7}} = 3.2$$

C_6H_5COOAg is 3.2 times more soluble in buffer than in pure water.

11. $CH_2ClCOOH + H_2O \rightleftharpoons CH_2ClCOO^- + H_3O^+$

$$K_a = 1.35 \times 10^{-3} \qquad \text{(given)}$$

$$pK_a = -\log K_a = -\log [1.35 \times 10^{-3}]$$

$$= 3 - 0.13 = 2.87$$

By Ostwald's dilution law,

$$[H_3O^+] = \sqrt{K_a \cdot C} = \sqrt{1.35 \times 10^{-3} \times 0.1}$$

$$[H_3O^+] = 1.16 \times 10^{-2} M$$

$$\text{pH of acid} = -\log [H_3O^+] = -\log (1.16 \times 10^{-2})\ M$$

$$pH = 2 - 0.06 = 1.94$$

0.1 M $CH_2ClCOONa$ (sod. chloroacetate) is basic due to hydrolysis.

$$CH_2ClCOO^- + H_2O \rightleftharpoons CH_2ClCOOH + OH^-$$

For a salt of strong base + weak acid,

$$pH = 7 + \frac{pK_a + \log C}{2} = 7 + \frac{2.87 + \log 0.1}{2}$$

$$pH = 7 + \frac{2.87 + (-1)}{2} = 7 + \frac{1.87}{2}$$

$$= 7 + 0.935 \approx 7.94$$

$$pH = 7.94$$

12. $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}; \qquad K_{sp} = 1.1 \times 10^{-12}$

$s \qquad 2s \qquad s$ (Solubility of Ag_2CrO_4 is s mol L^{-1})

$$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$$

$$K_{sp} = (2s)^2 \cdot s = 4s^3$$

or $$s^3 = \frac{K_{sp}}{4} = \frac{1.1 \times 10^{-12}}{4} = 0.275 \times 10^{-12}$$

$$s^3 = 2.75 \times 10^{-13}$$

$$3 \log s = \log 2.75 \times 10^{-13}$$

$$3 \log s = -13 + 0.4393 = -12.5607$$

$$\log s = \frac{-12.5607}{3} = -4.1869 = \bar{5}.8131$$

$$s = \text{antilog } \bar{5}.8131 = 6.503 \times 10^{-5}\ M$$

Solubility of $[Ag_2CrO_4] = 6.503 \times 10^{-5}$ M

$$AgBr \rightleftharpoons Ag^+ + Br^-; \quad K_{sp} = 5.0 \times 10^{-13}$$

$s \qquad s \qquad s$

(Solubility of AgBr is s mol L^{-1})

$$K_{sp} = [Ag^+][Br^-] = s \cdot s = s^2$$

or $$s = \sqrt{K_{sp}} = \sqrt{5.0 \times 10^{-13}}$$

$$= \sqrt{50 \times 10^{-14}}$$

$$s = 7.07 \times 10^{-7}\ M$$

Ratio of their solubilities

$$\frac{s\,(Ag_2CrO_4)}{s\,(AgBr)} = \frac{6.50 \times 10^{-5}\ M}{7.07 \times 10^{-7}\ M} = 91.93 \approx 92$$

Ag_2CrO_4 is 92 times more soluble than AgBr.

13. (a) Molecular mass of TlOH = 204 + 16 + 1 = 221 g mol^{-1}

Conc. in mol L^{-1} (molarity)

$$= \frac{\text{Mass of TlOH (g)}}{\text{Molar mass of TlOH} \times \text{Volume of solution (L)}}$$

$$= \frac{2}{221 \times 2} = 0.00452 = 4.52 \times 10^{-3}\ M$$

$$pH = -\log [OH^-] = -\log [4.52 \times 10^{-3}]$$

$$pOH = 3 + (-0.6551) = 2.344$$

$$pH + pOH = 14$$

or $$pH = 14 - 2.334 = 11.656 \approx 11.66$$

(b) Molecular mass of $Ca(OH)_2 = 40 + [(16+1) \times 2]$

$$= 74 \text{ g mol}^{-1}$$

Molarity, M

$$= \frac{\text{Mass of } Ca(OH)_2(g) \times 1000}{\text{Molar mass of } Ca(OH)_2 \times \text{Volume of solution (mL)}}$$

$$M = \frac{0.3 \times 1000}{74 \times 500} = 0.0081$$

One mole of $Ca(OH)_2$ gives 2 moles of OH^-. So

$$[OH^-] = 2 \times 0.0081 = 0.0162\ M$$

$$pOH = -\log [OH^-] = -\log [0.0162]$$

$$pOH = -\log [1.62 \times 10^{-2}]$$

$$= 2 + (-0.2095) = 1.7905 \approx 1.79$$

$$pH + pOH = 14 \quad \text{or } pH = 14 - 1.79 = 12.21$$

(c) Molecular mass of NaOH = 23 + 16 + 1 = 40

$$M = \frac{\text{Mass of NaOH}(g) \times 1000}{\text{Molar mass of NaOH} \times \text{Volume of solution (mL)}}$$

$$= \frac{0.3 \times 1000}{40 \times 200} = 0.0375$$

$$pOH = -\log [0.0375] = -\log [3.75 \times 10^{-2}]$$

$$pOH = 2 + (-0.5740) = 1.426 \approx 1.43$$

$$pH + pOH = 14 \quad \text{or} \quad pH = 14 - 1.43 = 12.57$$

(d) In case of dilution $M_1V_1 = M_2V_2$

$$13.6 \times 1 \text{ (mL)} = M_2 \times 1000 \text{ (mL)}$$

$$M_2 = \frac{13.6 \times 1}{1000} = 0.0136 = 1.36 \times 10^{-2}\ M$$

$$pH = -\log [1.36 \times 10^{-2}]$$

$$= 2 + (-0.1335) = 1.8665$$

$$pH = 1.87$$

14. 90.55% CO by mass means 90.55 g CO and 9.45 g CO_2 are present in 100 g mixture.

No. of moles of CO, $n_{CO} = \frac{90.55}{28} = 3.234$ mol

(Molar mass of CO = 28 g mol^{-1})

No. of moles of CO_2, $n_{CO_2} = \frac{9.45}{44} = 0.215$ mol

(Molar mass of CO_2 = 44 g mol^{-1})

Partial pressure of CO, $p_{CO} = x_{CO} \cdot p_{total}$

$$\left(x_{CO} = \frac{3.234}{3.234\ +\ 0.215} = 0.938\right)$$

$$p_{CO} = 0.938 \times 1\,\text{atm} = 0.938\ \text{atm}$$

Similarly, $p_{CO_2} = x_{CO_2} \cdot p_{total}$

$$\left(x_{CO_2} = \frac{0.215}{3.234\ +\ 0.215} = 0.062\right)$$

$$p_{CO_2} = 0.062 \times 1\,\text{atm} = 0.062\ \text{atm}$$

$$C(s)\ +\ CO_2\,(g) \rightleftharpoons 2\ CO(g)$$

$$K_p = \frac{p^2_{CO}}{p_{CO_2}} = \frac{(0.938)^2}{0.062} = 14.19$$

$$\Delta n_g = 2 - 1 = 1$$

$$K_p = K_c\ (RT)^{\Delta n_g}$$

$$K_c = \frac{K_p}{RT} \qquad (\because\ \Delta n_g = 1)$$

$$K_c = \frac{14.19}{0.0821 \times 1127} = 0.15336 \approx 0.153$$

15. $2BrCl(g) \rightleftharpoons Br_2(g)\ +\ Cl_2(g);\ K_c = 32$ at 500 K

Initial conc. 3.30×10^{-3} mol L^{-1} 0   0

Equili. conc. $(3.30 \times 10^{-3} - x)$ mol L^{-1} $\frac{x}{2}$ mol L^{-1} $\frac{x}{2}$ mol L^{-1}

$$K_c = \frac{[Br_2]\ [Cl_2]}{[BrCl]^2}$$

$$= \frac{x/2 \cdot x/2}{(3.30 \times 10^{-3} - x)^2} = 32$$

$$\frac{x^2}{4 \times (3.30 \times 10^{-3} - x)^2} = 32$$

$$\frac{x}{2 \times (3.30 \times 10^{-3} - x)} = \sqrt{32} = 5.656$$

$$\frac{x}{3.30 \times 10^{-3} - x} = 2 \times 5.656 = 11.312$$

$$x = 11.312(3.30 \times 10^{-3} - x)$$

$$x = 0.03732 - 11.312x$$

$$x + 11.312\ x = 0.03732$$

$$x = \frac{0.03732}{12.312} = 3.032 \times 10^{-3}\ \text{mol L}^{-1}$$

$$[BrCl]_{equili.} = (3.30 \times 10^{-3} - 3.032 \times 10^{-3})\ \text{mol L}^{-1}$$

$$= 2.68 \times 10^{-4}\ \text{mol L}^{-1}$$

16. $\text{pOH} = 14 - \text{pH} = 14 - 10.65 = 3.35$

$$\text{pOH} = -\log\,[OH^-]$$

$$-3.35 = \log\,[OH^-]$$

$$\therefore \quad [OH^-] = 4.466 \times 10^{-4}\ M$$

$$Ca(OH)_2 = Ca^{2+} + \underset{4.466 \times 10^{-4}\ M}{2OH^-}$$

$$\frac{[OH^-]}{2} = [Ca(OH)_2] = 2.2335 \times 10^{-4}\ M$$

Hence, in 250 mL, moles of

$$Ca(OH)_2 = \frac{2.2335 \times 10^{-4} \times 250}{1000} = 0.56 \times 10^{-4}$$

17. $\text{pH} = -\log\,(5 \times 10^{-10}) + \log\left[\frac{5 \times V}{V+10} \bigg/ \frac{10 \times 2}{V+10}\right]$

$$9 = -\log\,(5 \times 10^{-10}) + \log\frac{V}{4}$$

On solving, $V = 2$ mL

18. Weak monoacidic base, *e.g.*, BOH is neutralised as follows

$$BOH + HCl \longrightarrow BCl + H_2O$$

At equivalence point, all BOH get converted into salt. Remember! the concentration of H$^+$ (or pH of solution) is due to hydrolysis of the resultant salt (BCl, cationic hydrolysis here.)

$$\underset{C\,(1-h)}{B^+} + H_2O \rightleftharpoons \underset{Ch}{BOH} + \underset{Ch}{H^+}$$

Volume of HCl used up,

$$V_a = \frac{N_b V_b}{N_a} = \frac{2.5 \times 2 \times 15}{2 \times 5} = 7.5\ \text{mL}$$

Concentration of salt,

$$[BCl] = \frac{\text{conc. of base}}{\text{total volume}}$$

$$= \frac{2 \times 2.5}{5\ (7.5 + 2.5)}$$

$$= \frac{1}{10} = 0.1$$

$$K_h = \frac{Ch^2}{1-h} = \frac{K_w}{k_b}$$

(h should be estimated whether that can be neglected or not)

On calculating, $h = 0.27$ (significant, not negligible)

$$[H^+] = Ch = 0.1 \times 0.27 = 2.7 \times 10^{-2}\ M$$

19.

Salt	Solubility product	Solubility
MX	$S_1^2 = 4.0 \times 10^{-8}$	$S_1 = 2 \times 10^{-4}$
MX_2	$4S_2^3 = 3.2 \times 10^{-14}$	$S_2 = 2 \times 10^{-5}$
M_3X	$27S_3^4 = 2.7 \times 10^{-15}$	$S_3 = 1 \times 10^{-4}$

Thus, solubility order is $MX > M_3X > MX_2$.

20. $2NH_3 \rightleftharpoons N_2\ +\ 3H_2$

Initial moles a 0   0

At equilibrium $(a - 2x)$ x $3x$

Initial pressure of NH$_3$ if 'a' mole = 15 atm at 27°C. The pressure of 'a' mole of NH$_3$ = p atm at 347°C

$$\therefore \qquad \frac{15}{300} = \frac{p}{620}$$

$$\therefore \qquad p = 31\ \text{atm}$$

At constant volume and at 347°C,

$$\text{mole} \propto \text{pressure}$$

$$a \propto 31 \qquad \text{(before equilibrium)}$$

$$\therefore \quad (a-2x) \propto 50 \qquad \text{(after equilibrium)}$$

$$\therefore \quad \frac{(a-2x)}{a} = \frac{50}{31}$$

$$\therefore \quad x = \frac{19}{62}a$$

$$\therefore \text{ \% of } NH_3 \text{ decomposed} = \frac{2x}{a} \times 100 = \frac{2 \times 19a}{62 \times a} \times 100 = 61.29\%$$

21. $FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$;

Initial pressure 1.4 atm 0.80 atm

$$K_p = 0.265 \text{ at } 1050 \text{ K}$$

$$Q_p = \frac{p_{CO_2}}{p_{CO}} = \frac{0.80}{1.4} = 0.571 \quad [\because \text{Fe and FeO are solids.}]$$

$Q_p > K_p$, the reaction will go in reverse direction. Due to this pressure of CO_2 will decrease and that of CO will increase to attain equilibrium. Hence, $p_{CO_2} = (0.80 - p)$ and $p_{CO} = (1.4 + p)$

(Suppose p is the decrease in pressure of CO_2 and p is the increase in pressure of CO).

$$K_p = \frac{p_{CO_2}}{p_{CO}} = 0.265 = \frac{(0.80 - p)}{(1.4 + p)}$$

$$1.265\,p = 0.80 - 0.371$$

$$1.265\,p = 0.429$$

$$p = \frac{0.429}{1.265} = 0.339 \text{ atm}$$

Hence, at equilibium,

$$p_{CO_2} = 0.80 - 0.339 = 0.461 \text{ atm}$$

and $$p_{CO} = 1.4 + 0.339 = 1.739 \text{ atm}$$

22. $[S^{2-}] = 1 \times 10^{-19}$ M

10 mL of S^{2-} is mixed with 5 mL of 0.04 M solution of different solutes so that final volume of solution is 15 mL.

$$\therefore \quad [S^{2-}]_{mix} = \frac{10 \times 10^{-19}}{15} = 6.67 \times 10^{-20} \text{ M}$$

$$[M^{2+}] = \frac{5 \times 0.04}{15} = 1.33 \times 10^{-2} \text{ M}$$

where, $[M^{2+}] = Fe^{2+}, Mn^{2+}, Zn^{2+}$ or Cd^{2+}

$$[M^{2+}][S^{2-}]\ 1 = .33 \times 10^{-2} \times 6.67 \times 10^{-20}$$

Ionic product of $[M^{2+}][S^{2-}] = 8.87 \times 10^{-22}$

IP of $[M^{2+}][S^{2-}] > K_{sp}$ of ZnS and CdS

So, these ($CdCl_2$ and $ZnCl_2$) are precipitated as CdS and ZnS.

23. Since, value of K increases with rise in temperature, the reaction is endothermic.

Since, number of moles of gaseous products are greater than the number of moles of gaseous reactants. Thus, higher pressure favours the backward reaction, *i.e.,* more $N_2O_4(g)$ will be obtained, if $p_{product} > p_{reactant}$.

$$\Delta n_g = n_p - n_r > 0 \qquad \therefore \quad \Delta S > 0$$

24. $N_2O_4 \rightleftharpoons 2NO_2$

a 0 Initial

$a(1-\alpha)$ $2a\alpha$ At equilibrium

$$\text{Vapour density} = \frac{46}{1+\alpha} : 30.67$$

$$\text{So,} \quad (1+\alpha) = \frac{46}{30.67} = 1.5 \quad \text{or} \quad \alpha = 50\%$$

$$\text{Total pressure} = \frac{1.5 \times 1.5 \times 0.082 \times 300}{8.2} = 6.75 \text{ atm}$$

$$\text{So,} \quad K_p = \frac{4\alpha^2}{1-\alpha^2} = 9 \text{ atm}$$

$$\text{Density of mixture} = \frac{138}{8.2} \text{ g/L} = 16.83 \text{ g/L}$$

25. $$\text{Reaction quotient} = \frac{p^2_{NH_3}}{p_{N_2} \cdot p^3_{H_2}} = \frac{(0.05 \text{ atm})^2}{(0.05 \text{ atm})(3.0 \text{ atm})^3}$$

$$= 1.85 \times 10^{-3} \text{ atm}^{-2}$$

The value of K_p is 4.28×10^{-5} atm^{-2}. The numerical value of Q_p is more than that of K_p. The reaction goes towards the left and thus, ammonia decomposes into H_2 and N_2.

26. In aqueous solution, a salt of weak acid and a weak base acts as a buffer solution. The pH of a buffer solution do not change on dilution. Thus, pH of 0.01 M CH_3COONH_4 will not change on dilution. HCO_3^- from $NaHCO_3$ and $H_2PO_4^-$ from NaH_2PO_4 are amphiprotic anions. The pH of solution containing amphiprotic anions do not change on dilution.

27. $K_{sp} = 1.1 \times 10^{-11} = (1.4 \times 10^{-4})^{x+y} \cdot x^x \cdot y^y$

So, we have $x + y = 3$

$$\text{So,} \quad x^x \cdot y^y = \frac{1.1 \times 10^{-11}}{1.4 \times 1.4 \times 1.4 \times 10^{-12}} = 4$$

Hence, $x = 1,\ y = 2$

or $y = 1,\ x = 2.$

28. According to Le-Chatelier's principle with increase of pressure, equilibrium shifts in that direction in which lesser number of gaseous moles are produced.

29. In biological systems buffer system of carbonic acid and sodium bicarbonate is found in our blood. It maintains the pH of blood to a constant value of about 7.4.

30. H_2S is a weak acid and also a weak electrolyte, thus its ionisation is suppressed when small amount of strong electrolyte like HCl is added due to common ion effect.

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

$$HCl \longrightarrow \underbrace{H^+}_{\text{common ion}} + Cl^-$$

31. $$\begin{array}{l} (NH_4)_2CO_3 \longrightarrow 2NH_4^+ + CO_3^{2-} \\ \qquad 2H_2O \longrightarrow 2OH^- + 2H^+ \\ \qquad\qquad\qquad\quad \downarrow \qquad \downarrow \\ \qquad\qquad\quad NH_4OH + H_2CO_3 \\ \qquad\qquad\quad \text{weak base} \quad \text{weak acid} \end{array}$$

If K_b of $NH_4OH > K_a$ of H_2CO_3

The solution is basic.

Or if K_a of $H_2CO_3 > K_b$ of NH_4OH the solution is acidic.

32. $PCl_5 \longrightarrow PCl_3 + Cl_2$

At constant pressure, when He is added to the equilibrium, volume increases. Thus, in order to maintain the K constant, degree of dissociation of PCl_5 increases.

He is unreactive towards chlorine gas.

33. $CaCO_3(s) \overset{\Delta}{\rightleftharpoons} CaO(s) + CO_2(g) \qquad K_{p_1} = 8 \times 10^{-2}$

$$CO_2(g) + C(s) \longrightarrow 2CO(g) \qquad K_{p_2} = 2$$

$$K_p{}' = K_{p_1} \times K_{p_2}$$

$$= 8 \times 10^{-2} \times 2 = 16 \times 10^{-2}$$

$$K_p{}' = (p_{CO}(g))^2$$

$$p_{CO} = \sqrt{K_p{}'} = \sqrt{16 \times 10^{-2}} = 4 \times 10^{-1}$$

$$= 0.4 \text{ atm}$$

34. $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$

$$\begin{array}{llll} 0.5 & & & \text{Initial} \\ (0.5 - x) & & 2x & \text{At equilibrium} \end{array}$$

Total pressure $= 0.5 - x + 2x = 0.5 + x$

$$0.5 + x = 0.8$$

$$x = 0.8 - 0.5 = 0.3$$

$$p_{CO} = 2x = 2 \times 0.3 = 0.6 \text{ atm}$$

$$K = \frac{(p_{CO})^2}{p_{CO_2}} = \frac{(0.6)^2}{0.2} = 1.8 \text{ atm}$$

35. $K_p = K_c(RT)^{\Delta n}$

Here, $\qquad K_p = K_c, \quad \Delta n = 2 - 1 = 1$

$$(RT)^{\Delta n} = 1$$

$$(0.0821 \times T) = 1$$

$$T = \frac{1}{0.0821} = 12.18 \text{ K},$$

36. % of unprecipitated $Ag^+ = \dfrac{\text{unprecipitated } Ag^+}{\text{total } Ag^+ \text{ taken}} \times 100$

$$= \frac{1 - \left(\dfrac{149}{150}\right)}{1} \times 100 = 0.666\%$$

37. $K_{sp} = [Ag^+][IO_3^-]$

$$= \frac{(10 - x)}{500} \cdot \frac{(3 - x)}{500} = \frac{6.66 \times 10^3 \times 2}{25 \times 10000} = 5.3 \times 10^{-8}$$

38. Moles of $AgIO_3$ precipitated $= \dfrac{149}{150}$ millimol

Mass of $AgIO_3$ precipitated $= 285 \times \dfrac{149}{150}$ g $= 283.1$ g

39. $N_2(g) + O_2(g) \longrightarrow 2NO(g)$

$$K_c = \frac{[NO]^2}{[N_2][O_2]} = 4 \times 10^{-4}$$

$$2NO(g) \longrightarrow N_2(g) + O_2(g)$$

$$K_c{}' = \frac{1}{K_c} = \frac{[N_2][O_2]}{[NO]^2}$$

$$= \frac{1}{4 \times 10^{-4}} = \frac{10^4}{4}$$

$$NO(g) \longrightarrow \frac{1}{2} N_2(g) + \frac{1}{2} O_2(g)$$

$$K_c{}'' = \frac{[N_2]^{1/2}[O_2]^{1/2}}{[NO]}$$

$$= \sqrt{K_c{}'} = \sqrt{\frac{10^4}{4}} = \frac{100}{2} = 50$$

40. $HQ \longrightarrow H^+ + Q^-$

$$[H^+] = \sqrt{K_a C} \qquad \text{(by Ostwald's dilution law)}$$

$$[H^+] = 10^{-pH} = 10^{-3} \text{ M}$$

$$C = 0.1 \text{ M}$$

Thus, $\qquad 10^{-3} = \sqrt{K_a \times 0.1}$

$$10^{-6} = K_a \times 0.1$$

$\therefore \qquad K_a = 10^{-5}$

41. Let molar solubility of $Cr(OH)_3 = s$ mol L^{-1}

$$Cr(OH)_3(s) \rightleftharpoons \underset{s}{Cr^{3+}}(aq) + \underset{3s}{3OH^-}(aq)$$

$$K_{sp} = 1.6 \times 10^{-30}$$

$$= [Cr^{3+}][OH^-]^3$$

$$= (s)(3s)^3 = 27s^4$$

$\therefore \qquad s^4 = \dfrac{1.6 \times 10^{-30}}{27}$

$\therefore \qquad s = \sqrt[4]{\dfrac{1.6 \times 10^{-30}}{27}}$

42. Only in reaction (II) $H_2PO_4^-$, gives H^+ to H_2O, thus behaves as an acid.

43. $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-; \quad K_1 = 4.2 \times 10^{-7}$

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}; \qquad K_2 = 4.8 \times 10^{-11}$

$$K_1 >> K_2$$

$\therefore \qquad [H^+] = [HCO_3^-]$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

So, $\qquad [CO_3^{2-}] = K_2 = 4.8 \times 10^{-11}$

44. $K_{sp} = [Ag^+][Br^-] = 5.0 \times 10^{-13}$

$$[Ag^+] = 0.05\text{ M}$$

$$[Br^-] = \frac{5.0 \times 10^{-13}}{0.05} = 1 \times 10^{-11}\text{ M}$$

Moles of KBr $= 1 \times 10^{-11} \times 1 = 1 \times 10^{-11}$

Weight of KBr $= 1 \times 10^{-11} \times 120 = 1.2 \times 10^{-9}$ g

45. $Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$

$$K_{sp} = [Mg^{2+}][OH^-]^2$$

$$[OH^-] = \sqrt{\frac{K_{sp}}{[Mg^{2+}]}} = 10^{-4}$$

$$\text{pOH} = 4$$

and $\quad \text{pH} = 10$

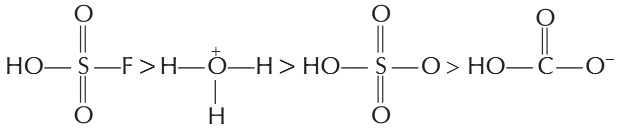
46. $K_{sp}[BaCO_3] = [Ba^{2+}][CO_3^{2-}]$

$$[Ba^{2+}] = \frac{K_{sp}}{[CO_3^{2-}]} = \frac{5.1 \times 10^{-9}}{1 \times 10^{-4}}$$

$$[Ba^{2+}] = 5.1 \times 10^{-5}\text{ M.}$$

47. As equation 'III' is obtained on adding equation 'I' and equation 'II', so $K_3 = K_1 \cdot K_2$.

48. Acidity order



$$HO-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-F > H-\overset{+}{\underset{H}{O}}-H > HO-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-O > HO-\overset{O}{\overset{\|}{C}}-O^-$$

(conjugate anion decreases acidity)

49.

Initially $\quad X \rightleftharpoons 2Y \quad$ 1 $\quad$ 0

At equilibrium $\quad 1 - x \quad 2x$

Total number of moles $= 1 + x$

$$K_{p_1} = \frac{\left[\frac{2x}{1+x} \cdot p_1\right]^2}{\left(\frac{1-x}{1+x}\right) \cdot p_1} = \frac{4x^2}{(1-x)} \cdot \frac{p_1}{(1+x)}$$

Initially $\quad Z \rightleftharpoons P + Q \quad$ 1 $\quad$ 0 $\quad$ 0

At equilibrium $\quad 1 - x \quad x \quad x$

Similarly, $\quad K_{p_2} = \frac{x^2}{(1-x)} \cdot \frac{p_2}{(1+x)}$

$$\frac{K_{p_1}}{K_{p_2}} = \frac{1}{9}$$

So, $\quad \frac{4 \times p_1}{p_2} = \frac{1}{9}$

$\Rightarrow \quad \frac{p_1}{p_2} = \frac{1}{36}$

50. For salt of weak acid and weak base

$$\text{pH} = -\frac{1}{2}[\log K_a + \log K_w - \log K_b]$$

$$= \frac{1}{2}\text{p}K_a + \frac{1}{2}\text{p}K_w - \frac{1}{2}\text{p}K_b$$

$$= \frac{1}{2} \times 4.80 + 7 - \frac{1}{2} \times 4.78 = 7.01$$

51. $AgIO_3(s) \rightleftharpoons Ag^+(aq) + IO_3^-(aq)$

Let solubility of $AgIO_3$ be S

$$K_{sp} = [Ag^+][IO_3^-]$$

$$1.0 \times 10^{-8} = S^2 \quad \text{or} \quad S = 1 \times 10^{-4}\text{ mol/L}$$

In 1000 mL moles of $AgIO_3$ dissolved $= 1 \times 10^{-4}$ mol

In 100 mL moles of $AgIO_3$ dissolved $= 1 \times 10^{-5}$ mol

Mass of $AgIO_3$ in 100 mL $= 1 \times 10^{-5} \times 283 = 2.83 \times 10^{-3}$

52. Equilibrium constant for the reaction,

$$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$$

$$K_c = \frac{1}{4.9 \times 10^{-2}}$$

and for, $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$$K_c = \left(\frac{1}{4.9 \times 10^{-2}}\right)^2$$

$$= \frac{10^4}{(4.9)^2} = 416.490$$

53. $\quad PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

Initially $\quad$ 1 $\quad$ 0 $\quad$ 0

At equilibrium $\quad (1 - x) \quad x \quad x$

Total number of moles at equilibrium $= (1 - x) + x + x = 1 + x$

$$p_{PCl_3} = \left[\frac{x}{1+x}\right] \times p$$

54. $\quad NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

Initially $\quad$ 1 $\quad$ 0.5 $\quad$ 0

At equilibrium $\quad (1 - x) \quad (0.5 + x) \quad x$

Total pressure at equilibrium $= p_{NH_3} + p_{H_2S}$

$$= 0.5 + x + x = 0.84$$

$\therefore \quad x = 0.17$ atm

$\therefore \quad p_{NH_3} = 0.50 + 0.17 = 0.67$ atm

$\quad p_{H_2S} = 0.17$ atm

$\therefore \quad K_p = p_{NH_3} \cdot p_{H_2S} = 0.67 \times 0.17 = 0.114$ atm

55. $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$

$$K_c = 1.8 \times 10^{-6} \text{ at } 184^\circ\text{ C } (= 457\text{ K})$$

$$R = 0.00831\text{ kJ mol}^{-1}\text{ K}^{-1}$$

$$K_p = K_c\,(RT)^{\Delta n_g}$$

where,

$$\Delta n_g = (\text{gaseous products} - \text{gaseous reactants})$$
$$= 3 - 2 = 1$$
$$\therefore \quad K_p = 1.8 \times 10^{-6} \times 0.00831 \times 457$$
$$= 6.836 \times 10^{-6} > 1.8 \times 10^{-6}$$

Thus, $K_p > K_c$

56. Conjugate base is formed by loss of H^+.

$$OH^- \longrightarrow \underset{\text{conjugate base}}{O^{2-}} + H^+$$

O^{2-} is the conjugate base of OH^-.

57. $MX_2 \rightleftharpoons \underset{S}{M^{2+}} + \underset{2S}{2X^-}$

$$K_{sp} = [M^{2+}][X^-]^2$$

If solubility be S, then

$$K_{sp} = (S)(2S)^2 = 4S^3$$
$$4S^3 = 4 \times 10^{-12}$$
$$\therefore \quad S = 1 \times 10^{-4}\ \text{M}$$
$$\therefore \quad M^{2+} = S = 1 \times 10^{-4}\ \text{M}$$

58. $K_p = K_c\,(RT)^{\Delta n_g}$

Δn_g = Sum of coefficients of gaseous products – sum of coefficients of gaseous reactants.

$$CO(g) + Cl_2(g) \longrightarrow COCl_2(g)$$
$$\therefore \quad \Delta n_g = 1 - 2 = -1$$
$$\therefore \quad K_p = K_c\,(RT)^{-1}$$
$$\therefore \quad \frac{K_p}{K_c} = (RT)^{-1} = \frac{1}{(RT)}$$

59.

Δn_g = – ve	$\Delta H°$ = – ve
Takes place with decrease in number of moles or pressure, hence increase in pressure shifts equilibrium in forward side.	Takes place with evolution of heat or increase in temperature, hence decrease in temperature shifts this equilibrium in forward side.

60. $HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^- + OH^-$

$$HPO_4^{2-} + H_2O \rightleftharpoons PO_4^{3-} + H_3O^+$$

$H_2PO_2^-$ is a conjugate base of H_3PO_2 (a monobasic acid) and does not give H^+, HPO_3^{2-} is a conjugate base of H_2PO_3 and does not ionise further, since H_3PO_3 is a dibasic acid.

7 Redox Reactions

JEE Main MILESTONE

- Oxidation Number
- Oxidation and Reduction
- Oxidising and Reducing Agent
- Redox Reactions
- Molecular and Ionic Equations
- Balancing of Redox Reactions

7.1 Oxidation Number

The real or imaginary charge which an atom appears to have in its combined state, is called **oxidation state** or **oxidation number** of that atom.

The oxidation number (or oxidation state) of an element in a compound is determined as the number of electrons that have passed from one atom of a given element to other atom (positive oxidation) or to one atom of a given element from other atom (negative oxidation). We can also say that, oxidation state is the oxidation number per atom.

The reaction which involves oxidation and reduction as its two half-reactions is called ***redox reaction.*** *Normally it is found that oxidation and reduction reactions are complementary to each other and occur simultaneously. Their simultaneous occurrence is seen in the form of redox reaction.*

Rules for Assigning Oxidation Number

The oxidation number of an element or atom can be calculated with the help of following rules

1. The oxidation number of an atom in its free or elemental state is zero, *e.g.*, oxidation number of H in H_2, S in S_8, P in P_4, O in O_2 or O_3 is zero.
2. Oxidation number of fluorine is always −1 in all of its compounds.
3. Oxidation number of oxygen is always −2 in all of its compounds except peroxides, superoxides and oxygen fluorides. In peroxides, its oxidation number is −1, in superoxides, its oxidation number is $-\frac{1}{2}$ while in OF_2 its oxidation number is +2.
4. The oxidation number of hydrogen in metallic hydrides is −1 while in rest of the compounds it has +1 oxidation number.
5. The oxidation number of an ion is equal to the electrical charge present on it.
6. For complex ions, the algebraic sum of oxidation numbers of all the atoms is equal to the net charge on the ion.
7. In case of neutral molecules, the algebraic sum of the oxidation numbers of all the atoms present in the molecule is zero.

(Wherever there is doubt, the more electronegative atom takes the lower oxidation number.)

The most common oxidation states of representative elements are tabulated below

Table 7.1 **Common Oxidation States of Representative Elements**

Group	Common oxidation states except zero in free state
1st (IA)	+1
2nd (IIA)	+2
13th (IIIA)	+3, +1
14th (IVA)	+4, +3, +2, +1, −1, −2, −3, −4
15th (VA)	+5, +3, +1, −1, −3 N → shows all possible oxidation states from +5 to −3 including $-\frac{1}{3}$ in N_3H.
16th (VIA)	+6, +4, +2, −2
17th (VIIA)	+7, +5, +3, +1, −1
18th (zero group)	Zero

Caution Point *Transition elements exhibit a large number of oxidation states due to involvement of $(n-1)d$ electrons also besides ns electrons.*

Hot Spot 1

FINDING Oxidation State

Finding oxidation state is an important topic of this chapter and easiest also as by just remembering a few rules, you can find the oxidation state of the desired element.

The various steps used to find out the oxidation state are

Step I Assign oxidation state of all other elements except the one, oxidation state which has to be found. (Use the rules for assigning oxidation states of elements.) *e.g.*, In $KMn0_4$, we have to find the oxidation state of Mn.

$$\overset{+1}{K}\overset{x}{Mn}\overset{-2}{0_4}$$

Step II The algebric sum of oxidation states of all the elements of a netural molecule is zero. (In case of ion, it is equal to charge on the ion.)

$KMn0_4$

$$+1 + x + (-2)4 = 0$$
$$+1 + x - 8 = 0$$
$$x - 7 = 0$$

or $$x = 7$$

Thus, the oxidation state of Mn is +7.

Sample **Problem 1** *Assign oxidation number to the underlined elements in each of the following species.* **[NCERT]**

(*i*) $NaH_2\underline{P}O_4$ (*ii*) $NaH\underline{S}O_4$

(*iii*) $H_4\underline{P}_2O_7$ (*iv*) $\underline{Mn}O_4^{2-}$

(*v*) $Ca\underline{O}_2$ (*vi*) $Na\underline{B}H_4$

(*vii*) $H_2\underline{S}_2O_7$ (*viii*) $KAl(\underline{S}O_4)_2\cdot 12H_2O$

Interpret (i) $NaH_2\underline{P}O_4$

Let the oxidation number of P be *x*. Writing the oxidation number of each atom above its symbol, we get $\overset{+1}{Na}\overset{+1}{H_2}\overset{x}{P}\overset{-2}{O_4}$

In neutral compounds, the sum of the oxidation numbers of all the atoms is zero.

$$\therefore \quad 1(+1) + 2(+1) + x + 4(-2) = 0$$
$$3 + x + (-8) = 0$$
$$x = 8 - 3 = 5$$

Hence, the oxidation number of P in NaH_2PO_4 is + 5.

(ii) $NaH\underline{S}O_4$

Let the oxidation number of S be *x*.

$$\overset{+1}{Na}\overset{+1}{H}\overset{x}{S}\overset{-2}{O_4}$$

$$1(+1) + 1(+1) + x + 4(-2) = 0$$
$$2 + x + (-8) = 0$$
$$x = +6$$

Hence, the oxidation number of S in $NaHSO_4$ is + 6.

(iii) $H_4\underline{P}_2O_7$

Let the oxidation number of P in $H_4P_2O_7$ be x.

$$\overset{+1}{H_4}\ \overset{x}{P_2}\ \overset{-2}{O_7}$$

$$4\,(+1) + 2(x) + 7\,(-2) = 0$$
$$4 + 2x + (-14) = 0$$
$$2x = +10 \quad \text{or} \quad x = +\frac{10}{2} = +5$$

Hence, the oxidation number of P in $H_4P_2O_7$ is + 5.

(iv) $\underline{Mn}O_4^{-2}$

Let the oxidation number of Mn in MnO_4^{2-} be x.

$$\overset{x}{Mn}\ \overset{-2}{O_4}{}^{-2}$$

$$x + 4\,(-2) = -2 \qquad [\because \text{Charge on the ion is } -2]$$
$$x - 8 = -2 \text{ or } x = +6$$

(v) $\underline{Ca}O_2$

Let the oxidation number of O be x.

$$\overset{+2}{Ca}\ \overset{x}{O_2}$$

(Ca is an alkaline earth metal, so its oxidation number is + 2.)

$$1(+2) + 2x = 0$$
$$2x = -2 \text{ or } x = -1$$

Hence, the oxidation number of O in CaO_2 is – 1.

(vi) $Na\underline{B}H_4$

Let the oxidation number of B be x.

$\overset{+1}{Na}\,\overset{x}{B}\,\overset{-1}{H}_4$ (In $NaBH_4$, H exists as hydride ion, H^-, so its oxidation number is – 1)

$$1(+1) + x + 4\,(-1) = 0$$
$$1 + x - 4 = 0 \text{ or } x = +3$$

Hence, the oxidation number of B in $NaBH_4$ is + 3.

(vii) $H_2\underline{S}_2O_7$

Let the oxidation number of S be x.

$$\overset{+1}{H_2}\ \overset{x}{S_2}\ \overset{-2}{O_7}$$

$$2\,(+1) + 2x + 7\,(-2) = 0$$
$$2 + 2x - 14 = 0$$
$$2x = +12 \quad \text{or} \quad x = +6$$

Hence, the oxidation number of S in $H_2S_2O_7$ is + 6.

(viii) $KAl(\underline{S}O_4)_2 \cdot 12H_2O$

Let the oxidation number of S in $KAl(SO_4)_2 \cdot 12H_2O$ be x.

$$\overset{+1}{K}\ \overset{+3}{Al}\ (\overset{x}{\underline{S}}\ \overset{-2}{O_4})_2 \cdot 12\,\overset{+1}{H_2}\overset{-2}{O}$$

$$1(+1) + 1(+3) + 2x + 8\,(-2) + 12\,(2 \times 1 + (-2)) = 0$$
$$4 + 2x - 16 = 0$$
$$2x = +12 \quad \text{or} \quad x = +6$$

Note H_2O is a neutral molecule, therefore sum of oxidation numbers of all atoms in H_2O is zero.
Hence, the oxidation number of S in $KAl(SO_4)_2 \cdot 12H_2O$ is + 6.

Fractional Oxidation States

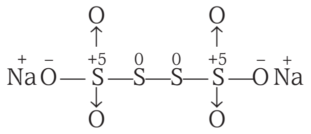
Fractional oxidation states are often used to represent the average oxidation states of several atoms in a structure. For example, in KO_2, the superoxide ion has a charge of −1 divided among two equivalent atoms, so each oxygen is assigned an oxidation state of −1/2. This ion is described as a resonance hybrid of two Lewis structures and each oxygen has oxidation state 0 in one structure and −1 in the other.

For the cyclopentadienyl ion $C_5H_5^-$, the oxidation state of C is $(-1) + (-1/5) = -6/5$. The −1 occurs because each C is bonded to one less electronegative H, and the −1/5 because the total ionic charge is divided among five equivalent C.

Exceptional Cases of Oxidation States

1. **Oxidation State of Sulphur in $Na_2S_4O_6$**

Let us see the structure of $Na_2S_4O_6$.



From the structure , it is clear that the sulphur atoms acting as donor atoms have + 5 oxidation number (each). On the other hand, the sulphur atom involved in pure covalent bond formation has zero oxidation number.

2. **Oxidation State of Fe in Fe_3O_4**

In FeO $\longrightarrow$ $x - 2 = 0, x = +2$
In Fe_2O_3 $\longrightarrow$ $2x - 6 = 0, x = +3$
In Fe_3O_4 $\longrightarrow$ $3x - 8 = 0, x = +8/3$(fractional)

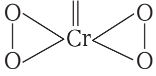
Here, in Fe_3O_4, oxidation number is the average of those in FeO and Fe_2O_3.

$$FeO + Fe_2O_3 = Fe_3O_4$$

Average oxidation number of Fe in

$$Fe_3O_4 = \frac{+2 + 2(+3)}{3} = +\frac{8}{3}$$

3. **Oxidation State of Chromium in CrO_5** CrO_5 has butterfly structure having two peroxo bonds as



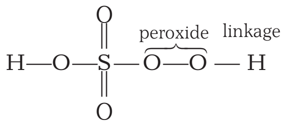
Per oxygen has (–1) oxidation state.

Let the oxidation state of chromium be '*x*'

$$x + 4(-1) + (-2) = 0$$
$$\therefore \qquad x = +6$$

4. **Oxidation State of S in H_2SO_5 and $H_2S_2O_8$**

   In H_2SO_5 (Caro's acid) one peroxide linkage is present.



$$H-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\overbrace{O-O}^{\text{peroxide linkage}}-H$$

   Thus, the oxidation number of S is obtained as

$$\underset{(\text{for H})}{2\times(+1)}+\underset{(\text{for S})}{x}+\underset{(\text{for O})}{3\times(-2)}+\underset{(\text{for O—O})}{2\times(-1)}=0$$

$$2+x-6-2=0 \text{ or } x=+6$$

   Similarly, in $H_2S_2O_8$, the oxidation number of S is + 6.

5. **Oxidation State of Cl in $CaOCl_2$** In $CaOCl_2$ (bleaching powder) or Ca(OCl) Cl, the two Cl atoms are in different oxidation states. The oxidation state of Cl^- is -1 and that present in OCl^- is + 1.

6. **Oxidation Number of Sulphur in $(CH_3)_2SO$** (dimethyl sulphoxide) Here, oxidation number of $O=-2$ oxidation number of each CH_3 group is + 1.

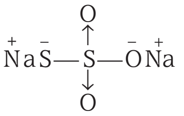
$$\therefore \quad +2+x-2=0 \text{ or } x=0$$

   Thus, sulphur lies in zero oxidation state.

7. **Oxidation Number of Sulphur in hypo, $Na_2S_2O_3$** Let the average oxidation number of sulphur be '*x*'.

$$\therefore \quad +2+2x-6=0 \quad \therefore\ x=+2$$

   Structure of hypo may be drawn as



$$\overset{+}{Na}\overset{-}{S}-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-\overset{-}{O}\overset{+}{Na}$$

   Here, the two sulphur atoms have different oxidation states

   (i) Oxidation number of donor sulpur atom is + 5. It gives up four electrons in coordination and one electron in covalent bond formation with oxygen.

   (ii) Sulphur, bonded with Na, lies in -1 state since one electron of Na lies towards the sulphur. Electrons of S–S bond are equally shared between two sulphur atoms.

   Thus, + 5 and -1 are two oxidation states of the two sulphur atoms.

Sample **Problem 2** *Oxidation state of nitrogen in hydrazoic acid is*

(*a*) -3 (*b*) -2
(c) $-1/2$ (*d*) $-1/3$

Interpret (*d*) Hydrazoic acid is N_3H.

$$N_3H$$

$$3x+1=0$$

$$3x=-1$$

$$x=-1/3$$

Oxidation number of nitrogen is $-1/3$.

Oxidation State in Covalent Compounds

We should take into consideration the following fundamental aspects of bonding while counting the oxidation state of covalently bonded molecules.

1. Single covalent bond contributes one unit for oxidation number.
2. Negative oxidation number is assigned to more electronegative atom and positive oxidation number to less electronegative atom.
3. Coordinate bond is represented by an arrow from donor atom to acceptor atom.

$$\underset{\text{donor}}{A} \longrightarrow \underset{\text{acceptor}}{B}$$

If donor atom is less electronegative and acceptor is more , then + 2 state is given to donor and -2 state is given to acceptor.

But it should be noted that if the donor is more electronegative than the acceptor, then contribution of coordinate bond for both atoms regarding oxidation state is negleted. *e.g.*,

(i) **Oxidation state of N and C in HCN**

$$H-C\equiv N$$

$$+1+a-3=0$$

$$a=+2$$

Carbon is in + 2 state and nitrogen is in -3 state. Each bond contributes -1 state to more electronegatve atom.

(ii) **Oxidation state of N and C in HNC** $H-N\equiv C$

Oxidation state of H = + 1
Oxidation state of nitrogen = $(-1)+(-2)+(0)=-3$

Covalent bond with hydrogen contributes (-1) and covalent bond with carbon contributes (-2) and there is zero contribution of coordinate bond. Let the oxidation state of carbon be '*x*'.

$$+1-3+x=0;\ x=+2$$

(iii) $Fe_{0.94}O$ (Oxidation state of iron is to be determined)

$$0.94x-2=0$$

$$x=2/0.94=200/94$$

(iv) NH_2-NH_2 (Oxidation state of nitrogen is to be determined)

$$2x+4=0$$

$$x=-2$$

Stock Notations

While naming the ion or compound, it is desirable to **put oxidation number per atom** (*i.e.,* oxidation state) in Roman figures within brackets (anion end with ate) (Table 7.2). Such representation is called *Stock notation* given by German chemist *Alfred Stock*.

For example, nitrogen forms five oxides, *i.e.*, N_2O, NO, NO_2, N_2O_4 and N_2O_5 having the oxidation number $+1, +2, +4, +4$ and $+5$ respectively. Therefore, according to Stock notation, they are represented as $N_2(I)O$, $N_2(II)O$, $N(IV)O_2$, $N_2(IV)O_4$, and $N_2(V)O_5$, respectively.

Note Hg_2Cl_2 is also called calomel and is an ionic compound while $HgCl_2$ is also called corrosive sublimate and is a covalent compound and poisonous. Antidote of this is white of an egg.

Table 7.2 **Naming the Acid and its Ions**

Oxoanions	Formula	Acids	Formula
Bromate (I)	BrO^-	Bromic (I)	$HBrO$
Bromate (III)	BrO_2^-	Bromic (III)	$HBrO_2$
Bromate (V)	BrO_3^-	Bromic (V)	$HBrO_3$
Bromate (VII)	BrO_4^-	Bromic (VII)	$HBrO_4$
Chromate (VI)	CrO_4^{2-}	Chromic (VI)	H_2CrO_4
Nitrate (V)	NO_3^-	Nitric	HNO_3
Nitrate (III)	NO_2^-	Nitrous	HNO_2
Phosphate (V)	PO_4^{3-}	Phosphoric	H_3PO_4
Sulphate (IV)	SO_3^{2-}	Sulphurous	H_2SO_3
Sulphate (VI)	SO_4^{2-}	Sulphuric	H_2SO_4
Peroxodisulphate (VI)	$S_2O_8^{2-}$	Peroxy -disulphuric	$H_2S_2O_8$

Sample **Problem 3** *Write the formulae for the following compounds.*

(i) Mercury (II) chloride	*(ii) Nickel (II) sulphate*
(iii) Tin (IV) oxide	*(iv) Thallium (I) sulphate*
(v) Iron (III) sulphate	*(vi) Chromium (III) oxide* **[NCERT]**

Interpret While writing the formula of a compound oxidation state (or valency) of cation is written as the subscript of anion and valency of anion is written as the subscript of cation.

Valency of chloride (Cl^-), sulphate (SO_4^{2-}) and oxide (O^{2-}) are $-1, -2$ and -2 respectively, valencies of metals are given in brackets.

Hence, the formulae of the given compounds is as

(i) $Hg\,(II)\,Cl_2$ (ii) $Ni\,(II)\,SO_4$ (iii) $Sn\,(IV)\,O_2$

(iv) $Th_2(I)\,SO_4$ (v) $Fe_2\,(III)\,(SO_4)_3$ (vi) $Cr_2\,(III)\,O_3$

Difference Between Valency and Oxidation Number

These two terms have different meanings as explained above in the Table 7.3

Table 7.3 **Difference Between Oxidation Number and Valency**

S.No.	Oxidation number	Valency
1.	Oxidation number is the residual charge left on the atom when other atoms are removed as ions.	It is the combining capacity of an element. It is also defined as the number of H atom or twice the number of O atoms with which an atom of the element reacts.
2.	It can be zero, *e.g.*, oxidation number of C in CH_2Br_2 is zero.	It can never be zero. It is always positive.
3.	It refers to the charge, which can be positive or negative, *e.g.*, in $CuCl_2$, the oxidation number of Cu is $+2$ and that of Cl is -1.	It is only a number and it is not assigned as positive or negative. For example, in $CuCl_2$, the valency of Cu is 2 and that of Cl is 1.
4.	It can have fractional value, *e.g.*, oxidation number of S in $K_2S_2O_8$ is $+5/2$.	It is always a whole number, since atoms always combine in simple whole numbers.
5.	Oxidation number of an element can be different in different compounds, *e.g.*, oxidation number of C in CH_4, C_2H_6, CH_3Br, CCl_4, and $CHBr_3$ are $-4, -3, -2, +4$ and $+2$, respectively.	It is fixed in all its compounds, *e.g.*, the valency of C is 4 in all its compounds, such as CH_4, C_2H_6, CH_3Br, CCl_4 and $CHBr_3$.

Applications of Oxidation Number

Oxidation number helps in comparing acidity and basicity of different substances. Moreover, these also help in naming compounds.

Some such applications are described below

(i) Acidic Character

Greater the oxidation number of the element forming oxyacids, greater the acid strength except for oxyacids of phosphorus Thus, acid strength increases as,

$$\left.\begin{array}{l} H_2\overset{+2}{S}_2O_3 < H_2\overset{+4}{S}O_3 < H_2\overset{+6}{S}O_4 \\ H\overset{-1}{Cl} < H\overset{+1}{Cl}O < H\overset{+3}{Cl}O_2 < H\overset{+5}{Cl}O_3 < H\overset{+7}{Cl}O_4 \end{array}\right\}$$

order of acid strength

(ii) Basic Strength

Greater the oxidation number of the element in conjugate bases, smaller the basic strength. Basic strength of conjugate bases of oxyacids of Cl will be in the order

$$ClO_4^- < ClO_3^- < ClO_2^- < ClO^-$$

(iii) Naming of Ternary Acids

Ternary acids (oxoacids) are compounds of hydrogen, oxygen and usually a non-metal. Non-metals that exhibit more than one oxidation state form more than one ternary acid. These ternary acids differ in the number of oxygen atoms they contain. The suffixes "-ous" and "-ic" indicate lower and higher oxidation states, respectively. The common ternary "-ic" acids are shown below.

Acids containing one fewer oxygen atom per central atom are named in the same way except that the "-ic" suffix is changed to "ous". **The oxidation number of the central element is lower by 2 in the "-ous"** acid than in the "-ic" acid.

Thus, oxoacids of chlorine can be named as

Formula	Oxidation number	Name
HClO	+1	Hypochlorous acid
$HClO_2$	+3	Chlorous acid
$HClO_3$	+5	Chloric acid
$HClO_4$	+7	Perchloric acid

Naming ternary acids and their anions.

Decreasing oxidation number of central atom ↓

Ternary acid	Anion
PerXXXic acid	PerXXXate
XXXic acid	XXXate
XXXous acid	XXXite
HypoXXXous acid	HypoXXXite

Decreasing number of oxygen atom of central atom ↓

The stem (XXX) represents the stem of the name *e.g.*, "nitr", "sulphur" or "chlor"

Ternary acids that have one fewer O atoms than the "-ous" acids (two fewer O atoms than the "-ic" acids) are named using the prefix "hypo-" and the suffix "-ous".

Formula	Oxidation number	Name
HClO	+1	Hypochlorous acid
H_3PO_2	+1	Hypophosphorus acid
HIO	+1	Hypoiodous acid
$H_2N_2O_2$	+1	Hyponitrous acid

Acids containing one more oxygen atom per central non-metal atom than the normal "-ic acid" are named "-per" acids.

Formula	Oxidation number	Name
$HClO_4$	+7	Perchloric acid
$HBrO_4$	+7	Perbromic acid
HIO_4	+7	Periodic acid

Check Point 1

1. In $H_2S_2O_3$, the oxidation number of S is + 6, not + 7, Explain.
2. In OF_2, the oxidation number of O is + 2, but not − 2, Explain.
3. Why the oxidation number of O in peroxide is − 1?
4. Why the oxidation state of H in metal hydrides is − 1?

7.2 Oxidation and Reduction

The term **oxidation** was first used for those chemical reactions in which oxygen is added to an element or a compound. The reverse of such a process can be defined as **reduction.** Both the above written terms can be defined in many ways as

Oxidation is a process which involves

(i) **Addition of oxygen *e.g.,***

$$2Mg + O_2 \longrightarrow 2MgO$$ (Oxidation of magnesium)

$$S + O_2 \longrightarrow SO_2$$ (Oxidation of sulphur)

$$2CO + O_2 \longrightarrow 2CO_2$$ (Oxidation of carbon monoxide)

(ii) **Removal of hydrogen *e.g.,***

$$H_2S + Cl_2 \longrightarrow 2HCl + S$$ (Oxidation of hydrogen sulphide)

$$4HI + O_2 \longrightarrow 2H_2O + 2I_2$$ (Oxidation of hydrogen iodide)

(iii) **Addition of an electronegative element *e.g.,***

$$Fe + S \longrightarrow FeS$$ (Oxidation of iron)

$$SnCl_2 + Cl_2 \longrightarrow SnCl_4$$ (Oxidation of stannous chloride)

$$2Fe + 3F_2 \longrightarrow 2FeF_3$$ (Oxidation of iron)

(iv) **Removal of an electropositive element *e.g.,***

$$2KI + H_2O_2 \longrightarrow 2KOH + I_2$$ (Oxidation of potassium iodide)

$$2K_2MnO_4 + Cl_2 \longrightarrow 2KCl + 2KMnO_4$$ (Oxidation of potassium manganate)

$$2KI + Cl_2 \longrightarrow 2KCl + I_2$$ (Oxidation of potassium iodide)

Reduction is just the reverse of oxidation. It is a process which involves

(i) **Removal of oxygen** *e.g.,*

$$CuO + C \longrightarrow Cu + CO$$ (Reduction of cupric oxide)

$$\underset{\text{steam}}{H_2O} + \underset{\text{coke}}{C} \longrightarrow \underbrace{CO + H_2}_{\text{water gas}}$$ (Reduction of water)

$$Fe_3O_4 + 4H_2 \longrightarrow 3Fe + 4H_2O$$

(Reduction of magnetic oxide *i.e.*, iron oxide)

(ii) **Addition of hydrogen** *e.g.*,

$$Cl_2 + H_2 \longrightarrow 2HCl \quad \text{(Reduction of chlorine)}$$

$$S + H_2 \longrightarrow H_2S \quad \text{(Reduction of sulphur)}$$

$$C_2H_4 + H_2 \longrightarrow C_2H_6 \quad \text{(Reduction of ethene)}$$

(iii) **Removal of an electronegative element** *e.g.*,

$$2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4$$

(Reduction of mercuric chloride)

$$2FeCl_3 + H_2 \longrightarrow 2FeCl_2 + 2HCl$$

(Reduction of ferric chloride)

$$2FeCl_3 + H_2S \longrightarrow 2FeCl_2 + 2HCl + S$$

(Reduction of ferric chloride)

(iv) **Addition of an electropositive element**

$$HgCl_2 + Hg \longrightarrow Hg_2Cl_2$$

(Reduction of mercuric chloride)

$$CuCl_2 + Cu \longrightarrow Cu_2Cl_2$$

(Reduction of cupric chloride)

Modern Concept

According to the modern concept, **loss of electrons** (*i.e.*, increase in the oxidation number) is called **oxidation** while **gain of electrons** (*i.e.*, decrease in the oxidation number) is called **reduction.**

Oil	**Ring**
oxidation is loss	reduction is gain

e.g., The equation shows a simple redox reaction which can obviously be described in terms of oxygen transfer.

$$CuO + Mg \longrightarrow Cu + MgO$$

Copper (II) oxide and magnesium oxide are both ionic. The metals obviously are not. If you rewrite this as an ionic equation, it becomes

Reduction by gain of electrons

$$Cu^{2+} + Mg \longrightarrow Cu + Mg^{2+}$$

Oxidation by loss of electrons

7.3 Oxidising and Reducing Agent

A substance which undergoes oxidation acts as **reducing agent** and the other one which undergoes reduction acts as **oxidising agent.**

In other words

In case of reducing agent

(i) loses one or more electrons
(ii) undergoes oxidation
(iii) oxidation number of atom increases

Table 7.4 **Some Important Reducing Agent**

Reducing agent	Effective change	Increase in oxidation number per atom
Iron (II) salts (acid)	$Fe^{2+} \longrightarrow Fe^{3+}$	1
Tin (II) salts (acid)	$Sn^{2+} \longrightarrow Sn^{4+}$	2
Ethanedioates (acid)	$C_2O_4^{2-} \longrightarrow CO_2$	1
Sulphites (acid)	$SO_3^{2-} \longrightarrow SO_4^{2-}$	2
Hydrogen sulphide	$S^{2-} \longrightarrow S$	2
Iodides (dilute acid)	$I^- \longrightarrow I$	1
Iodides (conc acid)	$I^- \longrightarrow I^+$	2
Metals, *e.g.*, Zn	$Zn \longrightarrow Zn^{2+}$	2
Hydrogen	$H \longrightarrow H^+$	1

An oxidising agent

(i) gains one or more electrons
(ii) undergoes reduction
(iii) oxidation number of atom decreases

$Mg, S, Cu, H_2S, HI, H_2, C, KI$ are reducing agents, while $O_2, Cl_2, F_2, H_2O_2, FeCl_3, CuCl_2, Fe_3O_4, CuO$, etc., are oxidising agents in the above examples. Some other examples are tabulated below.

Table 7.5 **Some Important Oxidising Agent**

Oxidising agent	Effective change	Decrease in oxidation number per atom
$KMnO_4$ in acid solution	$MnO_4^- \longrightarrow Mn^{2+}$	5
$KMnO_4$ in alkaline solution	$MnO_4 \longrightarrow MnO_2$	3
$K_2Cr_2O_7$ in acid solution	$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$	3
Dilute HNO_3	$NO_3^- \longrightarrow NO$	3
Concentrated HNO_3	$NO_3^- \longrightarrow NO_2$	1
Concentrated H_2SO_4	$SO_4^{2-} \longrightarrow SO_2$	2
Manganese (IV) oxide	$MnO_2 \longrightarrow Mn^{2+}$	2
Chlorine	$Cl_2 \longrightarrow Cl^-$	1
Chloric (I) acid	$ClO^- \longrightarrow Cl^-$	2
KIO_3 in dilute acid	$IO_3^- \longrightarrow I_2$	5
KIO_3 in concentrated acid	$IO_3^- \longrightarrow I^-$	6

Equivalent Mass of Oxidant/Reductant

Equivalent mass of oxidant/reductant is calculated by dividing their molecular mass by number of electrons taking part in the reaction, *i.e.*,

Equivalent mass of oxidising/reducing agent

$$= \frac{\text{mol. mass of oxidising / reducing agent}}{\text{no. of electrons taking part in the reaction}}$$

Hot Spot 2

FINDING Oxidising and Reducing Agent

Generally question based on oxidant, reductant, oxidised and reduced species has been seen in previous year JEE Main (AIEEE) examination papers so it is an important topic for this examination. The level of questions is generally easy.

Steps involved to find out these reagents are

Step I Find the oxidation state of each species. *e.g.*, in the equation

$$\overset{+1\ -2}{H_2S} + \overset{0}{O_2} \longrightarrow \overset{+1\ -2}{H_2O} + \overset{0}{2S}$$

Step II Find the atom/species oxidation state of which is increasing. This species is oxidised and is called the reducing agent. *e.g.,* In the above equation, oxidation state of S is increasing from −2 to 0, thus , it is oxidised and is called the reducing agent.

Step III Find the atom/species, oxidation state of which is decreasing. This species is reduced and is called the oxidising agent. *e.g.,* In the above equation, oxidation state of O is decreasing from 0 to −2 thus, it is reduced and is called the oxidising agent.

Sample **Problem 4** *In the following reaction which species is oxidised?*

$$K[Ag(CN)_2] + Zn \longrightarrow 2Ag + K_2[Zn(CN)_4]$$

(*a*) $[Ag(CN)_2]^-$ (*b*) $[Zn(CN)_4]^{2-}$

(*c*) Ag (*d*) Zn

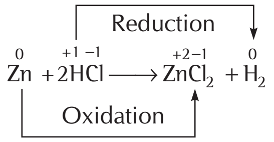
Interpret (*a*) In this reaction oxidation state of Zn is increasing from 0 to + 2. Thus, it is oxidised in this reaction.

Sample **Problem 5** *Identify the correct statement (s) in relation to the following reaction.* **[NCERT Exemplar]**

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$

(*a*) *Zinc is acting as an oxidant*
(*b*) *Chlorine is acting as a reductant*
(*c*) *Hydrogen ion is acting as an oxidant*
(*d*) *Zinc is acting as a reductant*

Interpret (*c, d*)



$$\overset{0}{Zn} + \overset{+1\ -1}{2HCl} \longrightarrow \overset{+2-1}{ZnCl_2} + \overset{0}{H_2}$$

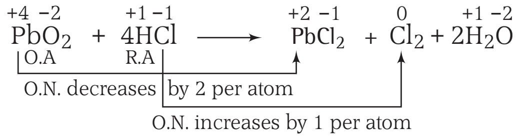
In the above reaction Zn is oxidised and H^+ is reduced so Zn acts as reducing agent and hydrogen ion (or HCl) as oxidising agent or oxidant.

7.4 Redox Reactions

These reactions involve oxidation as well as reduction as its two half reactions. In other words, those reactions in which oxidation and reduction processes occur simultaneously are called redox reactions. *e.g.,*

$$\overset{+4\ -2}{PbO_2} + \overset{+1\ -1}{4HCl} \longrightarrow \overset{+2\ -1}{PbCl_2} + \overset{0}{Cl_2} + \overset{+1\ -2}{2H_2O}$$

In PbO_2, Pb is in +4 oxidation state. Due to inert pair effect, Pb in + 2 oxidation state is more stable. So, Pb in +4 oxidation state (PbO_2) acts as an oxidising agent . It oxidises Cl^- to Cl_2 and itself gets reduced to Pb^{2+}.



$$\overset{+4\ -2}{PbO_2} + \overset{+1\ -1}{4HCl} \longrightarrow \overset{+2\ -1}{PbCl_2} + \overset{0}{Cl_2} + \overset{+1\ -2}{2H_2O}$$

Sample **Problem 6** *Which of the following reactions are redox reactions?* **[NCERT]**

(*I*) $CuO(s) + H_2(g) \longrightarrow Cu(s) + H_2O(g)$
(*II*) $Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$
(*III*) $4BCl_3(g) + 3LiAlH_4(s) \longrightarrow 2B_2H_6(g) + 3LiCl(s) + 3AlCl_3(s)$
(*IV*) $2K(s) + F_2(g) \longrightarrow 2K^+F^-(s)$
(*V*) $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$

(*a*) *I, III* and *IV* (*b*) *II, III* and *IV*

(*c*) *I, II* and *III* (*d*) *All of these*

Interpret (*d*) *Redox reactions are those reactions in which one reactant is oxidised while the other is reduced. So, first find the oxidation state of each element to find the substance undergoing oxidation or reduction, and then tell is it redox reaction or not?*

(i) $CuO(s) + H_2(g) \longrightarrow Cu(s) + H_2O(g)$

Assign oxidation numbers of each atom above its symbol.

$$\overset{+2\ -2}{CuO}(s) + \overset{0}{H_2}(g) \longrightarrow \overset{0}{Cu}(s) + \overset{+1\ -2}{H_2O}(g)$$

Oxidation number of Cu in CuO is + 2. It decreases from + 2 to zero in Cu. While oxidation number of hydrogen increases from 0 (in H_2) to +1 (in H_2O). This shows that CuO is reduced to Cu but H_2 is oxidised to H_2O. Hence, it is an example of redox reaction.

(ii) $\overset{+3\ -2}{Fe_2O_3}(s) + 3\overset{+2-2}{CO}(g) \longrightarrow 2\overset{0}{Fe}(s) + 3\overset{+4-2}{CO_2}(g)$

Oxidation number of Fe decreases from +3 (in Fe_2O_3) to zero (in Fe) and oxidation number of C increases from + 2 (in CO) to + 4 (in CO_2). This shows that Fe_2O_3 is reduced to Fe and CO is oxidised to CO_2. Hence, it is a redox reaction.

(iii) $4\overset{+3}{B}\overset{-1}{Cl_3}(g) + 3\overset{+1}{Li}\overset{+3}{Al}\overset{-1}{H_4}(s) \longrightarrow 2\overset{-3}{B_2}\overset{+1}{H_6}(g) + 3\overset{+1}{Li}\overset{-1}{Cl}(s) + 3\overset{+3}{Al}\overset{-1}{Cl_3}(s)$

Oxidation number of B decreases from + 3 (in BCl_3) to − 3 (in B_2H_6) and oxidation number of H increases from −1 (in $LiAlH_4$) to +1 (in B_2H_6). This shows that BCl_3 is reduced to B_2H_6 and $LiAlH_4$ is oxidised. Hence, it is a redox reaction.

(iv) $2\overset{0}{K}(s) + \overset{0}{F_2}(g) \longrightarrow 2\overset{+1}{K}\overset{-1}{F}(s)$

Oxidation number of K increases from zero (in K) to +1 (in KF) and oxidation number of F reduces from zero (in F_2) to −1 (in KF). This shows that K is oxidised and F_2 is reduced. Hence, it is a redox reaction.

(v) $4\overset{-3}{N}\overset{+1}{H_3}(g) + 5\overset{0}{O_2}(g) \longrightarrow 4\overset{+2}{N}\overset{-2}{O}(g) + 6\overset{+1}{H_2}\overset{-2}{O}(g)$

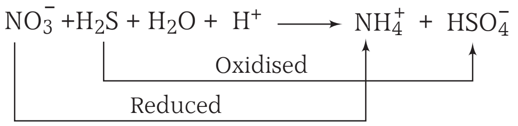
Oxidation number of N increases from − 3 (in NH_3) to +2 (in NO) and oxidation number of O decreases from zero (in O_2) to − 2 (in NO and H_2O). This shows that NH_3 is oxidised and O_2 is reduced. Hence, it is a redox reaction.

Types of Redox Reactions

Redox reactions are divided into two main types

(a) **Intermolecular Redox Reactions**

In such redox reactions, molecule of one reactant is oxidised whereas molecule of other reactant is reduced. *e.g.*,



$NO_3^- + H_2S + H_2O + H^+ \longrightarrow NH_4^+ + HSO_4^-$

(b) **Intramolecular Redox Reactions**

If one atom of a molecule is oxidised and other atom of same molecule is reduced then the reaction is called intramolecular redox reaction.

e.g., $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$

There are two types of nitrogen, one in NH_4^+ ion (oxidation number = −3) and the other in NO_3^- (oxidation number = +5). On decomposition, N_2O (oxidation number = + 1) is formed. Thus, NH_4^+ is oxidised to N_2O and NO_3^- is reduced to N_2O.

Since, both the elements are in the same initial substance, reactions of this kind are known as **intramolecular oxidation-reduction or redox reactions.**

In another example, $\underset{\text{(O.N.)}\ +5\ -1}{\underset{\uparrow\ \uparrow}{PCl_5}} \xrightarrow{\Delta} \underset{+3\ -1}{\underset{\uparrow\ \uparrow}{PCl_3}} + \underset{0}{\underset{\uparrow}{Cl_2}}$

Phosphorus (V) of PCl_5 is thus reduced to P(III) of PCl_3. Cl (−1) is oxidised to Cl_2(0).

Thus, it is an **intramolecular redox reaction.**

(c) **Disproportionation Reactions**

In such reactions, compounds are simultaneously formed that contain a given element in a more oxidised and more reduced state than the initial one. The initial substance displays functions of both an oxidising and a reducing agent. *Such reactions are possible if the relevant element is in an intermediate oxidation state in the initial compound.* In the following disproportionation reaction

$$4H_3PO_3 \longrightarrow 3H_3PO_4 + PH_3$$

Oxidation number of P (in H_3PO_3) is +3 which is the intermediate of +5 (in H_3PO_4) and −3 (in PH_3). Such substances have **oxidation-reduction duality.**

The reaction between chlorine and cold dilute sodium hydroxide solution is

$$Cl_2 + 2OH^- \longrightarrow Cl^- + ClO^- + H_2O$$

Obviously the chlorine has changed oxidation state because it has ended up in compounds starting from the original element. Checking all the oxidation states shows

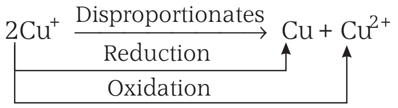
$$\underset{0}{\underset{\uparrow}{Cl_2}} + \underset{-2\ +1}{\underset{\uparrow\ \uparrow}{2OH^-}} \longrightarrow \underset{-1}{\underset{\uparrow}{Cl^-}} + \underset{+1\ -2}{\underset{\uparrow\ \uparrow}{ClO^-}} + \underset{+1\ -2}{\underset{\uparrow\ \uparrow}{H_2O}}$$

The chlorine is the only thing to have changed oxidation state. One atom has been reduced because its oxidation state has fallen. The other has been oxidised. This is a good example of disproportionation reaction.

Thus, a disproportionation reaction is one in which a single substance (element) is both oxidised and reduced.

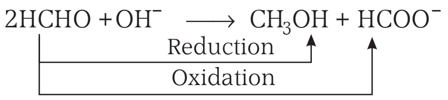
Other examples of disproportionation reaction (autoxidation-autoreduction) are

(i)



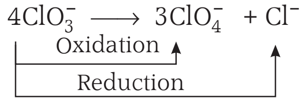
$2Cu^+ \xrightarrow{\text{Disproportionates}} Cu + Cu^{2+}$

(ii)



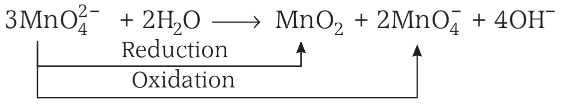
$2HCHO + OH^- \longrightarrow CH_3OH + HCOO^-$

(iii)



$4ClO_3^- \longrightarrow 3ClO_4^- + Cl^-$

(iv)



$3MnO_4^{2-} + 2H_2O \longrightarrow MnO_2 + 2MnO_4^- + 4OH^-$

(v) $$\begin{array}{l}\text{CHO}\\ |\\ \text{CHO}\end{array} + \text{OH}^- \longrightarrow \begin{array}{l}\text{CH}_2\text{OH}]\ \text{Reduction}\\ |\\ \text{COO}^-\ ]\text{Oxidation}\end{array}$$

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

Sample Problem 7 *Find the disproportionation reaction among the following.*

(a) $Te(s) + NO_3^-(aq) \longrightarrow TeO_2(s) + NO(g)$

(b) $H_2O_2(aq) + Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + H_2O(l)$

(c) $Mn(s) + NO_3^-(aq) \longrightarrow Mn^{2+}(aq) + NO_2(g)$

(d) $Mn^{3+}(aq) \longrightarrow MnO_2(s) + Mn^{2+}(aq)$

Interpret (d) (a) $\underset{0}{Te}(s) + \underset{+5}{N}O_3^-(aq) \longrightarrow \underset{+4}{Te}O_2(s) + \underset{+2}{N}O(g)$

Oxidation $Te(s) \longrightarrow TeO_2(s)$

Reduction $NO_3^-(aq) \longrightarrow NO(g)$

(b) $H_2\underset{-1}{O_2}(aq) + \underset{+2}{Fe^{2+}}(aq) \longrightarrow \underset{+3}{Fe^{3+}}(aq) + H_2\underset{-2}{O}(l)$

Oxidation $Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq)$

Reduction $H_2O_2(aq) \longrightarrow H_2O(l)$

(c) Oxidation $Mn(s) \longrightarrow Mn^{2+}(aq)$

Reduction $NO_3^-(aq) \longrightarrow NO_2(g)$

(d) Oxidation $Mn^{3+}(aq) \longrightarrow MnO_2(s)$

Reduction $Mn^{3+}(aq) \longrightarrow Mn^{2+}(aq)$

In this reaction, Mn^{3+} has been oxidised to $MnO_2(s)$ as well as reduced to $Mn^{2+}(aq)$. Thus, it is a **disproportionation reaction.**

Equivalent weight of the element of compound in disproportionation reaction Equivalent weight is the sum of the equivalent weights in oxidation and reduction reaction, *i.e.*, $(M/n_1 + M/n_2)$, where M is the molecular mass of the compound and n_1 and n_2 are the number of electrons in oxidation and reduction reactions, respectively. *e.g.*, the equivalent weight of P_4 in the disproportionation reaction shown below is

$$P_4 + 3\overset{\ominus}{O}H + 3H_2O \longrightarrow PH_3 + 3H_2PO_2^{\ominus}$$

$$12e^- + P_4 \longrightarrow 4PH_3 \qquad \text{(reduction)}$$

$$4x = 0 \quad 4x + 12 = 0$$

$$4x = -12 \qquad \text{(oxidation)}$$

$$P_4 \longrightarrow 4H_2PO_2^{\ominus} + 4e^-$$

$$4x = 0 \quad 8 + 4x - 16 = -4$$

$$4x = +4$$

$$\text{Eq. wt} = \left(\frac{M}{4} + \frac{M}{12}\right) = \left(\frac{31\times 4}{4} + \frac{31\times 4}{12}\right)$$

$$= \left(31 + \frac{31}{3}\right) = 41.33$$

Sample Problem 8 *For the reaction,*

$$3Br_2 + 6OH^{\ominus} \longrightarrow Br^{\ominus} + BrO_3^{\ominus} + 3H_2O$$

equivalent weight of Br_2 *(molecular weight M) is*

(a) $\frac{M}{2}$

(b) $\frac{M}{10}$

(c) $\left(\frac{M}{2} + \frac{M}{10}\right)$

(d) $\left(\frac{M}{6}\right)$

Interpret (c) Here, Br_2 disproportionates (simultaneous oxidation and reduction), so, its equivalent weight is the sum of equivalent weights of the half reactions.

$$2e^- + Br_2 \longrightarrow 2Br^{\ominus}\ (x = 2) \qquad \text{(reduction)}$$

$$Br_2 \longrightarrow 2BrO_3^{\ominus} + 10e^-\ (x = 10) \qquad \text{(oxidation)}$$

$$2x = 0 \quad 2x - 12 = -2 \Rightarrow 2x = 10$$

$$\therefore \qquad \text{Eq. wt} = \frac{M}{2} + \frac{M}{10}$$

Conproportionation Reaction

This reaction is the reverse of disproportionation reaction. For example, $Br^{\ominus}$ and $BrO_3^{\ominus}$ in acidic medium undergoes oxidation and reduction respectively to give Br_2.

$$2Br^{\ominus} \longrightarrow Br_2 + 2e^-] \times 5$$

$$12H^{\oplus} + 10e^- + 2BrO_3^{\ominus} \longrightarrow Br_2 + 6H_2O$$

$$2x - 12 = -2 \qquad 2x = 0$$

$$2x = 10$$

$$\overline{10Br^{\ominus} + 2BrO_3^{\ominus} + 12H^{\oplus} \longrightarrow 6Br_2 + 6H_2O}$$

Or $$5Br^{\ominus} + BrO_3^{\ominus} + 6H^{\oplus} \longrightarrow 3Br_2 + 3H_2O$$

Check Point 2

1. It is not possible to oxidise HNO_3. Explain it.
2. H_2S acts only as a reducing agent while SO_2 can act both as a reducing agent and an oxidising agent. Explain, why?
3. Why conproportionation reactions are called the reverse of disproportionation reactions?
4. $NaCl + KNO_3 \longrightarrow NaNO_3 + KCl$

   The above reaction is not a redox reaction. Explain, why?

7.5 Molecular and Ionic Equations

When the reactants and products have been written in molecular forms, the equation is termed as molecular equation *e.g.*, Consider the reaction between solutions of ferric chloride and stannous chloride. When they are mixed, ferrous chloride and stannic chloride are formed. The chemical change can be represented by the following equation

$$2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$$

Since, the reactants and products involved in the chemical change are ionic compounds, these will be present in the form of ions in the solution. So, the above chemical change can also be written in the following manner.

$$2Fe^{3+} + 6Cl^- + Sn^{2+} + 2Cl^- \longrightarrow 2Fe^{2+} + 4Cl^- + Sn^{4+} + 4Cl^-$$

or $$2Fe^{3+} + Sn^{2+} \longrightarrow 2Fe^{2+} + Sn^{4+}$$

The ferric ions combine with stannous ions to form ferrous ions and stannic ions. This is an **ionic equation** for the above chemical change.

The ions which do not undergo any electronic change during a chemical change are termed as **spectator ions.** The spectator ions are not included in the final balanced equations.

The rules to be followed for writing ionic equations are

(i) All soluble ionic compounds involved in a chemical change are expressed in ionic symbols while covalent substances are written in molecular form *i.e.*, H_2O, NH_3, NO_2, NO, SO_2, CO, CO_2, etc., are expressed in molecular form.

(ii) Highly insoluble ionic compound is expressed in molecular form.

(iii) The ions which are common and equal in number on both sides, *i.e.*, spectator ions, are cancelled.

(iv) Besides the atoms, the ionic charges must also be balanced on both the sides.

Sample **Problem 9** *Choose the correct ionic form of the following equation.*

$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \longrightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + 7H_2O + K_2SO_4$$

(*a*) $Cr_2O_7^- + 7H^+ + 6Fe^{2+} \longrightarrow 6Fe^{3+} + 2\,Cr^{3+} + 7H_2O$

(*b*) $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$

(c) $Cr_2O_7^{2-} + 7H + 6Fe^{3+} + 13SO_4^{2-} \longrightarrow 6Fe^{3+} + 13SO_4^{2-} + 2Cr^{3+} + 7H_2O$

(*d*) $Cr_2O_7^{2-} + 2K^+ + 14H^+ + 6Fe^{2+} \longrightarrow 6Fe^{3+} + 13SO_4^{2-} + 2Cr^{3+} + 2K^+$

Interpret (*b*) In this equation except H_2O, all are ionic in nature. Representing these compounds in ionic forms.

$$2K^+ + Cr_2O_7^{2-} + 14H^+ + 7SO_4^{2-} + 6Fe^{2+} + 6SO_4^{2-} \longrightarrow$$
$$6Fe^{3+} + 9SO_4^{2-} + 2Cr^{3+} + 3SO_4^{2-} + 2K^+ + SO_4^{2-} + 7H_2O$$

$2K^+$ ions and $13\,SO_4^{2-}$ ions are common on both sides, so these are cancelled. The desired ionic equation reduces to,

$$Cr_2O_7^{2} + 14H^+ + 6Fe^{2+} \longrightarrow 6Fe^{3+} + 2\,Cr^{3+} + 7H_2O$$

Total charges are equal on both sides; thus, the balanced ionic equation is the same as above.

Sample **Problem 10** *Write the following ionic equation in the molecular form if the reactants are chlorides.*

$$2Fe^{3+} + Sn^{2+} \longrightarrow 2Fe^{2+} + Sn^{4+}$$

(*a*) $FeCl_2 + SnCl_2 \longrightarrow FeCl_3 + SnCl_4$

(*b*) $Fe^{3+} + Sn^{2+} + Cl^- \longrightarrow Fe^{2+} + Sn^{4+} + Cl^-$

(*c*) $FeCl_3 + 2SnCl_2 \longrightarrow 2\,FeCl_2 + SnCl_4$

(*d*) $2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$

Interpret (*d*) For writing the reactants in molecular forms, the requisite number of chloride ions are added.

$$\underbrace{2Fe^{3+} + 6Cl^-} + \underbrace{Sn^{2+} + 2Cl^-}$$

or $$2FeCl_3 + SnCl_2$$

Similarly $8Cl^-$ ions are added on RHS to neutralise the charges.

$$\underbrace{2Fe^{2+} + 4Cl^-} + \underbrace{Sn^{4+} + 4Cl^-}$$

or $$2FeCl_2 + SnCl_4$$

Thus, the balanced molecular equation is

$$2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$$

7.6 Balancing of Redox Reactions

The redox reactions can be balanced through

1. Ion-electron method
2. Oxidation number method

1. Ion-Electron Method

The ion-electron method for balancing redox reactions was given by **Jette** and **Lamev** in 1927.

The method involves the following steps

Step I Write the redox reaction in ionic form.

Step II Split the redox reaction into its two half-reactions, *i.e.*, the oxidation-half and the reduction-half.

Step III Balance atoms of each half-reaction by using simple multiples (not applicable for hydrogen and oxygen)

Step IV For balancing H and O.

(i) Use simple multiples if possible.

(ii) **For acidic and neutral solutions** add water molecules to the side deficient in oxygen and H^+ to the side deficient in hydrogen.

(iii) **In case of alkaline solution** for each excess of oxygen add one water molecule to the same side and two OH^- ions on the other side. If hydrogen is still unbalanced add one OH^- ion for each excess of hydrogen on the same side and one water molecule to the other side.

Step V Add electrons to the side deficient in electrons, so as to equalise the charge on both the sides.

Step VI Multiply one or both the half-reactions by a suitable number so that the numbers of electrons become equal in both the equations.

Step VII Add the two balance half-reactions and cancel any term common to both the sides.
e.g., in the reaction,

$$Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO + H_2O$$

Stepwise approach is,

Step I Ionic equation.

$$Cu + H^+ + NO_3^- \longrightarrow Cu^{2+} + NO + H_2O$$

Step II and III Splitting of ionic reaction into two half-reactions.

$$Cu \xrightarrow{\text{Oxidation-half}} Cu^{2+}$$

$$NO_3^- \xrightarrow{\text{Reduction-half}} NO$$

Step IV Adding H_2O and H^+ to the side deficient in oxygen and hydrogen respectively (according to simple multiple approach)

$$Cu \xrightarrow{\text{Oxidation-half}} Cu^{2+};$$

$$NO_3^- + 4H^+ \longrightarrow NO + 2H_2O$$

Step V and VI Adding electrons to the side deficient in electrons

$$[Cu \xrightarrow{\text{Oxidation-half}} Cu^{2+} + 2e^-] \times 3$$

$$[NO_3^- + 4H^+ + 3e^- \xrightarrow{\text{Reduction-half}} NO + 2H_2O] \times 2$$

For balancing electrons, oxidation-half reaction is to be multiplied by 3 and the reduction-half reaction is to be multiplied by 2. Hence, we get,

$$3Cu \longrightarrow 3Cu^{2+} + 6e^- ;$$

$$2NO_3^- + 8H^+ + 6e^- \longrightarrow 2NO + 4H_2O$$

Step VII Adding both the half-reactions

$$3Cu + 2NO_3^- + 8H^+ \longrightarrow 3Cu^{2+} + 2NO + 4H_2O$$

Converting the complete reaction into molecular form (while doing so we add $6NO_3^-$ to both the sides), we get

$$3Cu + 2NO_3^- + 8H^+ + 6NO_3^- \longrightarrow 3Cu^{2+} + 2NO + 6NO_3^- + 4H_2O$$

or $3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

2. Oxidation Number Method

This method is based upon the fact that total increase in oxidation number must be equal to total decrease in oxidation number.

The stepwise approach is

Step I Write the skeleton equation (if not given) representing the chemical change.

Step II Assign oxidation number to the atoms in the equation and find out which atoms are undergoing oxidation and reduction. Write separate equations for the atoms undergoing oxidation and reduction.

Step III Find the change in oxidation number in each equation. Make the change equal in both the equations by multiplying with suitable integers. Add both the equations.

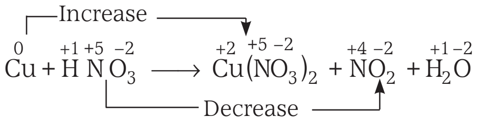
Step IV Complete the balancing. First balance those substance which undergone change in oxidation number and then other atoms except H and O. Lastly balance H and O by putting H_2O molecules whenever needed.

e.g., balance the equation,

$$Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO_2 + H_2O$$

Stepwise approach

Step I and II Writing oxidation numbers of all the atoms



$$\overset{0}{Cu} + \overset{+1}{H}\,\overset{+5}{N}\,\overset{-2}{O_3} \longrightarrow \overset{+2}{Cu}(\overset{+5}{N}\overset{-2}{O_3})_2 + \overset{+4}{N}\overset{-2}{O_2} + \overset{+1}{H_2}\overset{-2}{O}$$

Change in oxidation number is shown by arrows as,

$$\overset{0}{Cu} \xrightarrow{\text{Increase}} \overset{+2}{Cu}(NO_3)_2$$

$$H\overset{+5}{N}O_3 \xrightarrow{\text{Decrease}} \overset{+4}{N}O_2$$

Thus, in case of Cu, oxidation number is increased by 2 units while in the case of nitrogen, oxidation number is decreased by 1 unit.

Step III To make increase and decrease equal, the lower equation is to be multiplied by 2. Thus, the equation will be,

$$Cu + 2HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + H_2O$$

Step IV Balancing nitrate ions, H and O gave the result as,

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

Sample **Problem 11** *Balance the following equation in basic medium by ion-electron method and oxidation number methods and identify the oxidising agent and the reducing agent.* [**NCERT**]

$$P_4(s) + OH^-(aq) \longrightarrow PH_3(g) + H_2PO_2^-(aq)$$

Interpret $P_4(s) + OH^-(aq) \longrightarrow PH_3(g) + H_2PO_2^-(aq)$

By ion electron method

Reduction half reaction

$$\overset{0}{P_4}(s) \longrightarrow \overset{-3}{P}H_3(g) \qquad \text{...(i)}$$

$$\text{Balance P atoms } \underset{0}{\overset{0}{P_4}}(s) \longrightarrow 4\,\underset{-12}{\overset{-3}{P}}H_3(g) \qquad \text{...(ii)}$$

Balance oxidation number by adding electrons,

$$P_4(s) + 12e^- \longrightarrow 4PH_3(g) \qquad \text{...(iii)}$$

Balance charge by adding OH^- ions,

$$P_4(s) + 12e^- \longrightarrow 4PH_3(g) + 12OH^-(aq) \text{...(iv)}$$

Balance 'O' atoms by adding H_2O

$$12H_2O + P_4(s) + 12e^- \longrightarrow 4PH_3(g) + 12OH^-(aq) \text{ ...(v)}$$

Oxidation half reaction

$$P_4(s) \longrightarrow H_2PO_2^-(aq) \qquad \text{...(vi)}$$

Balance P atoms,

$$\overset{0}{P_4}(s) \longrightarrow 4H_2\overset{+1}{P}O_2^-(aq) \qquad \text{...(vii)}$$

Balance oxidation number by adding electrons,

$$P_4(s) \longrightarrow 4H_2PO_2^-(aq) + 4e^- \qquad \text{...(viii)}$$

Balance charge by adding OH^- ions

$$P_4(s) + 8OH^-(aq) \longrightarrow 4H_2PO_2^-(aq) + 4e^- \quad \text{...(ix)}$$

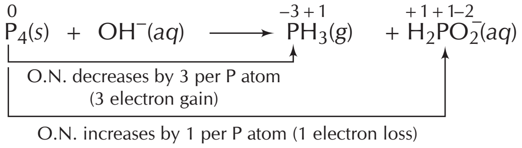
Oxygen and hydrogen are balanced automatically.

First multiply Eq. (ix) by 3 to equalise number of electrons gain and lose and add it to Eq. (v), Thus, we get,

$$4P_4(s) + 12OH^-(aq) + 12H_2O(l) \longrightarrow 4PH_3(g) + 12H_2PO_2^-(aq)$$

$$\text{or} \quad P_4(s) + 3OH^-(aq) + 3H_2O(l) \longrightarrow PH_3(g) + 3H_2PO_2^-(aq)$$

By oxidation number method



In a balanced chemical reaction loss of electrons = gain of electrons

So, multiply $H_2PO_2^-$ by 3 and we get

$$P_4(s) + OH^-(aq) \longrightarrow PH_3(g) + 3H_2PO_2^-$$

Multiply OH^- by 3 to balance the charge

$$P_4(s) + 3OH^-(aq) \longrightarrow PH_3(g) + 3H_2PO_2^-(aq)$$

Balance H by adding $3H_2O$ to LHS

$$P_4(s) + 3H_2O(l) + 3OH^-(aq) \longrightarrow PH_3(g) + 3H_2PO_2^-(aq)$$

In this equation P_4 acts both as an oxidising agent as well as a reducing agent.

WORKED OUT
Examples

Example 1 *In the reaction,*

$$H_2O_2 + Na_2CO_3 \longrightarrow Na_2O_2 + CO_2 + H_2O$$

the substance undergoing oxidation is

(*a*) H_2O_2 (*b*) Na_2CO_3
(*c*) Na_2O_2 (*d*) None of these

Solution (*d*) $\overset{+1}{H_2}\overset{-1}{O_2} + \overset{+1}{Na_2}\overset{+4}{C}\overset{-2}{O_3} \longrightarrow \overset{+1}{Na_2}\overset{-1}{O_2} + \overset{+4}{C}\overset{-2}{O_2} + \overset{+1}{H_2}\overset{-2}{O}$

Here, the oxidation state of all the elements remain the same as before. Thus, it does not involve oxidation or reduction processes. None of the elements changes its oxidation number.

Example 2 *In the following reaction,*

$$4P + 3KOH + 3H_2O \longrightarrow 3KH_2PO_2 + PH_3$$

(*a*) P *is only oxidised*
(*b*) P *is only reduced*
(*c*) P is *both oxidised as well as reduced*
(*d*) *None of the above*

+1 unit increases

Solution (*c*) $4\overset{0}{P} + 3KOH + 3H_2O \longrightarrow 3KH_2\overset{+1}{P}O_2 + \overset{-3}{P}H_3$

−3 unit decreases

Hence, P is both oxidised as well as reduced.

Example 3 *Which of the following is not a redox reaction?*

(*a*) $CaCO_3 \longrightarrow CaO + CO_2$
(*b*) $Na + H_2O \longrightarrow NaOH + \frac{1}{2}H_2$
(*c*) $MnCl_3 \longrightarrow MnCl_2 + \frac{1}{2}Cl_2$
(*d*) $O_2 + 2H_2 \longrightarrow 2H_2O$

Solution (*a*) In redox reactions, oxidation and reduction takes place simultaneously.

$$\overset{+2}{Ca}\,\overset{+4}{C}\overset{-2}{O_3} \longrightarrow \overset{+2}{Ca}\overset{-2}{O} + \overset{+4}{C}O_2$$

Since, in this reaction, there is no change in the oxidation state of elements, *i.e.*, there is no oxidation or reduction in this reaction. Thus, it is not a redox reaction. (All other given reactions involve the change in oxidation state, *i.e.*, oxidation and reduction.)

Example 4 *The equivalent weight of* H_2SO_4 *in the following reaction is*

$$Na_2Cr_2O_7 + 3SO_2 + H_2SO_4 \longrightarrow 3Na_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

(*a*) 98 (*b*) $\frac{98}{6}$ (*c*) $\frac{98}{2}$ (*d*) $\frac{98}{8}$

Solution (*b*) In this reaction, 6 moles of electron are involved with 1 mole of H_2SO_4.So, H_2SO_4 acts here as acidic medium.

$$6e^- + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} (x = 6) \text{ (reduction)}$$

$$2x - 14 = -2 \qquad 2x = 6$$
$$2x = 12$$

$$SO_2 \longrightarrow SO_4^{2-} + 2e^-] \times 3 \; (x = 6)$$

$$x - 4 = 0 \qquad x - 8 = -2$$
$$x = 4 \qquad x = 6$$

$$\text{So, equivalent weight of } H_2SO_4 = \frac{M}{6} = \frac{98}{6}$$

Example 5 *For the redox reaction,*

$$MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O$$

Correct stoichiometric coefficients of MnO_4^-, $C_2O_4^{2-}$ *and* H^+ *are respectively*

(*a*) 2, 16, 5 (*b*) 2, 5, 16
(*c*) 16, 5, 2 (*d*) 5, 16, 2

Solution (*b*) The following steps are involved to balance this equation.

(i) Split the equation into oxidation and reduction half- reactions.

$$MnO_4^- \longrightarrow Mn^{2+};$$
$$C_2O_4^{2-} \longrightarrow CO_2$$

(ii) Balance the atoms other than O and H.

$$MnO_4^- \longrightarrow Mn^{2+};$$
$$C_2O_4^{2-} \longrightarrow 2CO_2$$

(iii) Add H_2O to the side deficient in O and H^+ to the side deficient in H.

$$MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O;$$
$$C_2O_4^{2-} \longrightarrow 2CO_2$$

(iv) Balance the charge by adding electrons.

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$
$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$$

(v) Equalise the number of electrons and then add both the equations.

$$[MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$$
$$[C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-] \times 5$$
$$\overline{2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O}$$

Thus, the coefficients of MnO_4^-, $C_2O_4^{2-}$ and H^+ are respectively 2, 5 and 16.

Start **Practice** *for* JEE Main

Round I (Topically Divided Problems)

Oxidation State

1. Oxidation number of S in SO_4^{2-}
(a) +6 (b) +3
(c) +2 (d) −2

2. Oxidation number of nitrogen is highest in
(a) N_3H (b) N_2O_4
(c) NH_2OH (d) NH_3

3. In which of the following compounds, an element exhibits two different oxidation states? **[NCERT Exemplar]**
(a) NH_2OH (b) NH_4NO_3
(c) N_2H_4 (d) N_3H

4. The oxidation number of oxygen in OF_2 is
(a) + 2 (b) − 2
(c) + 1 (d) − 1

5. The oxidation number of Cr in CrO_5 is
(a) + 3 (b) + 5 (c) + 6 (d) 0

6. The oxidation states of iodine in HIO_4, H_3IO_5 and H_5IO_6 are respectively
(a) +1, + 3, + 7 (b) +7, + 7, + 3
(c) +7, + 7, + 7 (d) +7, + 5, + 3

7. In which of the following compounds, the oxidation number of iodine is fractional?
(a) IF_3 (b) IF_5 (c) I_3^- (d) IF_7

8. The oxidation number of an element in a compound is evaluated on the basis of certain rules. Which of the following rules is not correct in this respect? **[NCERT Exemplar]**
(a) The oxidation number of hydrogen is always +1.
(b) The algebraic sum of all the oxidation numbers in a compound is zero.
(c) An element in the free or the uncombined state bears oxidation number zero.
(d) In all its compounds, the oxidation number of fluorine is −1

9. The oxidation number of chromium in potassium dichromate is
(a) +2 (b) +4
(c) +6 (d) +8

10. In the conversion of Br_2 to BrO_3^-, the oxidation number of Br changes from
(a) zero to +5 (b) +1 to +5
(c) zero to −3 (d) +2 to +5

11. In permonosulphuric acid (H_2SO_5), the oxidation number of sulphur is
(a) +8 (b) +4
(c) +5 (d) +6

12. The oxidation number of N and Cl in $NOClO_4$ respectively are
(a) +2 and + 7 (b) +3 and + 7
(c) −3 and + 5 (d) +2 and − 7

13. The largest oxidation number exhibited by an element depends on its outer electronic configuration. With which of the following outer electronic configurations the element will exhibit largest oxidation number? **[NCERT Exemplar]**
(a) $3d^1 4s^2$ (b) $3d^3 4s^2$
(c) $3d^5 4s^1$ (d) $3d^5 4s^2$

14. Find the oxidation state of C_1 and C_2 in the following compound. $\overset{2}{\underline{C}}H_3\overset{1}{\underline{C}}H_2OH$ **[NCERT]**
(a) 0, 2 (b) −2, 0
(c) −2, −2 (d) −2, +2

15. Oxidation state of C in $\underline{C}H_3\underline{C}OOH$ is **[NCERT]**
(a) 0 (b) 1
(c) 2 (d) 3

16. The oxidation state of two sulphur atoms in $H_2S_2O_8$ is
(a) −6 (b) −2
(c) +6 (d) −4

17. When $K_2Cr_2O_7$ is converted into K_2CrO_4, the change in oxidation number of chromium is
(a) 0 (b) 5 (c) 7 (d) 9

Redox Reactions

18. Which of the following is the best description of the behaviour of bromine in the reaction given below?

$$H_2O + Br_2 \longrightarrow HOBr + HBr$$

(a) Proton acceptor only
(b) Both oxidised and reduced
(c) Oxidised only
(d) Reduced only

19. Which of the following is not an intermolecular redox reaction?
(a) $MgCO_3 \longrightarrow MgO + CO_2$
(b) $O_2 + 2H_3 \longrightarrow 2H_3O$
(c) $K + H_2O \longrightarrow KOH + (1/2)H_2$
(d) $MnBr_3 \longrightarrow MnBr_2 + (1/2)Br_2$

20. Which conversion is an oxidation?
(a) $SO_4^{2-} \longrightarrow SO_3^{2-}$ (b) $Cu^{2+} \longrightarrow Cu$
(c) $H^+ \longrightarrow H$ (d) $H^- \longrightarrow H$

21. In the reaction,

$$3Cl_2 + 6NaOH \longrightarrow NaClO_3 + 5NaCl + 3H_2O$$

the element which loses as well as gains electrons is
(a) Na (b) O
(c) Cl (d) None of these

22. Of the following reactions, only one is a redox reaction. Identify this reaction.
(a) $Ca(OH)_2 + 2HCl \longrightarrow CaCl_2 + 2H_2O$
(b) $2S_2O_7^{2-} + 2H_2O \longrightarrow 2SO_4^{2-} + 4H^+$
(c) $BaCl_2 + MgSO_4 \longrightarrow BaSO_4 + MgCl_2$
(d) $Cu_2S + 2FeO \longrightarrow 2Cu + 2Fe + SO_2$

23. White phosphorus reacts with caustic soda, the products are PH_3 and NaH_2PO_2. This reaction is an example of
(a) oxidation (b) reduction
(c) disproportionation (d) neutralisation

24. Which of the following is the strongest reducing agent in aqueous medium?
(a) Mg (b) Na (c) Li (d) Ca

25. In the reaction,

$$2FeCl_3 + H_2S \longrightarrow 2FeCl_2 + 2HCl + S$$

(a) $FeCl_3$ acts as an oxidising agent
(b) Both H_2S and $FeCl_3$ are oxidised
(c) $FeCl_3$ is oxidised while H_2S is reduced
(d) H_2S acts as an oxidising agent

26. Which of the following is the strongest oxidising agent?
(a) I_2 (b) F_2
(c) Cl_2 (d) Br_2

27. In the reaction, $SO_2 + 2H_2S \longrightarrow 3S + 2H_2O$ the substance that oxidises is
(a) H_2S (b) SO_2
(c) S (d) H_2O

28. Which of the following acts as an oxidising agent?
(a) HNO_3
(b) Cl_2
(c) $FeCl_3$
(d) All of the above

29. Identify disproportionation reaction **[NCERT Exemplar]**
(a) $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$
(b) $CH_4 + 4Cl_2 \longrightarrow CCl_4 + 4HCl$
(c) $2F_2 + 2OH^- \longrightarrow 2F^- + OF_2 + H_2O$
(d) $2NO_2 + 2OH^- \longrightarrow NO_2^- + NO_3^- + H_2O$

30. MnO_4^{2-} undergoes disproportionation reaction in acidic medium but MnO_4^- does not because **[NCERT Exemplar]**
(a) In MnO_4^{2-}, Mn is in intermediate oxidation state
(b) In MnO_4^-, Mn is in lowest oxidation state
(c) In MnO_4^-, Mn is in intermediate oxidation state
(d) None of the above

31. Which of the following is a redox reaction?
(a) H_2SO_4 with NaOH
(b) In atmosphere, O_3 from O_2 by lightening
(c) Nitrogen oxides from nitrogen and oxygen by lightening
(d) Evaporation of H_2O

32. The reaction,

$$Cl_2(g) + 2OH^-(aq) \longrightarrow ClO^-(aq) + Cl^-(aq) + H_2O(l)$$

represents the process of bleaching. Identify and name the species that bleaches the substances due to its oxidising action. **[NCERT Exemplar]**
(a) Cl^- (b) Cl_2
(c) OH^- (d) ClO^-

33. Whenever a reaction between an oxidising agent and a reducing agent is carried out **[NCERT]**
(a) a compound of lower oxidation state is formed if the reducing agent is in excess
(b) a compound of higher oxidation state is formed if the oxidising agent is in excess
(c) Both (a) and (b)
(d) None of the above

Balancing of Redox Reactions

34. The coefficients of I^-, IO_3^- and H^+ in the redox reaction, $I^- + IO_3^- + H^+ \longrightarrow I_2 + H_2O$ in the balanced form respectively are

(a) 5,1,6 (b) 1,5,6 (c) 6,1,5 (d) 5,6,1

35. In the equation $NO_2^{\ominus} + H_2O \longrightarrow NO_3^{\ominus} + 2H^{\oplus} + ne^-$ n stands for

(a) 1 (b) 2 (c) 3 (d) 4

36. The value of n in

$$MnO_4^- + 8H^+ + ne^- \longrightarrow Mn^{2+} + 4H_2O \text{ is}$$

(a) 5 (b) 4 (c) 2 (d) 3

37. $aK_2Cr_2O_7 + bKCl + cH_2SO_4 \longrightarrow xCrO_2Cl_2 + yKHSO_4 + zH_2O$

The above equation balances when

(a) $a = 2, b = 4, c = 6$ and $x = 2, y = 6, z = 3$
(b) $a = 4, b = 2, c = 6$ and $x = 6, y = 2, z = 3$
(c) $a = 6, b = 4, c = 2$ and $x = 6, y = 3, z = 2$
(d) $a = 1, b = 4, c = 6$ and $x = 2, y = 6, z = 3$

38. In the reaction, $8Al + 3Fe_3O_4 \longrightarrow 4Al_2O_3 + 9Fe$ the number of electrons transferred from the reductant to the oxidant is

(a) 8 (b) 4
(c) 16 (d) 24

39. The value of 'n' in the reaction $Cr_2O_7^{2-} + 14H^+ + nFe^{2+} \longrightarrow 2Cr^{3+} + nFe^{3+} + 7H_2O$ will be

(a) 2 (b) 3
(c) 6 (d) 7

40. The Mn^{3+} ion is unstable in solution and undergoes disproportionation to give Mn^{2+}, MnO_2 and H^+ ion. The balanced ionic equation for the reaction is **[NCERT]**

(a) $Mn^{3+} + 2H_2O \longrightarrow Mn^{2+} + 4H^+ + MnO_2$
(b) $2Mn^{3+} + H_2O \longrightarrow Mn^{2+} + 2H^+ + MnO_2$
(c) $2Mn^{3+} + 2H_2O \longrightarrow Mn^{2+} + MnO_2 + 4H^+$
(d) None of the above

Round II (Mixed Bag)

Only One Correct Option

1. What are the oxidation numbers of the three I atoms, in KI_3? **[NCERT]**

(a) 0, 0, −1 (b) −1, 0, −1
(c) $0, -\frac{1}{3}, 0$ (d) $-\frac{1}{3}, -\frac{1}{3}, 0$

2. Which of the following acts as an oxidising as well as reducing agent?

(a) Na_2O (b) Na_2O_2
(c) $NaNO_3$ (d) $NaNO_2$

3. During a redox titration involving a solution containing Fe^{2+} ions against MnO_4^- in the presence of excess of H^+ ions, the number of electrons that gets transferred is

(a) 6 (b) 5 (c) 4 (d) 2

4. When sulphur dioxide is passed in an acidified $K_2Cr_2O_7$ solution, the oxidation state of sulphur is changed from

(a) 4 to 0 (b) 4 to 2 (c) 4 to 6 (d) 6 to 4

5. In the following reaction,

$$M^{x+} + MnO_4^- \longrightarrow MO_3^- + Mn^{2+} + \frac{1}{2}O_2$$

If one mole of MnO_4^- oxidises 2.5 moles of M^{x+} then the value of x is

(a) 5 (b) 3 (c) 4 (d) 2

6. $3KClO_3 + 3H_2SO_4 \longrightarrow 3KHSO_4 + HClO_4 + 2ClO_2 + H_2O$

Equivalent weight of $KClO_3$ is

(a) $\frac{M}{4}$ (b) $\frac{M}{2}$ (c) $\left(M + \frac{M}{2}\right)$ (d) $\left(\frac{M}{4} + \frac{M}{2}\right)$

7. The equivalent weight of HNO_3 (molecular weight = 63) in the following reaction is

$$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

(a) $\frac{4 \times 63}{3}$ (b) $\frac{63}{5}$ (c) $\frac{63}{3}$ (d) $\frac{63}{8}$

8. A mole of N_2H_4 loses 10 moles of electrons to form a new compound Y. Assuming that all the nitrogen appears in the new compound, what is the oxidation state of nitrogen in Y? (There is no change in the oxidation number of hydrogen.)

(a) −1 (b) −3 (c) +3 (d) +5

9. Which of the following reactions do not involve oxidation reduction?

I. $2Rb + 2H_2O \longrightarrow 2RbOH + H_2$
II. $2CuI_2 \longrightarrow 2CuI + I_2$
III. $NH_4Br + KOH \longrightarrow KBr + NH_3 + H_2O$
IV. $4KCN + Fe(CN)_2 \longrightarrow K_4[Fe(CN)_6]$

(a) I, II (b) I, III
(c) I, III, IV (d) III, IV

10. In which of the following pairs is there the greatest difference in the oxidation numbers of the underlined elements?

(a) $\underline{N}O_2$ and $\underline{N}_2O_4$
(b) $\underline{P}_2O_5$ and $\underline{P}_4O_{10}$
(c) $\underline{N}_2O$ and $\underline{N}O$
(d) $\underline{S}O_2$ and $\underline{S}O_3$

11. Cerric ammonium sulphate and potassium permanganate are used as oxidising agents in acidic medium for the oxidation of ferrous ammonium sulphate to ferric sulphate. The ratio of number of moles of cerric ammonium sulphate required per mole of ferrous ammonium sulphate to the number of moles of $KMnO_4$ required per mole of ferrous ammonium sulphate, is

(a) 5.0
(b) 0.2
(c) 0.6
(d) 2.0

12. Oxidation states of X, Y, Z are $+2, +5$ and -2 respectively. Formula of the compound formed by these will be

(a) X_2YZ_6
(b) XY_2Z_6
(c) XY_5
(d) X_3YZ_4

13. In which of the following reactions hydrogen is acting as an oxidising agent?

(a) With Li to form LiH
(b) With I_2 to give HI
(c) With S to give H_2S
(d) None of these

14. The number of peroxide bonds in perxenate ion $[XeO_6]^{4-}$ is

(a) 0
(b) 2
(c) 3
(d) 1

15. Oxidation states of the metal in the minerals haematite and magnetite, respectively, are

(a) II, III in haematite and III in magnetite
(b) II, III in haematite and II in magnetite
(c) II in haematite and II, III in magnetite
(d) III in haematite and II, III in magnetite

16. Mn^{2+} can be converted into Mn^{7+} by reacting with

(a) SO_2
(b) Cl_2
(c) PbO_2
(d) $SnCl_2$

17. While sulphur dioxide and hydrogen peroxide can act as oxidising as well as reducing agents in their reactions, ozone and nitric acid act only as oxidants. This is because **[NCERT]**

(a) in SO_2 and H_2O_2, S and O are in their lowest oxidation state
(b) in O_3 and HNO_3, N and O are in their highest oxidation state
(c) in O_3 and HNO_3, N and O are in their lowest oxidation state
(d) Both (a) and (b)

18. Thiosulphate reacts differently with iodine and bromine in the reactions given below **[NCERT Exemplar, NCERT]**

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$
$$S_2O_3^{2-} + 2Br_2 + 5H_2O \longrightarrow 2SO_4^{2-} + 4Br^- + 10H^+$$

Which of the following statements justifies the above dual behaviour of thiosulphate?

(a) Bromine is a stronger oxidant than iodine
(b) Bromine is a weaker oxidant than iodine
(c) Thiosulphate undergoes oxidation by bromine and reduction by iodine in these reactions
(d) Bromine undergoes oxidation and iodine undergoes reduction in these reactions

19. Which of the following statements is not correct?

(a) The oxidation number of S in $(NH_4)_2S_2O_8$ is $+6$
(b) The oxidation number of Os in OsO_4 is $+8$
(c) The oxidation number of S in H_2SO_5 is $+8$
(d) The oxidation number of O in KO_2, is $-1/2$

More than One Correct Option

20. Which of the following reactions should be balanced in basic medium?

(a) $NH_3 + MnO_4^{\ominus} \longrightarrow MnO_2 + NO_2$
(b) $Cr(OH)_2 + I_2 \longrightarrow Cr(OH)_2 + 2I^{\ominus}$
(c) $HNO_3 + Fe^{2+} \longrightarrow Fe^{3+} + NO_2$
(d) $H_2O_2 + Fe^{3+} \longrightarrow O_2 + Fe^{2+}$

21. Which of the following statements is/are correct?

In the reaction

$$xCu_3P + yCr_2O_7^{2-} \longrightarrow Cu^{2+} + H_3PO_4 + Cr^{3+}$$

(a) Cu in Cu_3P is oxidised to Cu^{2+} whereas P in Cu_3P is also oxidised to PO_4^{3-}
(b) Cu in Cu_3P is oxidised to Cu^{2+} whereas P in Cu_3P is reduced to H_3PO_4
(c) In the conversion of Cu_3P to Cu^{2+} and H_3PO_4 11 electrons are involved
(d) The value of x is 6

22. Which of the following statements about the following reaction is / are wrong?

$$2Cu_2O(s) + Cu_2S(s) \longrightarrow 6Cu(s) + SO_2(g)$$

(a) Both Cu_2O and Cu_2S are reduced
(b) Only Cu_2S is reduced
(c) Cu_2S is the oxidant
(d) Only Cu_2O is reduced

23. Which of the following has/have been arranged in order of decreasing oxidation state of sulphur?

(a) $H_2S_2O_7 > Na_2S_4O_6 > Na_2S_2O_3 > S_8$
(b) $SO^{2+} > SO_4^{2-} > SO_3^{2-} > HSO_4^-$
(c) $H_2SO_5 > H_2SO_3 > SCl_2 > H_2S$
(d) $H_2SO_5 > SO_2 > H_2S > H_2S_2O_8$

24. Which of the following statements(s) is/are not true about the following decomposition reaction?

$$2KClO \longrightarrow 2KCl + 3O_2$$ **[NCERT** Exemplar**]**

(a) Potassium is undergoing oxidation
(b) Chlorine is undergoing oxidation
(c) Oxygen is reduced
(d) None of the species are undergoing oxidation or reduction

Assertion and Reason

Directions (Q. Nos. 25 to 27) *Each of these questions contains two statements : Statement* I (*Assertion*) *and Statement* II (*Reason*). *Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes* (*a*), (*b*), (*c*), (*d*) *given below*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

25. Statement I Among halogens fluorine is the best oxidant .

Statement II Fluorine is the most electronegative atom. **[NCERT** Exemplar**]**

26. Statement I In the reaction between potassium permanganate and potassium iodide, permanganate ions act as oxidising agent.

Statement II Oxidation state of manganese changes from +2 to +7 during the reaction. **[NCERT** Exemplar**]**

27. Statement I The decomposition of hydrogen peroxide to form water and oxygen is an example of disproportionation reaction.

Statement II The oxygen of peroxide is in –1 oxidation state and it is converted to zero oxidation state in O_2 and –2 oxidation state in H_2O. **[NCERT** Exemplar**]**

Comprehension Based Questions

Directions (Q. Nos. 28 to 30) Consider the following unbalanced redox reaction

$$H_2O + AX + BY \longrightarrow HA + OY + X_2B$$

The oxidation number of X is – 2, and neither X nor water is involved in the redox process.

28. The element(s) undergoing oxidation is / are

(a) A	(b) B
(c) Y	(d) B or Y or both

29. The possible oxidation states of B and Y in BY are respectively

(a) +1, – 1	(b) +2, – 2
(c) +3, – 3	(d) All of these

30. If the above reaction is balanced with smallest whole number coefficients, the sum of the stoichiometric coefficients of all the compounds is

(a) 9	(b) 8
(c) 7	(d) 6

Directions (Q. Nos. 31 to 34) Redox equations are balanced either by ion electron method or by oxidation number method. Both methods lead to the correct form of the balanced equation. The ion electron method has two advantages, so some chemists prefer to use the ion electron method for redox reactions carried out in dilute aqueous solution, where free ions have more or less independent existence.

The oxidation state method for redox reactions is mostly used for solid chemicals or for reactions in concentrated acid media.

31. For the reaction

$$K_4[Fe(CN)_6] \longrightarrow Fe^{3+} + CO_2 + NO_3^{\ominus}$$

the n-factor is

(a) 1	(b) 11
(c) $\frac{5}{3}$	(d) 61

32. For the reaction,

$$FeS_2 \longrightarrow Fe^{3+} + SO_2$$

the n-factor is

(a) 1	(b) 11
(c) 28	(d) 61

33. For the reaction,

$$2Br_2 + 2NaOH \longrightarrow NaBrO_3 + NaBr + H_2O$$

the n-factor is

(a) 11	(b) 28
(c) 61	(d) $\frac{5}{3}$

34. For the reaction,

$$As_2S_3 \longrightarrow As^{5+} + SO_4^{2-}$$

the n-factor is

(a) 11	(b) 28
(c) 61	(d) $\frac{5}{3}$

Previous Years' Questions

35. What products are expected from the disproportionation reaction of hypochlorous acid? [AIEEE 2006]

(a) $HClO_3$ and Cl_2O
(b) $HClO_2$ and $HClO_4$
(c) HCl and Cl_2O
(d) HCl and $HClO_3$

36. Which of the following chemical reactions depicts the oxidising behaviour of H_2SO_4? [AIEEE 2006]

(a) $2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$
(b) $Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O$
(c) $NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$
(d) $2PCl_5 + H_2SO_4 \longrightarrow 2POCl_3 + 2HCl + SO_2Cl_2$

37. The oxidation state of chromium in the final product formed by the reaction between KI and acidified potassium dichromate solution is [AIEEE 2005]

(a) + 3 (b) + 2
(c) + 6 (d) + 4

38. Oxidation number of Cl in $CaOCl_2$ (bleaching powder) is [AIEEE 2004]

(a) zero, since it contains Cl_2
(b) −1, since it contains Cl^-
(c) +1, since it contains ClO^-
(d) +1 and −1, since it contains ClO^- and Cl^-

39. MnO_4^- is a good oxidising agent in different medium changing to

$$MnO_4^- \longrightarrow Mn^{2+} \longrightarrow MnO_4^{2-} \longrightarrow MnO_2 \longrightarrow Mn_2O_3$$

Changes in oxidation number respectively are [AIEEE 2002]

(a) 1, 3, 4, 5 (b) 5, 4, 3, 2
(c) 5, 1, 3, 4 (d) 2, 6, 4, 3

40. Which of the following is a redox reaction? [AIEEE 2002]

(a) $NaCl + KNO_3 \longrightarrow NaNO_2 + KCl$
(b) $CaC_2O_4 + 2HCl \longrightarrow CaCl_2 + H_2C_2O_4$
(c) $Ca(OH)_2 + 2NH_4Cl \longrightarrow CaCl_2 + 2NH_3 + 2H_2O$
(d) $2K[Ag(CN)_2] + Zn \longrightarrow 2Ag + K_2[Zn(CN)_4]$

Answers

Round I

1. (a)	**2.** (b)	**3.** (b)	**4.** (a)	**5.** (c)	**6.** (c)	**7.** (c)	**8.** (a)	**9.** (c)	**10.** (a)
11. (d)	**12.** (b)	**13.** (d)	**14.** (c)	**15.** (a)	**16.** (c)	**17.** (a)	**18.** (b)	**19.** (a)	**20.** (d)
21. (c)	**22.** (d)	**23.** (c)	**24.** (c)	**25.** (a)	**26.** (d)	**27.** (a)	**28.** (d)	**29.** (d)	**30.** (a)
31. (c)	**32.** (d)	**33.** (c)	**34.** (a)	**35.** (b)	**36.** (a)	**37.** (d)	**38.** (d)	**39.** (c)	**40.** (c)

Round II

1. (a)	**2.** (d)	**3.** (b)	**4.** (c)	**5.** (b)	**6.** (c)	**7.** (a)	**8.** (c)	**9.** (d)	**10.** (d)
11. (a)	**12.** (b)	**13.** (a)	**14.** (a)	**15.** (d)	**16.** (c)	**17.** (b)	**18.** (a)	**19.** (c)	**20.** (a,b)
21. (a,c,d)	**22.** (b,c,d)	**23.** (a,c)	**24.** (a,b,c,d)	**25.** (a)	**26.** (c)	**27.** (a)	**28.** (d)	**29.** (d)	**30.** (b)
31. (d)	**32.** (b)	**33.** (d)	**34.** (b)	**35.** (a)	**36.** (a)	**37.** (a)	**38.** (d)	**39.** (c)	**40.** (d)

the Guidance

Round I

1. The sum of oxidation states of all elements in an ion is equal to charge on it.

Let the oxidation state of S in $SO_4^{2-} = x$

$\therefore \quad x + (-2 \times 4) = -2$ or $x = +6$

2. In N_3H

Oxidation number of $N = -\frac{1}{3}$

In N_2O_4 oxidation number of $N = +4$

In NH_2OH oxidation number of $N = -1$

In NH_3 oxidation number of $N = -3$

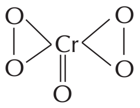
Hence, in N_2O_4 the oxidation number of nitrogen is highest.

3. NH_4NO_3 is actually NH_4^+ and NO_3^-. In NH_4^+, oxidation state of N is −3 and in NO_3^- oxidation state of N is + 5.

4. $\overset{+2}{O}\overset{-1\times2}{F_2}$: $x - 2 = 0 \Rightarrow x = 2$

$\therefore$ Oxidation number of O = + 2

5.



i.e., it has four peroxide bonded oxygen each having an oxidation number of −1 and one double bond in which oxidation number of O is −2.

Therefore, $x + 4 \times (-1) + 1 \times (-2) = 0$

$\therefore \quad x = +6$

6. The oxidation state of iodine in HIO_4 is + 7 as

$$1 + x + 4(-2) = 0$$
$$x = +7$$

The oxidation state of iodine in H_3IO_5 is + 7 as

$$3 + x + 5(-2) = 0$$
$$x = +7$$

The oxidation state of iodine in H_5IO_6 is + 7 as

$$5 + x + 6(-2) = 0$$
$$x = +7$$

7. Oxidation number of iodine in the given species is as follows

Oxidation number of iodine in $IF_3 = +3$

Oxidation number of iodine in $I_3^- = -\frac{1}{3}$

Oxidation number of iodine in $IF_5 = +5$

Oxidation number of iodine in $IF_7 = +7$

9. Let the oxidation number of Cr be x

$\therefore$ For $K_2Cr_2O_7$

$$+1 \times 2 + 2x + 7(-2) = 0$$
$$2 + 2x - 14 = 0$$
$$2x = 12$$
$$x = 6$$

10. Bromine has zero oxidation state because it is in free state.

$$\overset{0}{Br_2} \longrightarrow BrO_3^-$$

Let the oxidation number of Br in BrO_3^- is x.

$$x + (-2 \times 3) = -1$$
$$x + (-6) = -1$$
$$x = +6 - 1$$
$$= +5$$

So, oxidation number changes from 0 to + 5.

11. Permonosulphuric acid (H_2SO_5) has two oxygen atoms in peroxide linkage, hence,

$$2(+1) + x + 2(-1) + 3(-2) = 0$$
$$2 + x - 2 - 6 = 0$$

$\therefore \quad x = +6$

12. Oxidation number of N in NO^+ is

$$(1 \times x) + 1 \times (-2) = +1$$
$$x = +3$$

Oxidation number of Cl in ClO_4^- is

$$(1 \times x) + 4 \times (-2) = -1$$

$\therefore \quad x = +7$

13. Maximum oxidation state for d-block elements $= (n-1)$ unpaired $de^- + nse^-$

For $3d^5, 4s^2$ configuration,

Maximum oxidation number = 5 + 2 = 7

14. $\underline{C}H_3\underline{C}H_2OH$

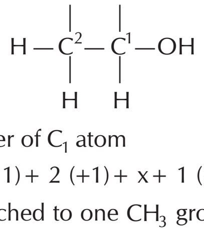
$$\overset{x}{C_2}\overset{+1}{H_6}\overset{-2}{O}$$

$$2x + 6(+1) + 1(-2) = 0$$
$$2x = -4$$

or $\quad x = -2$

Therefore, the average oxidation number of C is −2.

Let us consider the structure of CH_3CH_2OH



$$H-\overset{H}{\underset{H}{C^2}}-\overset{H}{\underset{H}{C^1}}-OH$$

Oxidation number of C_1 atom

$$= 1(+1) + 2(+1) + x + 1(-1) = 0$$

[$\therefore C_1$ atom is attached to one CH_3 group (oxidation number = + 1), two H atoms and one —H group (Ox. no. = −1)]

$\therefore \qquad x = -2$

Oxidation number of C_2 atom $= 3(+1) + x + 1(-1) = 0$

[C_2 atom is attached to three H-atoms and one $—CH_2OH$ group (Ox. no. $= -1$)]

$\therefore y = -2$

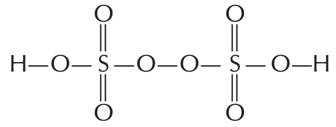
15. $\underline{C}H_3\underline{C}OOH$

$$\overset{x}{C_2}\overset{+1}{H_4}\overset{-2}{O_2}$$

$$2x + 4(+1) + 2(-2) = 0$$

$$2x + 4 + (-4) = 0 \text{ or } x = 0$$

16. The chemical structure of $H_2S_2O_8$ is as follows



$$\underset{\text{For H}}{2x(+1)} + \underset{\text{For S}}{2 \times x} + \underset{\text{For O}}{6 \times (-2)} + \underset{\text{For O–O}}{2 \times (-1)} = 0$$

$$+2 + 2x - 12 - 2 = 0$$

$$2x = +12$$

$$x = +6$$

17. Let the oxidation state of Cr in $K_2Cr_2O_7 = x$

$$(+1 \times 2) + 2x + (-2 \times 7) = 0$$

or $\qquad +2 + 2x - 14 = 0$

$\therefore \qquad x = +6$

Let the oxidation state of Cr in $K_2CrO_4 = x$

$$+1 \times 2 + x + (-2 \times 4) = 0$$

$$2 + x - 8 = 0$$

$$x = 6$$

$\therefore$ Change in oxidation state of Cr is zero when it changes from $K_2Cr_2O_7$ to K_2CrO_4.

18. It is a disproportionation reaction.

19. Intermolecular redox reaction and redox reactions are same.

20. Loss of an electron or increase in oxidation number is oxidation process. *i.e.,*

$$H^- \longrightarrow H + e^-$$

21. It is a disproportionation reaction, so Cl_2 undergoes both oxidation and reduction.

Oxidation

22. $\overset{+1}{Cu_2}\overset{-2}{S} + 2\overset{+2}{Fe}\overset{-2}{O} \longrightarrow 2\overset{0}{Cu} + 2\overset{0}{Fe} + \overset{+4}{S}\overset{-2}{O_2}$

Reduction

Reduction

In this reaction Cu and Fe undergo reduction while sulphur undergoes oxidation. Hence, this is a redox reaction.

23. In this reaction phosphorus is simultaneously oxidised and reduced. It is a disproportionation reaction.

$$\overset{0}{P_4} + 3NaOH + 3H_2O \longrightarrow 3Na\overset{+1}{H_2}PO_2 + \overset{-3}{P}H_3$$

24. In an aqueous medium, Li is the strongest reducing agent, since the high negative enthalpy of hydration compensates high IE_1.

25. $e^- + Fe^{3+} \longrightarrow Fe^{2+}$ (Reduction)

Therefore, $FeCl_3$ acts as an oxidising agent.

26. Reduction potential order is $F_2 > Cl_2 > Br_2 > I_2$.

So, F_2 is the strongest oxidising agent.

(Moreover, F_2 has great tendency to get reduced into F^- due to its highly electronegative nature.)

28. All these substances can accept electrons and can decrease their oxidation number and hence, all these act as oxidising agent.

$$H\overset{+5}{N}O_3 \longrightarrow \overset{+4}{N}O_2 \text{ or } \overset{+2}{N}O$$

$$Cl_2 \longrightarrow 2Cl^-$$

$$\overset{+3}{Fe}Cl_3 \longrightarrow \overset{+2}{Fe}Cl_2$$

Oxidation

29. $2\overset{+4}{N}O_2 + 2OH^- \longrightarrow \overset{+3}{N}O_2^- + \overset{+5}{N}O_3^- + H_2O$

Reduction

Since in this reaction, the same element , *i.e.,* N is reduced as well as oxidised, so it is a disproportionation reaction.

Note In OF_2, oxidation state of F is -1.

30. In MnO_4^{2-}, the oxidation number of Mn is $+6$. It can increase its oxidation number (to $+7$) or decrease its oxidation number to $+4, +3, +2, 0$). Hence, it undergoes disproportionation reaction is acidic medium.

$$3\overset{+6}{Mn}O_4^{2-} + 4H^+ \longrightarrow 2\overset{+7}{Mn}O_4^- + \overset{+4}{Mn}O_2 + 2H_2O$$

Ox. no. increases by 1 per atom

Ox. no. decreases by 2 per atom

In MnO_4^-, Mn is in its highest oxidation state, *i.e.,* $+7$. It can only decrease its oxidation number. Hence, it cannot undergo disproportionation reaction.

31. a. Neutralisation

b. It is the change of an element in one form (oxidation state $= 0$) to another form.

c. Redox reaction [$\overset{0}{N_2} + \overset{0}{O_2} \longrightarrow \overset{\neq 0 \neq 0}{NO}$]

d. Physical change

32. $\overset{0}{Cl_2}(g) + 2\overset{-2\,+1}{OH^-}(aq) \longrightarrow \overset{+1\,-2}{ClO^-}(aq) + \overset{-1}{Cl^-}(aq) + \overset{+1\,-2}{H_2O}(l)$

In this reaction, oxidation number of Cl increases from 0 (in Cl_2) to 1 (in ClO^-) as well as decreases from 0 (in Cl_2) to -1 (in Cl^-). So, it acts as both reducing agent as well as oxidising agent. This is an example of disproportionation reaction. In this reaction, ClO^- species bleaches the substances due to its oxidising action. [In hypochlorite ion (ClO^-), Cl can decrease its oxidation number from $+1$ to 0 or -1.]

33. Both the statements are correct. This can be proved by following example.

P_4 is a reducing agent and Cl_2 is an oxidising agent.

(i) $\underset{\text{Excess}}{\overset{0}{P_4}}\ (s) + 6Cl_2(g) \longrightarrow \underset{\text{Lower oxidation state of P}}{4\overset{+3}{P}Cl_3}$

(ii) $\underset{\text{Excess}}{\overset{0}{P_4}(s) + 10Cl_2(g)} \longrightarrow \underset{\text{Higher oxidation state of P}}{4\overset{+5}{P}Cl_5}$

Therefore, when P_4 (reducing agent) is in excess, PCl_3 is formed in which oxidation state of P is +3 and if Cl_2 (oxidising agent) is in excess, PCl_5 is formed in which oxidation state of P is + 5.

34. $I^- + \overset{+5}{I}O_3^- + H^+ \longrightarrow \overset{0}{I_2} + H_2O$

$$2I^- \longrightarrow I_2 + 2e^-]\times 5 \qquad \ldots(i)$$

$$10e^- + 2\overset{+5}{I}O_3^- \longrightarrow \overset{0}{I_2} \qquad \ldots(ii)$$

On adding Eq. (i) and (ii), we get

$$10I^- + 2IO_3^- \longrightarrow 6I_2$$

To balance O atom, add $6H_2O$ molecules on RHS and $12H^+$ on LHS, then

$$10I^- + 2IO_3^- + 12H^+ \longrightarrow 6I_2 + 6H_2O$$

or $\quad 5I^- + IO_3^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$

35. $NO_2^{\ominus} + H_2O \longrightarrow NO_3^{\ominus} + 2H^{\oplus} + 2e^-$

Balance charge on both sides.

36. $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

37. $\underset{1}{a}K_2Cr_2O_7 + \underset{4}{b}KCl + \underset{6}{c}H_2SO_4 \longrightarrow \underset{2}{x}CrO_2Cl_2 + \underset{6}{y}KHSO_4 + \underset{3}{z}H_2O$

38. $8Al \longrightarrow 8Al^{3+} + 24e^-$

$9Fe^{8/3+} + 24e^- \longrightarrow 9Fe$

39. $Cr_2O_7^{2-} + 14H^+ + nFe^{2+} \longrightarrow 2Cr^{3+} + nFe^{3+} + 7H_2O$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ (reduction)...(i)

$Fe^{2+} \longrightarrow Fe^{3+} + e^-$ (oxidation) ...(ii)

Eq. (ii) is multiplied by 6

$$6Fe^{2+} \longrightarrow 6Fe^{3+} + 6e^-$$

Thus, balanced equation is

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

Hence, the value of *n* is 6

40. The skeletal equation is,

$$Mn^{3+}(aq) \longrightarrow Mn^{2+}(aq) + MnO_2(s) + H^+(aq)$$

Reduction half reaction

$$Mn^{3+}(aq) + e^- \longrightarrow Mn^{2+} \qquad \ldots(i)$$

Oxidation half reaction

$$Mn^{3+}(aq) \longrightarrow \overset{+4}{Mn}O_2 + e^- \qquad \ldots(ii)$$

Balance charge by adding $4H^+$ to RHS and then balance O atoms by adding $2H_2O$ to LHS

$$Mn^{3+}(aq) + 2H_2O(l) \longrightarrow MnO_2(s) + e^- + 4H^+(aq) \qquad \ldots(iii)$$

By adding (i) and (iii) we get

$$2Mn^{3+}(aq) + 2H_2O(l) \longrightarrow Mn^{2+} + MnO_2(s) + 4H^+(aq)$$

This represents the final balanced redox reaction (disproportionation reaction).

Round II

1. $\overset{+1}{K}\overset{x}{I_3}$

$1(+1) + 3x = 0$ or $x = -\frac{1}{3}$

Therefore, the average oxidation number of I is $-\frac{1}{3}$. It is wrong because oxidation number cannot be fractional. Let us consider the structure of KI_3.

$\overset{+}{K}(I-I\leftarrow I)^{-1}$, In this structure, a coordinate bond is formed between I_2 molecule and I^- ion. Hence, the oxidation number of three I atoms in KI_3 are 0, 0 (in I_2) and −1 respectively.

2. $NaNO_2$ (sodium nitrite) acts both as oxidising as well as reducing agent because in it N-atom is in + 3 oxidation state (intermediate oxidation state).

Oxidising property

$$2NaNO_2 + 2KI + 2H_2SO_4 \longrightarrow Na_2SO_4 + K_2SO_4 + 2NO + 2H_2O + I_2$$

Reducing property

$$H_2O_2 + NaNO_2 \longrightarrow NaNO_3 + H_2O$$

3. $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

$[Fe^{2+} \longrightarrow Fe^{3+} + e^-]\times 5$

$MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

∴ Five electrons gets transferred.

4. Acidified $K_2Cr_2O_7$ solution oxidises SO_2 into $Cr_2(SO_4)_3$.

$$3\overset{+4}{S}O_2 + K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(\overset{+6}{S}O_4)_3 + H_2O$$

Hence, oxidation state of sulphur changes from + 4 to + 6.

5.

Oxidation

Change in oxidation state = 2

$$5M^{x+} + 2\overset{+7}{Mn}O_4^- \longrightarrow \overset{+5}{M}O_3^- + Mn^{2+} + \frac{1}{2}O_2$$

Change in oxidation state = 5

Reduction

$$x + 2 = 5$$

$$\therefore \quad x = 5 - 2 = +3$$

6. Disproportionation reaction.

$$\mathrm{ClO_3^{\ominus}} \longrightarrow \mathrm{ClO_4^{\ominus}} + 2\,e^-(x=2)\ \text{(oxidation)}$$

$x-6=-1$ $\quad$ $x-8=-1$

$x=5$ $\quad$ $x=7$

$$e^- + \mathrm{ClO_3^{\ominus}} \longrightarrow \mathrm{ClO_2}\,(x=1)\ \text{(reduction)}$$

$x=5$ $\quad$ $x-4=0$

$x=4$

$$\text{Equivalent weight} = M + \frac{M}{2}$$

7. In this case only 2 moles of $\mathrm{NO_3^{\ominus}}$ undergo reduction.

$$3e^- + \mathrm{NO_3^-} \longrightarrow \mathrm{NO}\,(x=3)\ \text{(reduction)}$$

$x-6=-1$ $\quad$ $x-2=0$

$x=5$ $\quad$ $x=2$

6 moles of $\mathrm{HNO_3}$ are not changing so $6\mathrm{NO_3^{\ominus}}$ are added in the reaction to get 3 moles of $\mathrm{Cu(NO_3)_2}$.

$$\text{Equivalent weight} = M + \frac{M}{3} = \frac{4M}{3} = \frac{4\times 63}{3}$$

8. $\mathrm{N_2H_4} \longrightarrow 2Y + 10e^-$

$2x+4=0 \quad 2y=2x$

$2x=-4$

$$\underbrace{\uparrow\;2x-(-4)=10\;\uparrow}_{x=3}$$

9. I. $\mathrm{Rb} \longrightarrow \mathrm{Rb^+} + e^-$ (Oxidation)

$$\mathrm{H_2O} + e^- \longrightarrow \overset{\ominus}{\mathrm{O}}\mathrm{H} + \frac{1}{2}\mathrm{H_2}\ \text{(Reduction)}$$

Hence, redox reaction.

II. $e^- + \mathrm{Cu^{2+}} \longrightarrow \mathrm{Cu^+}$ (Reduction)

$$2\mathrm{I}^{\ominus} \longrightarrow \mathrm{I_2} + 2e^-\ \text{(Oxidation)}$$

Hence, redox reaction.

III. $\overset{\oplus}{\mathrm{N}}\mathrm{H_4} \longrightarrow \mathrm{NH_3}$ (No change in oxidation number)

$x=-3$ $\quad$ $x=-3$

Hence, reaction is not redox.

IV. No change in the oxidation number of either $\mathrm{Fe^{2+}}$ or $\mathrm{CN^{\ominus}}$ in both reactant and product, hence, not redox reaction.

10. (a) $\mathrm{NO_2}(x=4), \mathrm{N_2O_4}(x=4)$

Difference in oxidation state of $\mathrm{N}=0$

(b) $\mathrm{P_2O_5}$ and $\mathrm{P_4O_{10}}$ (Difference in oxidation state of P is zero)

(c) $\mathrm{N_2O}\,(x=1)$ and $\mathrm{NO}\,(x=2)$,

Difference in oxidation state of $\mathrm{N}=1$.

(d) $\mathrm{SO_2}\,(x=4)$ and $\mathrm{SO_3}\,(x=6)$

Difference in oxidation state of $\mathrm{S}=2$

11. $\mathrm{Fe^{2+}} + \mathrm{Ce^{4+}} \longrightarrow \mathrm{Fe^{3+}} + \mathrm{Ce^{3+}}$

$$5\mathrm{Fe^{2+}} + \mathrm{MnO_4^-} + 8\mathrm{H^+} \longrightarrow 5\mathrm{Fe^{3+}} + \mathrm{Mn^{2+}} + 4\mathrm{H_2O}$$

$$\therefore \frac{\text{Moles of cerric ammonium sulphate}}{\text{Moles of potassium permanganate}} = \frac{1}{1/5} = 5.0$$

12. The oxidation state of X, Y and Z are $+2, +5$ and -2 respectively.

I. In $X_2YZ_6 = 2\times 2 + 5 + 6(-2) \neq 0$

II. In $XY_2Z_6 = 2 + 5\times 2 + 6(-2) = 0$

III. In $XY_5 = 2 + 5\times 2 \neq 0$

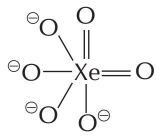
IV. In $X_3YZ_4 = 3\times 2 + 5 + 4(-2) \neq 0$

Hence, the formula of the compound is XY_2Z_6.

13. $\mathrm{Li} + \overset{0}{\mathrm{H_2}} \longrightarrow 2\,\overset{+1\,-1}{\mathrm{Li\,H}}$

Oxidation number of hydrogen is decreasing from 0 to −1. So, $\mathrm{H_2}$ is acting as oxidising agent in this reaction.

14. No peroxide bond in $[\mathrm{XeO_6}]^{4-}$. Structure is



15. Haematite is $\mathrm{Fe_2O_3}$, in which oxidation number of iron is III. Magnetite is $\mathrm{Fe_3O_4}$ which is infact a mixed oxide $(\mathrm{FeO\cdot Fe_2O_3})$, hence iron is present in both II and III oxidation state.

16. $2\mathrm{MnCl_2} + 5\mathrm{PbO_2} + 6\mathrm{HNO_3} \longrightarrow$

$$2\mathrm{HMnO_4} + 2\mathrm{PbCl_2} + 3\mathrm{Pb(NO_3)_2} + 2\mathrm{H_2O}$$

17. An element, in its lowest oxidation state, can behave only as reductant while in its highest oxidation state can behave only as oxidants. In intermediate oxidation states, elements can behave as oxidant as well as reductant.

(i) In $\mathrm{SO_2}$, S is in + 4 oxidation state. It can have minimum oxidation number − 2 and maximum oxidation number + 6. Therefore, S in $\mathrm{SO_2}$ can either decrease or increase its oxidation number. So, $\mathrm{SO_2}$ can act both as oxidising as well as reducing agent.

(ii) In $\mathrm{H_2O_2}$, O is in − 1 oxidation state. It can have minimum oxidation number − 2 and maximum oxidation number zero (+1 and +2 also possible in $\mathrm{O_2F_2}$ and $\mathrm{OF_2}$ respectively). Therefore, 'O' in $\mathrm{H_2O_2}$ can either decrease or increase its oxidation number. So, $\mathrm{H_2O_2}$ can act both as oxidising as well as reducing agent.

(iii) In $\mathrm{O_3}$, O is in zero oxidation state. It cannot increase its oxidation number, it can only decrease its oxidation number from zero to − 1 or − 2. So, ozone can act only as an oxidising agent.

(iv) In $\mathrm{HNO_3}$, the oxidation number of N is +5. It is maximum. So, N in $\mathrm{HNO_3}$ can only decrease its oxidation number. So, it can act as an oxidising agent only.

18. $2\,\overset{+2}{\mathrm{S}}_2\overset{-2}{\mathrm{O}}{}_3^{2-}(aq) + \overset{0}{\mathrm{I}}_2(s) \longrightarrow \overset{2.5}{\mathrm{S}}_4\overset{2-}{\mathrm{O}}{}_6^{2-}(aq) + 2\mathrm{I^-}(aq)$

$$\overset{+2}{\mathrm{S}}_2\overset{-2}{\mathrm{O}}{}_3^{2-}(aq) + 2\,\overset{0}{\mathrm{B}}\mathrm{r_2}(l) + 5\mathrm{H_2O}(l) \longrightarrow$$

$$2\overset{+6}{\mathrm{S}}\overset{2-}{\mathrm{O}}{}_4^{2-}(aq) + 4\mathrm{Br^-}(aq) + 10\mathrm{H^+}(aq)$$

Bromine being stronger oxidising agent than I_2, oxidises S of $S_2O_3^{2-}$ to SO_4^{2-} whereas I_2 oxidises it only into $S_4O_6^{2-}$ ion.

19. (a) $(N\overset{+1}{H}_4)_2S_2O_8^{2-}$

$\therefore$ Oxidation state of S $= +6$

(Since $S_2O_8^{2-}$ has one peroxide bond)

(b) Oxidation state of Os $= +8$

(c) Oxidation state of S in $H_2SO_5 = +6$

(Since it has one peroxide bond)

(d) $K^{1+}O_2^{1-}$ oxidation state of O $= -1/2$

20. In (a) $MnO_4^{\ominus} \longrightarrow MnO_2$ occurs only in basic medium

In (b) $Cr(OH)_2 \longrightarrow Cr(OH)_3$ occurs only in basic medium. (c) and (d) occurs only in acidic medium.

21.

$$4H_2O + \overset{+1\times 3}{Cu_3}\overset{-3}{P} \longrightarrow 3Cu^{2+} + H_3PO_4 + 11e^- + 5H^{\oplus}] \times 6$$

$$6e^- + 14H^{\oplus} + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O] \times 11$$

$$6Cu_3P + 124H^{\oplus} + 11Cr_2O_7^{2-} \longrightarrow 18Cu^{2+} + 6H_3PO_4 + 22Cr^{3+} \times 53H_2O$$

22. In Cu_2O and Cu_2S, the oxidation state of Cu is $+1$. So they are reduced to $Cu^0 (Cu^{1+} + e^- \longrightarrow Cu^0)$

23. (a)

$$\left.\begin{array}{r} H_2S_2O_7 : 2 + 2x - 14 = 0 \Rightarrow x = 6 \\ Na_2S_4O_6 : 2 + 4x - 12 = 0 \Rightarrow x = 2.5 \\ Na_2S_2O_3 : 2 + 2x - 6 = 0 \Rightarrow x = 2 \\ S_8 : 8x - 0 \Rightarrow x = 0 \end{array}\right] \text{Oxidation state of S}$$

(c) H_2SO_5 (Peroxo linkage) Oxidation state of S $= +6$

$H_2SO_3 : 2 + x - 6 = 0$

Oxidation state of S $= +4$

$SCl_2 : x - 2 = 0$ Oxidation state of S $= +2$

$H_2S : 2 + x = 0$ Oxidation state of S $= -2$

24.

Reduction

$$2\,\overset{+1}{K}\,\overset{+5}{Cl}\,\overset{-2}{O_3} \longrightarrow 2\,\overset{+1}{K}\overset{-1}{Cl} + 3\,\overset{0}{O_2}$$

Oxidation

25. Fluorine being most electronegative element is the best oxidant.

26.

$$10KI + 2K\overset{+7}{Mn}O_4 + 8H_2SO_4 \longrightarrow 2\overset{+2}{Mn}SO_4 + 6K_2SO_4 + 8H_2O + 5I_2$$

27.

Oxidation

$$2H_2\overset{-1}{O_2} \longrightarrow 2H_2\overset{-2}{O} + \overset{0}{O_2}$$

Reduction

Thus, the above reaction is an example of disproportionation reaction.

28. Oxidation state of $X = -2 \Rightarrow \overset{+2}{A}\overset{-2}{X}$

Oxidation state of $O = -2 \Rightarrow \overset{-2}{O}\overset{+2}{Y}$

Oxidation state of $X = -2, \Rightarrow \overset{-2\times 2}{X_2}\overset{+4}{B}$

$$\therefore \quad \overset{+2}{A}\overset{-2}{X} + BY + H_2O \longrightarrow \overset{+1}{H}\overset{-1}{A} + \overset{-2}{O}\overset{+2}{Y} + \overset{-2\times 2}{X_2}\overset{+4}{B}$$

$$e^- + A^{2+} \longrightarrow A^{1-} \text{ (reduction)}$$

$$\overset{+a}{B}\overset{-a}{Y} \longrightarrow B^{4+} + Y^{2+} \text{ (oxidation)}$$

Therefore, B or Y or both might have been oxidised.

29. In BY, the oxidation state of $B \le +2$

Oxidation state of $Y \le +2$.

If the oxidation state of B is +1 and that of Y is −1, then both will be oxidised.

If the oxidation state of B is +2 and that of Y is −2, then both will be oxidised.

If the oxidation state of B is +3 and that of Y is −3, then both will be oxidised.

30.

$$A^{2+} + H^{\oplus} + 3e^- \longrightarrow HA] \times 2$$

$$BY + H_2O \longrightarrow B^{4+} + OY + 2H^{\oplus} + 6e^-$$

$$2A^{2+} + BY + H_2O \longrightarrow 2HA + B^{4+} + OY$$

Or

$$\underset{2}{\underline{2AX}} + \underset{1}{\underline{BY}} + \underset{1}{\underline{H_2O}} \longrightarrow \underset{2}{\underline{2HA}} + \underset{1}{\underline{BX_2}} + \underset{1}{\underline{OY}} = 8$$

$$2 + 1 + 1 + 2 + 1 + 1$$

The sum of all the coefficients is 8.

31. $\overset{+1\times 4}{K_4}\left[Fe^{2+}(\overset{-1\times 6}{CN})_6\right]^{-4}$ Oxidation state of Fe is +2

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

$$6(CN)^{\ominus} \longrightarrow 6CO_2 + 12e^-$$

$6(x - 3 = -1)$ $\quad$ $6(x - 4 = 0)$

$6(x = 2)$ $\quad$ $6(x = 4)$

$$6(CN)^{\ominus} \longrightarrow 6NO_3^{\ominus} + 48e^-$$

$\left(\begin{array}{c}\text{Oxidation number} \\ \text{of } N = -3\end{array}\right)$ $\quad$ $6(x - 6 = -1)$

$6(x = 5)$

$$Fe^{2+}(CN)_6]^{4-} \longrightarrow Fe^{3+} + 6CO_2 + 6NO_3^{\ominus} + 61e^-$$

32.

$$Fe^{2+} \longrightarrow Fe^{3+} + e^- \text{ Total } e^- = 11$$

$$S_2^{2-} \longrightarrow 2SO_2 + 10e^-$$

$2x = -2$ $\quad$ $2x - 8 = 0$

$2x = 8$

33.

$$Br_2 \longrightarrow 2BrO_3^{\ominus} + 10e^-$$

$2x = 0$ $\quad$ $2x - 12 = -2$

$2x = 10$

$$2e^- + Br_2 \longrightarrow 2Br^{\ominus}] \times 5$$

$$\underline{6Br_2 \longrightarrow 2BrO_3^{\ominus} + 10Br^{\ominus}}$$

$$\text{Equivalent weight of } Br_2 = \frac{6\,[Br_2]}{10} = \frac{3}{5}$$

$$n\text{-factor} = \frac{5}{3}$$

34. $As_2^{3+} \longrightarrow 2As^{5+} + 4e^-$

$2x=6 \qquad 2x=10$

$S_3^{2-} \longrightarrow 3SO_4^{2-} + 24e^- \quad n\text{-factor} = 28$

$3x=-6 \qquad 3x-24=-6$

$3x=18$

35. $3HOCl \longrightarrow 2HCl + HClO_3$

36. $2\overset{-1}{H I} + H_2\overset{+6}{S}O_4 \longrightarrow \overset{0}{I_2} + \overset{+4}{S}O_2 + 2H_2O$

$$\underset{\text{oxidising agent}}{H_2SO_4} \text{ Reduced to} \longrightarrow SO_2$$

37. $Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 7H_2O + 3I_2$

$Cr_2O_7^{2-}$ is reduced to Cr^{3+}.

Thus, final state of Cr is +3.

38. $CaOCl_2$ is written basically as Ca(OCl)Cl

$OCl^- \longrightarrow$ Cl has + 1 oxidation state

$Cl^- \longrightarrow$ Cl has − 1 oxidation state

39. $\overset{+7}{Mn}O_4^- \longrightarrow Mn^{2+}$ change 5

$\longrightarrow \overset{+6}{Mn}O_4^{2-}$ change 1

$\longrightarrow \overset{+4}{Mn}O_2$ change 3

$\longrightarrow \overset{+3}{Mn_2}O_3$ change 4

40. (a) $\overset{+1}{Na}\overset{-1}{Cl} + \overset{+1}{K}\overset{-1}{NO_3} \longrightarrow \overset{+1}{Na}\overset{-1}{NO_3} + \overset{+1}{K}\overset{-1}{Cl}$

(b) $\overset{+2}{Ca}\,C_2\overset{-2}{O_4} + 2\,\overset{+1}{H}\overset{-1}{Cl} \longrightarrow \overset{+2}{Ca}\overset{-1}{Cl_2} + \overset{+1}{H_2}\,C_2\,\overset{-2}{O_4}$

(c) $\overset{+2}{Ca}(O\overset{-1}{H})_2 + 2\,\overset{+3}{N}\,\overset{+1}{H}_4\overset{-1}{Cl} \longrightarrow \overset{+2}{Ca}\overset{-1}{Cl_2} + 2\,\overset{-3}{N}\overset{+1}{H_3} + 2\,\overset{+1}{H_2}\overset{-2}{O}$

In all these cases during reaction, there is no change in oxidation state of ion or molecule or constituent atom, these are simply ionic reactions.

(d) $2K[Ag(CN)_2] + Zn \longrightarrow 2Ag + K_2[Zn(CN)_4]$

$Ag^+ \longrightarrow Ag$ gain of e^-, reduction

$Zn \longrightarrow Zn^{2+}$ loss of e^-, oxidation.

8

Classification of Elements and Periodicity in Properties

JEE Main MILESTONE

- Earlier Attempts to Classify Elements
- Long Form of Periodic Table
- Classification of Elements
- Prediction of Group, Period and Block of an Element
- Nomenclature of the Elements having Atomic Number > 100
- Periodic Properties
- Elements Showing Highest and Lowest Properties

8.1 Earlier Attempts to Classify Elements

Several attempts have been made for the classification of elements into groups and it leads to the development of periodic law and Periodic Table *e.g.*,

Prout's Hypothesis

This hypothesis, given in 1815, is also called **unitary theory** as according to it hydrogen atom was considered as the fundamental unit from which all other atoms were made.

In Periodic Table the elements are arranged in rows and columns. Using the position of an element in the Periodic Table, it is possible to predict its chemical behaviour. The regular gradation in the properties is called periodicity and such properties are called periodic properties.

Dobereiner's Triads

Dobereiner, between 1815-1829, gave his law of triads. A triad is a certain group of three elements with similar properties. According to him, in the triads the atomic weight of the middle element was approximately the arithmetic mean of the other two, *e.g.,*

Element	Li	Na	K
Atomic weight	7	23	39

Mean of atomic masses $= \frac{7+39}{2} = 23$

Similarly,

Element	Cl	Br	I
Atomic weight	35.5	80	127

Mean of atomic masses $= \frac{35.5+127}{2} = 81.25$

and

Element	**Ca**	**Sr**	**Ba**
Atomic weight	40	88	137

$$\text{Mean of atomic masses} = \frac{40 + 137}{2} = 88.5$$

But in some triads, all the three elements possessed nearly equal atomic masses, *e.g.,* Fe, Co, Ni, Os, Ir, Pt, etc., hence, the law was rejected.

Newland's Law of Octaves

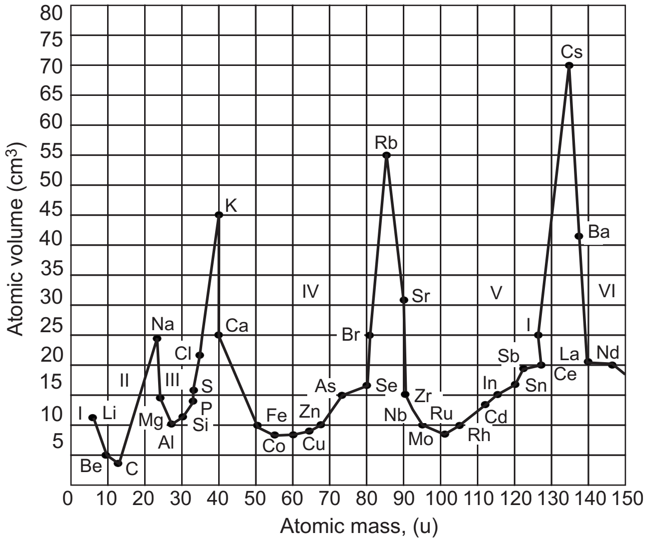
Newland in 1864 presented the **law of octaves** which is considered as first serious attempt to classify the elements. According to this law, if the known elements were arranged in increasing order of atomic weight, the 8th element starting from a given one, was a kind of repetition of the first, like the 8th note in the octave of music, *i.e.,*

Sa	Re	Ga	Ma	Pa	Dha	Ne
H	Li	Be	B	C	N	O
F	Na	Mg	Al	Si	P	S

The above law worked quite well for lighter elements but failed in the case of heavier elements. Moreover, after the discovery of noble gases, it is the ninth element that resembles with the first, which is not in accordance to the law.

Lothar Meyer's Atomic Volume Curve

Lothar Meyer presented the classification in the form of a curve between atomic volume and atomic masses and said, "the properties of the elements were the periodic functions of their atomic volumes".



Lothar Meyer's curve

He calculated atomic volumes with the help of the formula

$$\text{Atomic volume} = \frac{\text{molecular mass}}{\text{density}}$$

The findings of Meyer were

1. Alkali metals having the largest atomic volumes occupy the maxima of the curve.
2. The alkaline earth metals (Mg, Ca, Sr, Ba) occupy the mid point positions on the descending portions of the curve.
3. Halogens occupy positions on ascending portions before inert gases.
4. The transition elements occupy minima of the curve.

Remember that **Lothar Meyer** (Germany) and **Mendeleef** (Russia) quite independently evolved identical classification of elements in 1869. Both of them showed the connection between the periodicity of properties and atomic masses of elements, with the difference that Mendeleef considered the chemical properties while Lothar Meyer considered the physical properties of elements in their explanations.

Mendeleef's Periodic Law

It states the properties of elements are the periodic function of their atomic masses. In other words, if the elements are arranged in the order of their increasing atomic weights, after a regular interval similar properties of elements are repeated.

His law infact was an impressive version of the law of octaves and formed the basis for the modern classification of elements in the form of a table, called *Periodic Table*.

In his original table, Mendeleef arranged the elements in horizontal rows but subsequently he modified the original table and rearranged the elements in vertical rows.

Mendeleef's original table consisted of 8 vertical columns, called *groups* and 12 horizontal rows, called *series* or *periods*.

When Mendeleef presented the Periodic Table only 63 elements were known and a number of gaps were left for unknown elements. The properties of those unknown elements were also predicted on the basis of periodic law, which helped future scientists in the discovery of such elements.

Zero group was not known at Mendeleef's time. It was added later on in the modified Mendeleef's Periodic Table.

Uses of Mendeleef's Periodic Table

1. Atomic weights of elements were determined with the help of Periodic Table.
   Atomic weight = Valency × Equivalent weight.
2. Atomic weight of elements were corrected. Atomic weight of Be was calculated to be $3 \times 4.5 = 13.5$ by considering its valency 3 but, Mendeleef calculated it $2 \times 4.5 = 9$
3. In Mendeleef's Periodic Table two consecutive members differ by two or three units in the atomic weight. Where this gap was more, the gaps were left in the Periodic Table. This helped in discovering of new elements.

Defects of Mendeleef's Periodic Table

1. Position of hydrogen is uncertain. It has been placed in IA and VIIA groups because of its resemblance with elements of both the groups.
2. No separate positions were given for isotopes.
3. No separate group for lanthanides and actinides.
4. Although there is no resemblance except valency of subgroups A and B, they have been put in the same group.
5. Order of increasing atomic weights is not strictly followed in the arrangement of elements in the Periodic Table. *e.g.,* Co (At. wt. 58.9) is placed before I (127) and Ar (39.9) before K (39).

Modern Periodic Table

Moseley, while working in Rutherford's team in 1913, studied the wavelength of the characteristic X-rays by using different metals as anti-cathode and showed that the square root of the frequency of a line (of X-ray spectrum) is related to the atomic number, Z of the target material as

$$\sqrt{\nu} = a(Z - b)$$

where, a = proportionality constant
b = another constant (It has same value for all the lines of X-rays spectrum)
Z = atomic number.

He thereby showed that atomic number is more fundamental property of an element than its atomic mass and on this basis gave a law, which states *"The physical and chemical properties of the elements are periodic functions of their atomic numbers"*.

The Moseley's law is called *"modern periodic law"* and considered as the basis of *modern Periodic Table*.

The characteristics of this table are

1. The table consists of 9 vertical columns, called the **groups** and 7 horizontal rows, called the **periods**.
2. The groups are marked 0 to VIII out of which group I to VII are subdivided into subgroups A and B.
3. The group IA elements (Li, Na, K, Rb, Cs and Fr) are called **alkali metals** and the group II A elements (Be, Mg, Ca, Sr,Ba and Ra) are called **alkaline earth metals**. Elements in group VII A (F, Cl, Br, I and At) are known as **halogens** and elements in group VIII A (He, Ne, Ar, Kr, Xe and Rn) are called *noble gases* or *rare gases*.
4. The group VIII has three similar elements placed together in one place. These are called **transition triads,** *e.g.,* Fe, Co and Ni; Ru, Rh and Pd; Os, Ir and Pt etc.
5. Starting from hydrogen to heaviest elements uranium, there are 92 elements which are arranged in different periods as follows :

1st period	2 elements	Shortest period
2nd period	8 elements	Ist short period
3rd period	8 elements	IInd short period
4th period	18 elements	Ist long period
5th period	18 elements	IInd long period
6th period	32 elements	Longest period
7th period	6 elements	Incomplete period

6. In the 6th period, 14 elements from lanthanum ($Z = 57$) to lutetium ($Z = 71$) are given one position in 3rd B group, termed as *rare earths* or *lanthanides*.
7. Afterwords, 14 elements from actinium ($Z = 89$) to lawrencium ($Z = 103$) are also added to same place and called them *actinides*.
8. Every period starts from a member of alkali group and ends with a member of zero group. The first period however starts with hydrogen.
9. There is a gradual change in properties seen from one end to the other.

8.2 Long Form of Periodic Table

The Modern Periodic Table was further modified to *extended form* or *long form of Periodic Table*. This modification was not done by a single person, but it incorporates the modifications by many scientists especially *Rang, Werner, Bohr, Bury* etc.

This table is just graphical representation of *Aufbau principle*. The electronic configuration based classification of elements was given by Bohr that's why the table is also called **Bohr's Periodic Table.**

In this table, elements are arranged in increasing order of atomic number (Z) (same as that seen in modern Periodic Table). The isotopes are all grouped together as they have the same atomic number.

The table contains 7 periods (representing 7 orbits) and 18 groups (1–18). The concept of subgroup A and B is removed and groups are given no. 1 to 18. The transitional triad elements of modern Periodic Table (group 8) are included in group 8, 9 and 10. The name of zero group is changed to group 18.

A new period begins with the occupancy of new energy shell (principal quantum number) by the first electron. Thus, a period begins with the element having ns^1configuration ($n = 1, 2, 3, \ldots$ for 1st, 2nd and 3rd period respectively).

A period usually terminates at electronic configuration $ns^2\, np^6$ except 1st period which terminates on $1s^2$ as K orbit lacks p -orbital.

The 3rd group is the largest group of Periodic Table containing 32 elements.

On the basis of electronic configuration, elements are classified into following **four groups**

1. Inert gases
2. Representative elements
3. Transitional elements
4. Inner-transitional elements

(Although such a classification is convenient for the understanding of chemical properties, it overlooks the specific characteristics of individual atoms.)

Representative elements (*s*-block elements)

Transition elements (*d*-block elements)

Representative elements (*p*-block elements)

Noble gases

1 H $1s^1$

Period Number	GROUP NUMBER 1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 ←	9 VIII	10 →	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 0
1																		2 He $1s^2$
2	3 Li $2s^1$	4 Be $2s^2$											5 B $2s^22p^1$	6 C $2s^22p^2$	7 N $2s^22p^3$	8 O $2s^22p^4$	9 F $2s^22p^5$	10 Ne $2s^22p^6$
3	11 Na $3s^1$	12 Mg $3s^2$											13 Al $3s^23p^1$	14 Si $3s^23p^2$	15 P $3s^23p^3$	16 S $3s^23p^4$	17 Cl $3s^23p^5$	18 Ar $3s^23p^6$
4	19 K $4s^1$	20 Ca $4s^2$	21 Sc $3d^14s^2$	22 Ti $3d^24s^2$	23 V $3d^34s^2$	24 Cr $3d^54s^1$	25 Mn $3d^54s^2$	26 Fe $3d^64s^2$	27 Co $3d^74s^2$	28 Ni $3d^84s^2$	29 Cu $3d^{10}4s^1$	30 Zn $3d^{10}4s^2$	31 Ga $4s^24p^1$	32 Ge $4s^24p^2$	33 As $4s^24p^3$	34 Se $4s^24p^4$	35 Br $4s^24p^5$	36 Kr $4s^24p^6$
5	37 Rb $5s^1$	38 Sr $5s^2$	39 Y $4d^15s^2$	40 Zr $4d^25s^2$	41 Nb $4d^45s^1$	42 Mo $4d^55s^1$	43 Tc $4d^55s^2$	44 Ru $4d^75s^1$	45 Rh $4d^85s^1$	46 Pd $4d^{10}$	47 Ag $4d^{10}5s^1$	48 Cd $4d^{10}5s^2$	49 In $5s^25p^1$	50 Sn $5s^25p^2$	51 Sb $5s^25p^3$	52 Te $5s^25p^4$	53 I $5s^25p^5$	54 Xe $5s^25p^6$
6	55 Cs $6s^1$	56 Ba $6s^2$	57 La* $5d^16s^2$	72 Hf $4f^{14}5d^26s^2$	73 Ta $5d^36s^2$	74 W $5d^46s^2$	75 Re $5d^56s^2$	76 Os $5d^66s^2$	77 Ir $5d^76s^2$	78 Pt $5d^96s^1$	79 Au $5d^{10}6s^1$	80 Hg $5d^{10}6s^2$	81 Tl $6s^26p^1$	82 Pb $6s^26p^2$	83 Bi $6s^26p^3$	84 Po $6s^26p^4$	85 At $6s^26p^5$	86 Rn $6s^26p^6$
7	87 Fr $7s^1$	88 Ra $7s^2$	89 Ac** $6d^17s^2$	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cp	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
	Alkali metals	Alkaline earth metals									Coinage metals					Chalcogen	Halogen	

Inner-transition elements (*f*-block elements)

*Lanthanides $4f^n5d^{0-1}6s^2$	58 Ce $4f^25d^06s^2$	59 Pr $4f^35d^06s^2$	60 Nd $4f^45d^06s^2$	61 Pm $4f^55d^06s^2$	62 Sm $4f^65d^06s^2$	63 Eu $4f^75d^06s^2$	64 Gd $4f^75d^16s^2$	65 Tb $4f^95d^06s^2$	66 Dy $4f^{10}5d^06s^2$	67 Ho $4f^{11}5d^06s^2$	68 Er $4f^{12}5d^06s^2$	69 Tm $4f^{13}5d^06s^2$	70 Yb $4f^{14}5d^06s^2$	71 Lu $4f^{14}5d^16s^2$
**Actinides $5f^n6d^{0-2}7s^2$	90 Th $5f^16d^17s^2$	91 Pa $5f^26d^17s^2$	92 U $5f^36d^17s^2$	93 Np $5f^46d^17s^2$	94 Pu $5f^66d^07s^2$	95 Am $5f^76d^07s^2$	96 Cm $5f^76d^17s^2$	97 Bk $5f^96d^07s^2$	98 Cf $5f^{10}6d^07s^2$	99 Es $5f^{11}6d^07s^2$	100 Fm $5f^{12}6d^07s^2$	101 Md $5f^{13}6d^07s^2$	102 No $5f^{14}6d^07s^2$	103 Lr $5f^{14}6d^17s^2$

Two super heavy elements, element 113 and element 115 have been discovered by scientist. Element 113 is produced *via* the alpha decay of element 115. Experiment of this discovery was made between July 14 and August 10, 2003. The results have been published in Physical Review C.

8.3 Classification of Elements

Depending upon the orbital in which last electron enters, the elements are classified as

s-Block Elements

The ***s*-block** elements are present on the extreme left in the Periodic Table. All of these are highly reactive metals except hydrogen.

Their general electronic configuration is:

$$[\text{inert gas}]\ ns^x\ \ (x = 1, 2)$$

If $x = 1$, elements constitute a group of *alkali metals* placed in group 1 (IA) and if $x = 2$, elements constitute a group of *alkaline earth metals* placed in group 2 (IIA).

Alkali metals form monovalent cations while alkaline earth metals form divalent cations.

The important characteristics of elements of this block are

1. They are soft metals with low melting and boiling points.
2. They posses metallic character and reactivity of metal increases down the group .
3. They are highly electropositive and having low ionisation enthalpies.
4. Most of the metals of this block impart characteristic colour to the flame.
5. They are strong reducing agents and good conductor of heat and electricity.
6. Na, Mg and Al all have extensive three-dimensional atomic networks, which are held together by forces characteristic of the metallic state.

p-Block Elements

These elements are present in the right portion of Periodic Table. A clear demarcation line separates the metals and non-metals here. Semi-metals are present along the sides of line. This line begins from B, runs in a *zig-zag* manner and terminates at Po. *Thus, this is the only block that contains metals, semi-metals and non-metals.*

General electronic configuration of *p*-block elements is $\boldsymbol{ns^2np^x}$ (where, $x = 1$ to 6). Group number of an element of this block is $(2 + x)$ A based on old system like IIIA, IVA, ... etc., and $(12 + x)$ based on new IUPAC system like, 13, 14, 15, ..., etc.

Metals are solids generally but Hg is liquid at room temperature. Non-metals may be solid, liquid or gas.

Si is a metalloid; it has a giant three-dimensional structure in which the Si atoms are held together very strongly. Starting with phosphorus, the elements exist in simple, discrete molecular units (P_4, S_8, Cl_2 and Ar) which have low melting points and boiling points.

These elements mostly form covalent compounds.

d-Block Elements

The elements having incompletely filled *d*- orbitals in the ground state or in excited or chemically combined state are called *transitional elements* (*d*-families) or *d-block elements*. All the elements of *d-block* are present in the middle portion of Periodic Table, in between the *s* and *p*-block elements and are all metals.

By the strict definition, *lutetium* (Z=71) and *lawrencium* (Z=103) should be included in the *d*-families, but their properties justifies their inclusion in the inner-transitional elements. Further, as in these elements $4f$ and $5f$ levels are just filled up, these can be termed as the *bridging elements* between transition (*d*-block) and inner-transition (*f*-block) elements.

There are three complete series of 10 transition elements, called $3d$($_{21}$Sc to $_{30}$Zn), $4d$($_{39}$Y to $_{48}$Cd) and $5d$($_{57}$La; $_{72}$Hf to $_{80}$Hg) whereas, $6d$ series is incomplete. $_{21}$Sc is the lightest transition metal.

Although by definition zinc (group 12) does not belong to the *d*-family but for chemical reasons it is classified as *d*-block elements with d^{10} configuration.

The transitional elements show striking resemblances to one another in their characteristics such as melting and boiling points, metallic nature, etc., as they have almost same outermost shell configuration.

The general electronic configuration of the shells of transitional elements is therefore

$$(n-1)\,s^2p^6d^xns^{1\text{ or }2}$$

here, $x = 1$ to 10 for d-1 to d-10 families.

or $\quad (n-1)d^xns^y$

where, x = number of electrons in $(n-1)d$-orbital

= 1 to 10 (except 4 and 9)

y = number of electrons in ns-orbital.

= 2 in all cases [except in group 6(VIB) and 2(IB), $y = 1$]

According to IUPAC (new pattern) group = $(x + y)$, but old group number is decided by

1. group number is [$(x + y)$B], if $x < 6$
2. group number is [VIII], if $x = 6, 7, 8$
3. group number is [yB], if $x = 10$

Important characteristics of elements of this block are

1. These are hard, ductile and malleable metals with high melting and boiling points.
2. Ionisation energy is between s and *p*- block elements.
3. They show variable oxidation states and are good conductors of heat and electricity.
4. They form both ionic and covalent compounds. These compounds are generally coloured and paramagnetic in nature. Most of the transition metals form alloys.

f-Block Elements

The *inner-transition* elements or *f*-block elements have their $(n-2)f$ orbitals incompletely filled. There are 2 series of inner-transition elements, namely, $4f$ and $5f$ series. The $4f$ series begins with *cerium* ($Z = 58$) and ends on *lutetium* (Z=71) and the $5f$ series contains elements from *thorium* (Z=90) to *lawrencium* (Z=103).

The members of $4f$ series are called *lanthanons* or *rare earth* or *lanthanides* as these follow *lanthanum* ($Z = 57$) in their properties.

The member of $5f$ series are called *actinons* or *actinides* as these follow *actinium* (Z=89) in their properties.

The generalised electronic configuration of $4f$ and $5f$ series is

$$(n-2)f^{1-14}\,(n-1)s^2p^6d^{0-1}ns^2 \text{ i.e.,}$$

for $4f$ series, $4f^{1-14}, 5s^2p^6d^{0-1}, 6s^2$

for $5f$ series, $5f^{1-14}, 6s^2p^6d^{0-1}, 7s^2$

The elements of both the series show striking resemblance in their properties due to almost similar configurations of their outer two shells and same size.

The *f*-**block** elements are positioned in the bottom portion of Periodic Table and are included in the 3rd group (III B of modern Periodic Table). This group is considered as the largest group of Periodic Table. Elements with atomic number greater than 92 (U_{92}) are called the *transuranium elements*. All these elements are man-made through artificial nuclear reactions. At present, transuranium elements with atomic numbers up to 118 have been reported.

The tendency to lose f-electrons is more seen in the case of actinons as their electrons are less firmly held by the nuclear charge in comparison with those of $4f$ family.

Lanthanides show reduction in their sizes from left to right, called the *Lanthanide contraction***.** This can be explained on the basis of constant *poor screening* or *shielding effect* of *f*- electrons by other *f*-electrons.

Important characteristics of elements of this block are

1. They are heavy metals with high melting and boiling points.
2. They show variable oxidation states and compounds are generally coloured.
3. Most of the elements of the actinide series are radioactive.

Sample **Problem 1** *An element belongs to 3rd period and group-13 of the Periodic Table. Which of the following properties will be shown by the element?* **[NCERT Exemplar]**

(a) *Good conductor of electricity*

(b) *Liquid, metallic*

(c) *Solid, metallic*

(d) *Solid, non-metallic*

Interpret (*a, c*) Except B, all elements of group 13 are metallic. These exists as solid. Being metallic in nature, it (Al) is good conductor of electricity.

8.4 Prediction of Group, Period and Block of an Element

We can easily predict the group, period and block of an element from its electronic configuration by the following ways

1. Principal quantum number of the valence shell corresponds to the period of an element.
2. The orbital containing the last electron indicates the block of an element.
3. The group of an element is predicted from the number of electrons in the valence shell or a penultimate shell ($n-1$) as follows
   - (i) **For *s*-block elements**, group number is equal to the number of valence electrons.
   - (ii) **For *p*-block elements** group number is equal to 10 + number of electrons in the valence shell.
   - (iii) **For *d*-block elements,** group number is equal to the number of electrons in $(n-1)$ *d*-subshell + number of electrons in valence shell (n^{th} shell).

     Alternately you can calculate group number = Number of electrons in (penultimate shell + valence shell) −8.
   - (iv) **For *f*-block elements,** group number is always $III^{rd}/3B$.

Sample **Problem 2** *In terms of period and group where would you locate the element with $Z = 114$?* [**NCERT**]

(a) *7 period 14 group* (b) *6 period 14 group*
(c) *6 period 4 group* (d) *7 period 4 group*

Interpret (*a*) In order to solve out such problems, first write electronic configuration of the given element. Highest value of *n* shows the period of element and group number = 10 + number of electrons in *ns* and *np* shells.

$$_{114}Z = {}_{86}[\text{Rn}]\, 7s^2, 5f^{14}, 6d^{10}, 7p^2$$

In the Periodic Table, the element with $Z = 114$ is located in Block – *p*-block (as last electron enters in *p*-subshell).

Period – 7th (as $n = 7$ for valence shell)

Group – 14th (for *p*-block elements, group number = 10 + number of electrons in the valence shell which is 7th here).

Sample **Problem 3** *Which of the following is not an actinoid?* [**NCERT** Exemplar]

(a) *Curium* ($Z = 96$)
(b) *Californium* ($Z = 98$)
(c) *Uranium* ($Z = 92$)
(d) *Terbium* ($Z = 65$)

Interpret (*d*) Element from atomic number 89 to 103 are called actinides. Thus, terbium ($Z = 65$) is not an actinoid.

8.5 Nomenclature of the Elements having Atomic Number >100

CNIC (Commission on Nomenclature of Inorganic Chemistry) appointed by IUPAC in 1994, approved official names for elements with atomic number 104 to 109. For the elements having $Z > 109$, IUPAC recommended a nomenclature to be followed for naming these elements until their names are officially recognised. This nomenclature is based on the Latin words for the atomic numbers of the elements.

The names are derived by using roots for the three digits in the atomic number of the elements and adding the ending -ium. The roots for the numbers are as

Digit	0	1	2	3	4	5	6	7	8	9
Name	nil	un	bi	tri	quad	pent	hex	sept	oct	enn
Abbreviation	n	u	b	t	q	p	h	s	o	e

e.g., the element with atomic number 109 will be named as *un-nil-ennium* and symbolised as *une* (u for 1, *n* for 0 and e for 9).

Table 8.1 **IUPAC Nomenclature of Elements with Atomic Number Above 100**

Atomic number	Name	Symbol	IUPAC official name	IUPAC Symbol
101	Un-nil-unnium	Unn	Mendelevium	Md
102	Un-nil-bium	Unb	Nobelium	No
103	Un-nil-trium	Unt	Lawrencium	Lr
104	Un-nil-quadium	Unq	Rutherfordium	Rf
105	Un-nil-pentium	Unp	Dubnium	Db
106	Un-nil-hexium	Unh	Seaborgium	Sg
107	Un-nil-septium	Uns	Bohrium	Bh
108	Un-nil-octium	Uno	Hassnium	Hs
109	Un-nil-ennium	Une	Meitnerium	Mt
110	Un-un-nillium	Uun	Darmstadtium*	Ds
111	Un-un unnium	Uuu	Roentgenium*	Rg
112	Un-un-bium	Uub	**	
113	Un-un-trium	Uut	**	
114	Un-un-quadium	Uuq	**	
115	Un-un-pentium	Uup	**	
116	Un-un-hexium	Unh	**	
117	Un-un-septium	Uus	***	
118	Un-un-octium	Uno	***	

*IUPAC approved the name on August 16, 2003.

• IUPAC name announced on 1 Nov, 2004.

**Reported but not fully authenticated.

***Elements yet to be reported.8.7 Periodic Properties

Check Point 1

1. Why do elements in the same group have similar physical and chemical properties?
2. Predict the position of the element in the Periodic Table satisfying the electronic configuration $(n-1)\,d^3\,ns^2$ for $n = 4$.
3. The elements having atomic number 118 and 120 are yet to be discovered. In which family/group would you place them when discovered? Also give the IUPAC names of these elements.

8.6 Periodic Properties

In a period and as well as in a group there is a regular gradation (gradual increase or decrease in a particular property) in physical and chemical properties of elements with the change in atomic number. *This regular gradation in properties is called periodicity*. The main cause of periodicity in properties is the repetition of similar electronic configuration at regular intervals.

Before discussing the periodic properties, it is essential to know screening or shielding effect, as it greatly affects the periodic properties.

Screening or Shielding Effect

Electrons present in the inner orbits of an atom are themselves attracted more towards the nucleus and decreases the nuclear attractive forces on the electrons of outermost orbit. This is due to the reason, that the actual force of attraction on these valence electrons is decreased by the repulsive forces between electrons acting in opposite direction. Such an effect *in which the electrons of inner orbits work as a curtain between the nucleus and the electrons of outermost orbit is called screening or shielding effect.*

The magnitude of screening effect depends upon the number of inner electrons *i.e.,* higher the number of inner electrons, greater shall be the value of screening effect.

The screening effect and effective nuclear charge (the charge felt by the electrons of a particular orbit) are very closely related. *Slater* gave the relation between them which is written as :

$$Z' = Z - \sigma$$

where, Z' = effective nuclear charge

Z = atomic number

σ = screening constant or *Slater's constant*

There are some simple rules for estimating the degree to which electrons in the various types of orbitals shield other electrons from the nucleus and hence, for estimating the Z_{eff} experienced by other electrons.

1. For finding σ, write the full electronic configuration, rearrange it in the following groupings. Group *ns* and *np* orbitals together while all other types of orbitals are grouped separately, *e.g.*,

   $(1s)\,(2s, 2p)\,(3s, 3p)\,(3d)\,(4s, 4p)\,(4d)\,(4f)\,(5s, 5p)\ldots$
2. Electrons to the right of the group of electrons in question, contribute nothing to the shielding of that group of electrons.
3. All other electrons in the same group as the electron in question, shield that electron to an extent of 0.35 unit of nuclear charge each.
4. If the electron in question is a *s* or *p*-electron.
   - (i) All electrons with principal quantum number one less than the electron in question, shield it to an extent of 0.85 unit of nuclear charge each.
   - (ii) All electrons with principal quantum number two or more less than the electron in question, shield it completely *i.e.,* to an extent of 1 unit.
5. If the electron in question is a *d* or *f* electron.

   All electrons to the left of the group of the electron in question, shield the *d* or *f* electron completely (to an extent of 1 unit). This is due to poor penetration effect of *d* or *f* electron.
6. Sum the shielding constants from steps 2-5 and subtract them from the actual nuclear charge (Z) of the atom in question to obtain the Z_{eff} felt by the electron in question.

Thus, in short the value of Slater's constant can be given as

$$\sigma = (0.35 \times \text{no. of } e^- \text{ in } n\text{th orbit} + 0.85 \times \text{no. of } e^- \text{ in } (n-1)\text{th orbit} + 1 \times \text{rest of the } e^-)$$

[Take 0.30 instead of 0.35 for 1st orbit *i.e.,* ($n = 1$)]

Trends of Screening Constant and Z_{eff}

The magnitude of σ increases across a period or down the group for the elements of groups 1, 2, 13, 14, 15, 16, 17.

The magnitude of effective nuclear charge, Z' increases in a period but it remains almost same in the case of elements of groups 1, 2, 13, 14, 15, 16, 17.

Screening effect of all the inner electrons is not equal. It also depends upon the subshell in which electrons are present. For a given orbit, the screening effect of electron belonging to different subshells decreases in the order

$$s > p > d > f$$

The screening effect of *d* and *f*-orbitals is taken as almost constant.

Caution Points

(*i*) *For second period with n valence electrons,*

$$Z' = 0.65\,(1 + n)$$

(*ii*) *For third period with n valence electrons*

$$Z' = 1.55 + 0.65\,n$$

(*iii*) *For higher periods with d and f-orbitals variation may differ.*

Factors Affecting Atomic Radius

Atomic radius is affected by serval factors which are as follows

1. As the number of shells in an atom increases, atomic radii increases.
2. Atomic radii varies inversely with nuclear charge, *i.e.,*

   $$\text{Atomic radii} \propto \frac{1}{\text{nuclear charge}}$$
3. Atomic radii varies directly with shielding effect, *i.e.,* greater the shielding effect, larger will be the atomic radii.
4. Atomic radii is shorter in case of electrovalent compounds.
5. As the bond order increases, atomic radii decreases.

Hot Spot 1

Trends in Atomic Radii

Variation of atomic and ionic radii of different elements along a period and a group is the very important topic for JEE Main and AIEEE examination. The questions are generally based on order of radii and easy in nature.

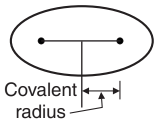
Atomic and Ionic Radius

It is defined as the distance from the centre of the nucleus to the outermost shell of electrons. The definition is imaginary because according to quantum mechanics there is no certainty about the exact position of an electron in an atom. Thus, for practical purposes, atomic radius can be defined in four ways

(a) Covalent Radius

It is defined as **the half of the internuclear distance between two identical or almost identical atoms bonded by a single covalent bond.**

For a diatomic molecule,



Distance $(A - A)$ = radius of A + radius of A

or $d = 2r_A$ or $r_A = \dfrac{d}{2}$

Similarly, for a heteronuclear diatomic molecule,

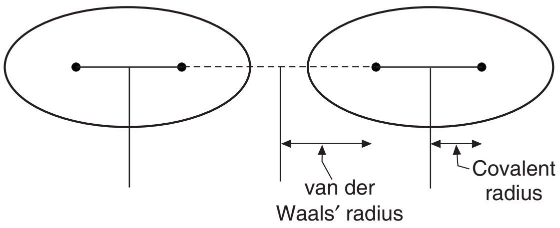
Distance $(A - B)$ = radius of A + radius of B

The above relations hold good only when the bond is purely covalent.

(b) van der Waals' Radius

It is defined as **half of the internuclear distance between the nuclei of two non-bonded adjacent atoms belonging to different molecules having identical atoms in solid state.** This radius is taken into consideration for those cases where intermolecular attractive forces are less strong, *e.g.,* weak dispersion forces. The examples of such molecules are molecules of noble gases, saturated molecules etc.

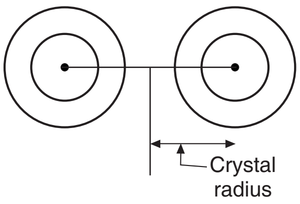
The covalent radius is always smaller than van der Waals' radius for a given element.



Representation of different radii

(c) Crystal Radius

The atomic radius of metals and inert gases in solid state is called their **crystal radius** and is defined as **half of the inter-nuclear distance between two non-bonded adjacent atoms in closed packed crystal lattice.**



Representation of crystal radius

A crystal radius is 10-15% greater than the covalent radius of a particular atom but is smaller than its van der Waals' radius.

The variations in atomic radii of various elements show the following trend

1. Atomic radii of elements increases on moving down the group due to increase in the number of shells by a factor of 1 and increase in screening effect, which reduces effective nuclear charge.
2. Atomic radius of elements decreases while moving from left to right in a period. This is due to the fact that effective nuclear charge increases as number of inner electrons remain the same throughout the period and the change occur only in the number of valence electrons.

However, in case of transition elements, atomic radii remains almost same because the electrons add to penultimate, *i.e.,* $(n-1)\,d$ subshell. Consequently, the increased nuclear charge is almost compensated by the screening effect.

Sample **Problem 4** *Choose the correct order of atomic radii of fluorine and neon (in pm) out of the options given below.*

[NCERT Exemplar]

(*a*) 72, 160 (*b*) 160, 160 (*c*) 72, 72 (*d*) 160, 72

Interpret (*a*) Atomic radius of F is expressed in terms of covalent radius while atomic radius of neon is usually expressed in terms of van der Waals' radius. van der Waals' radius of an element is always larger than its covalent radius. Therefore, atomic radius of F is smaller than atomic radius of Ne (F = 72 pm, Ne = 160 pm).

(d) Ionic Radius

For ions, it is difficult to consider all the above written radii as cations and anions have differences in their sizes. The above written methods are used for identical or almost identical atoms. For ions, thus we have to consider the imaginary definition written in the beginning *i.e.*, the distance between the centre of nucleus and its outermost shell or the distance between the nucleus and the point at which nucleus exerts its influence, in an ion **is called ionic radius.** For the determination of cationic and anionic radii, X-ray diffraction techniques are used.

Radii of Cation

The radius of cation is always smaller than its neutral atom, because of increase in the effective nuclear charge on electrons left and decrease in the number of orbits for most of the cases.

If various cations have same number of electrons (isoelectronic), the cation having greater number of proton is smallest in size.

	Na^+ >	Mg^{2+} >	Al^{3+}
Number of e^- :	10	10	10
Number of p :	11	12	13

Greater is the positive charge on the cation of a given atom, smaller is its ionic radius. *e.g.,*

$$Fe^+ > Fe^{2+} > Fe^{3+}$$

Similarly, $Sn > Sn^{2+} > Sn^{4+}$

Radius of Anion

Radius of anion is always greater than its neutral atom. It is due to decrease in effective nuclear charge.

In case of isoelectronic anions, the anion having greater number of protons is smallest in size. *e.g.,*

	N_3^- >	O^{2-} >	F^-
Number of e^-	10	10	10
Number of p	7	8	9

Greater is the negative charge on an atom, greater is its radius. *e.g.*, out of O^{2-}, O^- and O the order of size is $O^{2-} > O^- > O$.

Trend in Ionic Radius

In case of isoelectronic species, the ionic radii decreases with increase in atomic number.

In a group, the ionic radius of cation as well as anion increases on moving downwards.

The above written generalised facts for cations and anions can be evaluated with the help of formula $\frac{Z}{e} \propto \frac{1}{r}$

where, Z = atomic number of element, e = number of electrons

r = radius of ion

The formula must be used separately for cation and anions.

Sample **Problem 5** *Consider the isoelectronic species,* Na^+, Mg^{2+}, F^- *and* O^{2-}. *The correct order of increasing length of their radii is* **[NCERT Exemplar]**

(*a*) $F^- < O^{2-} < Mg^{2+} < Na^+$ (*b*) $Mg^{2+} < Na^+ < F^- < O^{2-}$

(*c*) $O^{2-} < F^- < Na^+ < Mg^{2+}$ (*d*) $O^{2-} < F^- < Mg^{2+} < Na^+$

Interpret (*b*) In case of isoelectronic species

$$\text{ionic radii} \propto \frac{1}{\text{atomic number}}$$

Ion	Mg^{2+} <	Na^+ <	F^- <	O^{2-}
Atomic number.	(12)	(11)	(9)	(8)

Thus, ionic radii have the following order

$$Mg^{2+} < Na^+ < F^- < O^{2-}$$

Ionisation Energy

The *ionisation energy* of an element is defined as *"the amount of energy required to remove an electron from the outermost orbit of an isolated gaseous atom."* (When such a definition is written in the terms of work done, *i.e.,* the amount of work done in removing an electron, the property is called *ionisation potential*)

The unit of ionisation energy is **kJ/mol** (when the property is written as ionisation potential, the units are taken as **eV/atom.**) This is denoted by word I.

An atom can have as many ionisation energies as number of electrons it has. These are denoted as I_1, I_2, I_3, … etc., for 1st electron, 2nd electron, 3rd electron and so on respectively.

The value of second ionisation energy (I_2) *is always greater than first ionisation energy* (I_1). Similarly that of I_3 is greater than I_2 and so on. The reason for such an increase is increased effective nuclear charge after removal of one electron from the neutral atom resulting in more difficulty in removing the second electron from the outermost orbit of cation formed.

Factors Affecting Ionisation Enthalpy

Important factors that affect the Ionisation Enthalpy are as follows.

1. The ionisation energy of an element depends upon its size as

   $$\text{IE} \propto \frac{1}{\text{size of atom / ion}}$$

   i.e., smaller the atom/ion, larger will be the ionisation energy.

2. Atoms and ions having inert gas configuration *i.e.,* stable (half-filled) configuration have high ionisation energy *i.e.,* it is relatively easy to remove an electron from a partially filled valence shell, where Z_{eff} is lower but it is relatively difficult to remove an electron from an atom or ion that has a filled valence shell, when Z_{eff} is higher.

3. The order of energy required to remove an electron from different subshells (if rest of the conditions are same) is

   $$s > p > d > f$$

   It is due to the closeness of above written subshells with the nucleus. Out of the four given subshells, the *s*-subshell is nearest to the nucleus while *f*-subshell is farthest from the nucleus.

Hot Spot 2

Trends in Ionisation Energy

Questions based on order of ionisation enthalpy have been seen frequently in AIEEE and JEE Main examination, which reveals the importance of the topic for this examination. The level of the question is generally easy and sometimes moderate.

In general, the first ionisation energy decreases in a regular way on descending the main groups.

On moving across a period, the atomic size decreases and nuclear charge increases and therefore the force of attraction exerted by the nucleus on the electron in outermost shell increases. Hence, (IE) increases along a period from left to right.

Exceptions of above written trend are

1. **First ionisation energy of group 2 (IIA) elements is greater than the corresponding elements of group 13(IIIA).** It is due to the presence of fully filled *s*-orbitals in case of group 2 elements (their outermost electronic configuration is ns^2). It is always difficult to pull out electron from stable configuration.
2. **First ionisation energies of group 15(VA) elements is greater than the corresponding elements of group 16(VIA).** It is due to the presence of stable half-filled electronic configuration in group 15 elements. (Their outermost electronic configuration is ns^2np^3).
3. In case of transition elements opposite trends are observed. Thus, $(\text{IE})_1$ of the corresponding elements of 3*d* and 4*d*-series are almost similar but these are smaller than the $(\text{IE})_1$ of the 5*d*-series elements. Certainly the higher values of ionisation energies of the 5*d*-transition elements are consistent with the relatively small size of the atoms.

Sample **Problem 6** *The first ionisation enthaplies of* Na, Mg, Al *and* Si *are in the order* **[NCERT Exemplar]**

(*a*) $\text{Na} < \text{Mg} > \text{Al} < \text{Si}$ (*b*) $\text{Na} > \text{Mg} > \text{Al} > \text{Si}$
(*c*) $\text{Na} < \text{Mg} < \text{Al} < \text{Si}$ (*d*) $\text{Na} > \text{Mg} > \text{Al} < \text{Si}$

Interpret (a) Follow the following steps to solve out such problems.

	Steps	Apply
Step I	Write the electronic configuration to find position in the Periodic Table.	$\text{Na}_{11} = [\text{Ne}]3s^1$, $\text{Mg}_{12} = [\text{Ne}]3s^2$, $\text{Al}_{13} = [\text{Ne}]3s^2 3p^1$, $\text{Si}_{14} = [\text{Ne}]3s^2,3p^2$
Step II	Arrange them in the order as they are in the Periodic Table.	1 2 13 14 Na Mg Al Si
Step III	Follow the general trend and also keep in mind the exception.	The IP increases along a period from left to right but IP of Mg is higher than that of Al due to completey filled 3*s* orbital in Mg.
Step IV	On the above basis find the order.	The order of IP is $\text{Na} < \text{Mg} > \text{Al} < \text{Si}$. Thus, (a) is the correct option.

Important Facts Related to Ionisation Enthalpy

1. Transition elements have almost same ionisation enthalpy. However, the first ionisation enthalpy of elements of group 12 (IIB) is higher than their immediate neighbours. This is because of the stable configuration, *i.e.*, $(n-1)\,d^{10}ns^2$ of these elements.
2. Alkali metals have the lowest and inert gases have the highest IE in a period.
3. Among all the known elements, He has the highest and Cs has the lowest ionisation energy.
4. As the ionisation energy increases, basic character of hydroxides increases. Thus, IE gives a rough idea about basic character of hydroxides.
5. The IE, of the metalloids generally fall between those of metals and non-metals. The difference in IE suggests why metals always form cations and non-metals form anions.
6. Metallic or electropositive character of elements increases as the value of ionisation potential decreases. So, in a group moving from top to bottom, metallic or electropositive character increases because IP value decreases. In a period, moving from left to right the values of IP increases so metallic or electropositive character decreases. Non-metallic character increases.
7. The relative reactivity of the metals increases with the decrease in IP values. The IP values of inert gases are

very high. So they are almost inactive. In a group moving from top to bottom the reactivity of metal atoms increases because their IP value decreases.

8. The reducing power of elements increases as the values of IP decreases because tendency to lose the electron increases. The reducing power increases on going down a group because the IP value decreases.

$$\text{Li} > \text{Cs} > \text{Rb} > \text{K} > \text{Na}$$

Electron Gain Enthalpy

The energy liberated when an extra electron is added to an isolated gaseous atom is called the *electron affinity* (A_e) of that atom while the energy change occurring during this process is called the *electron gain enthalpy* ($\Delta e_g H$). The units of electron affinity or electron gain enthalpy are eV/atom or kJ/g-atom.

Electron affinity and electron gain enthalpy have same magnitude but opposite sign. Indeed electron affinities are defined at absolute zero while electron gain enthalpy at 298 K. These two quantities at a given temperature are related as

$$\Delta e_g H = -A_e - \frac{5}{2}RT$$

For the process, $\text{Cl}(g) + e^- \longrightarrow \text{Cl}^-(g) + E_A$

Electron affinity is positive but $\Delta_{eg}H$ is negative.

Electron affinity describes the tightness with which an atom binds the extra electron added to it *i.e., greater the value of* $\boldsymbol{A_e}$ (energy liberated) *or* $\Delta e_g H$, *greater is the binding force.*

The value of $\Delta e_g H$ second onwards is always positive, *i.e.*, here for addition of electron, energy is to be absorbed from the system. *e.g.*, the electron affinity of oxygen has positive value (141kJ/mol), which means that the process

$$\text{O}(g) + e^- \longrightarrow \text{O}^-(g); \Delta H = -141\text{kJ/mol}$$

is exothermic. On the other hand, the electron affinity of the O^- ion is highly negative (−780kJ/mol), which means the process

$$\text{O}^-(g) + e^- \longrightarrow \text{O}^{2-}(g); \Delta H = 780\text{kJ/mol}$$

is endothermic even though O^{2-} ion has a stable noble gas configuration. This process is unfavourable in the gas phase because the resulting increase in electron-electron repulsion outweighs the stability gained by achieving a noble gas configuration. In solid phase, the process becomes favoured because O^{2-} ions stabilized by the adjacent cations to form ionic lattice releasing lattice energy.

Factors Affecting Electron Gain Enthalpy

Various factors which affect the $\Delta e_g H$ *are*

1. Magnitude of $\Delta e_g H \propto Z_{\text{eff}}$
2. Magnitude of $\Delta e_g H \propto \dfrac{1}{\text{atomic size}}$
3. Magnitude of $\Delta e_g H \propto$ penetrating power

   Therefore, the order of $\Delta e_g H$ is $s > p > d > f$.
4. Stability of half-filled and completely filled orbitals.

Hot Spot 3

Trends in Electron Gain Enthalpy

It is again an important topic of the chapter JEE Main examination. Here generally the questions are based on exceptions and their cause, although here also their level is not typical.

In a period, the electron gain enthalpy (negative) increases on moving from left to right. Thus, the tendency to accept electrons in a period and the electron gain enthalpy values become more and more negative. **The halogens have the highest electron affinity values in a given period.**

The value of electron gain enthalpy (negative) in a group decreases. This variation is related with the size of atom and electron density in the outermost shell of the atom concerned.

There are few exceptions also to the above written trend.

1. **$\Delta e_g H$ of the elements of group 2 (IIA) and group 15 (VA) is positive.** It is due to the presence of outer fully filled *s*-orbital in 2 group and half-filled *p*-orbital in 15 group because of which these atoms do not have the tendency to accept electron.
2. The noble gases have no or very little tendency to accept electrons, thus all the noble gases have electron gain enthalpy more than zero. This means that the anions of noble gases (if formed) would be inherently unstable.
3. In general, the $\Delta e_g H$ values (negative) of the elements of third **period are higher than the $\Delta e_g H$ values of the elements of second period.** It is due to small radius and high electron density in the outermost orbit of second period elements. The small size signifies limited capacity to release energy, while high electron density signifies greater repulsive forces which extra electron experiences while it is to be added *e.g.*, the $\Delta e_g H$ value of Cl is higher than that of F as Cl belongs to 3rd period while F belongs to 2nd period.
4. The electron gain enthalpy of metals are generally lower (less negative) than those of non-metals.
5. It has been found that elements having higher negative values of $\Delta e_g H$ *e.g.*, F_2, Cl_2, O_2, Br_2 etc., are good oxidants.

***Sample* Problem 7** *Among halogens, the correct order of amount of energy released in electron gain (electron gain enthalpy) is* **[NCERT Exemplar]**

(*a*) $F > Cl > Br > I$
(*b*) $F < Cl < Br < I$
(*c*) $F < Cl > Br > I$
(*d*) $F > Cl < Br < I$

Interpret (*c*) To solve out such problem, follow the same steps as shown in sample problem 6.
From this you get the order $F < Cl > Br > I$

***Sample* Problem 8** *Electronic configuration of some elements is given in column I and their electron gain enthalpies are given in column II. Match the electronic configuration with electron gain enthalpy and select the correct option.*

	Column I (Electronic configuration)		Column II (Electron gain enthalpy /kJ mol^{-1})
A.	$1s^2, 2s^2, 2p^6$	(i)	-53
B.	$1s^2, 2s^2, 2p^6, 3s^1$	(ii)	-328
C.	$1s^2, 2s^2, 2p^5$	(iii)	-141
D.	$1s^2, 2s^2, 2p^4$	(iv)	$+48$

[NCERT Exemplar]

Codes

	A	B	C	D		A	B	C	D
(*a*)	(i)	(ii)	(iii)	(iv)	(*b*)	(iv)	(iii)	(ii)	(i)
(*c*)	(iv)	(i)	(ii)	(iii)	(*d*)	(i)	(iv)	(iii)	(ii)

Interpret (*c*) Except (B), all configurations of elements belong to the second period and along a period as the number of electrons increases, $\Delta e_g H$ increases except in case of half or completely filled orbitals where $\Delta e_g H$ is positive.

For B, $\Delta e_g H$ is very less as it is an alkali metal but negative. Thus, the correct match is

A–(iv); B–(i); C–(ii); D–(iii)

Electronegativity and Electronegative Character

The tendency of an atom to attract the shared pair of electrons towards itself in a covalent bond is called *electronegativity* of that atom. Remember it is different from *electronegative character of an atom* which is infact the tendency of an element to form the anion by gaining the electron. *The first term is comparative while the second term is used for a single atom.*

Factors Affecting the Magnitude of Electronegativity

Various factors affecting the magnitude of electronegativity are as follows

1. As the atomic radius of the elements increases, the electronegativity value decreases.
   $$\text{Electronegativity} \propto \frac{1}{\text{Atomic radius}}$$
2. The electronegativiy value increases as the effective nuclear charge on the atomic nucleus increases.
   $$\text{Electronegativity} \propto \text{Effective nuclear charge } (Z_{\text{eff}})$$
3. The electronegativity increases as the oxidation state (*i.e.,* the number of positive charge) of the atom increases.
4. If the *s*-character in the hybridisation state of the atom increases, electronegativity also increases because *s*-electrons are comparatively near to the nucleus *e.g.,* the electronegativity values of C-atom in various hybridisation states are as under

Hybridisation states	sp^3	sp^2	sp
s-character	25%	33.33%	50%
Electronegativity	2.48	2.75	3.25

$$\longrightarrow$$

s-character is increasing,

So, the electronegativity value is increasing.

Trends in Electronegativity

Different tends shown by electronegativity along periods and groups are given below

1. In a period, on moving from left to right, the electronegativity increases due to the increase in effective nuclear charge/increase in ionisation energy.
2. In a period the electronegativity value of IA group elements (alkali metal) is minimum and that of VIIA (halogens) is maximum/with decrease in ionisation energy.
3. In a group on moving from top to bottom, the electronegativity decreases because atomic radius increases.
4. The electronegativity value of F is maximum and that of Cs is minimum in the Periodic Table.

Diagonal Relationship and Electronegativity

As we move from left to right across a period, the increased nuclear charge holds the electrons more tightly to the atom. On moving downwards one place in a group, the extra shell of electrons decreases the attraction of the nucleus for the outer electrons. A *diagonal* move means that these effects tend to compensate for one another.

The electronegativity increases as we go from Li to Be but it decreases as we move from Be to Mg. As we move diagonally, these two effects partly cancel each other and there is no marked change in electronegativity and thus, Li and Mg have close values of electronegativities. Because of this, Li and Mg show similarity in properties–*a diagonal relationship* (between elements lying diagonally in Periodic Table). *e.g.,* Li—Mg, Be—Al and B—Si

Measurement of Electronegativity

Since electronegativity is a tendency and tendencies cannot be measured accurately, electronegativity of different elements is calculated on different scales.

Some important of these scales are as

(i) **Pauling scale** at which F is the most electronegative element of the Periodic Table. The electronegativity of fluorine is arbitrarily assigned 4.0 by Pauling. The electronegativity of other elements is calculated against this standard. The calculations are done with the help of bond energies used in the formula

$$X_A - X_B = 0.208\sqrt{\Delta}$$

where, $\Delta = E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}$

$X_A - X_B$ = electronegativity difference between two atoms A and B.

E_{A-B}, E_{A-A}, and E_{B-B} are the bond energies of the molecules AB, A_2 and B_2 respectively.

Some other elements have following values of electronegativity based on Pauling's scale.

						H
						2.1
Li	Be	B	C	N	O	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na	Mg	Al	Si	P	S	Cl
0.9	1.2	1.5	2.8	2.1	2.5	3.0
K	Ca	Ga	Ge	As	Se	Br
0.8	1.0	1.6	1.8	2.0	2.4	2.8
Rb						I
0.8						2.5
Cs						
0.7						

***Sample* Problem 9** *The electronegativity of carbon if* $E_{\text{H—H}} = 104.2\ kcal\ mol^{-1}$, $E_{\text{C—C}} = 83.1\,kcal\ mol^{-1}$, $E_{\text{C—H}} = 98.8\ kcal\ mol^{-1}$, $X_{\text{H}} = 2.1$, *is*

(a) 2.1 (b) 3.7 (c) 2.6 (d) 2.9

Interpret (c) We know that,

$$X_{\text{C}} - X_{\text{H}} = 0.208\sqrt{\Delta}$$
$$\Delta = E_{\text{C—H}} - \sqrt{E_{\text{C—C}} \times E_{\text{H—H}}}$$
$$= 98.8 - \sqrt{83.1 \times 104.2}$$
$$= 98.8 - 93.05 = 5.74$$

$$\therefore \quad X_C - X_H = 0.208\sqrt{5.74}$$

$$X_C - X_H = 0.498$$

$$X_C = 0.498 + X_H$$

$$= 0.498 + 2.1$$

$$= 2.59 \approx 2.6$$

(ii) **Mulliken scale** at which electronegativity is determined from the values of A_e and IE of atom. This method is not much in use. On this scale electronegativity is denoted by word chi (χ) which can be calculated as

$$\chi = \frac{\text{IE} + A_e}{2}$$

1. If IE and A_e are determined in eV then

$$\chi = (\text{IE} + A_e) / 5.6 \text{ eV}$$

2. If IE and A_e are determined in kJ/g-atom then

$$\chi = (\text{IE} + A_e) / 125 \text{ kcal/g-atom}$$

3. If IE and A_e are in kJ/mol then

$$\chi = (\text{IE} + A_e) / 544 \text{ kJ/mol}$$

***Sample* Problem 10** *The ionisation energy and electron affinity of an element are 12.0 eV and 3.8 eV respectively. Its electronegativity on the Pauling scale is*

(a) 3.0 (b) 4.0

(c) 3.5 (d) 2.7

Interpret (d) Electronegativity on the Mulliken's scale $= \frac{1}{2}(12.0 + 3.8) = 7.9$. But since Mulliken's values are nearly 2.8 times as large as Pauling values, therefore, electronegativity of the element on the more commonly used Pauling scale is $\frac{7.9}{2.8} = 2.7$.

(iii) **Allred-Rochow's scale** is considered as the real scale as it is based upon covalent radius of an atom. According to Allred-Rochow, electronegativity is a force which is exerted by the nucleus on the electrons of outermost orbit *i.e.*,

$$E_n = \frac{0.359 \times Z_{\text{eff}}}{r^2} + 0.744$$

where, r = covalent radius

$Z_{\text{effective}}$ = effective nuclear charge

Applications of Electronegativity

1. The electronegativity values are used to predict the nature of $A - B$ bond as
   (i) Greater is the difference in the electronegativity of elements A and B, greater will be the ionic character of bond between A and B or weaker will be the covalent character.
   (ii) If electronegativities of A and B are equal or difference is very small, the bond between A and B is supposed to be purely covalent.
2. The electronegativity value also gives an idea about the bond lengths. As the electronegativity difference increases, bond length decreases.
3. If the electronegativity difference of covalently bonded atoms (Δx) increases, the bond energy of the covalent bond also increases *e.g.,* the order of the H—X bond strength is H — F > H — Cl > H — Br > H — I.

   As the bond strength is decreasing, the acid strength is increasing. So order of increasing acid strength is HF < HCl < HBr < HI. The acidic nature of the oxides of normal elements increase as we move from left to right in a period.
4. In a period from left to right the electronegativity of the elements increases.

   The order of acidic or basic nature of the oxides of third period elements may be given under

$$\underrightarrow{\text{Na}_2\text{O} \quad \text{MgO} \quad \text{SiO}_2 \quad \text{P}_2\text{O}_5 \quad \text{SO}_3 \quad \text{Cl}_2\text{O}_7}$$

   Basic nature is decreasing or acidic nature is increasing.
5. The metallic character decreases as the electronegativity of the elements increases. On moving from left to right in a period, the electronegativity of the elements increases. So the metallic character decreases. On moving down a group, the electronegativity of the elements decreases. So the metallic character increases.

Electropositive or Metallic Character

The tendency of an element to form the cation by the loss of electron is called its *electropositive character* or *metallic character*. Thus, metals are the elements which have the tendency to lose electrons.

Trend in Periodic Table The variation of electropositive or metallic character in the Periodic Table will be seen as

→Decrease (across the period)
↓ Electropositive or metallic character
Increase (down the group)

This tendency varies inversely with ionisation energy of an element.

Check Point 2

1. Why does the van der Waals' radius of an element is always larger than the covalent radius?
2. Explain, why cations are smaller and anions are larger than their parent atoms?
3. The first IP of Na is lower as compared to Mg but reverse is true for second IP. Explain, why?
4. The formation of F^- from F is exothermic whereas that of O^{2-} from O is endothermic. Explain.

Periodic Trends in Chemical Properties

(a) Valency

It is the combining capacity of an element and can never be equal to zero. It is only a number and is not assigned as positive or negative. *e.g.,* the valency of C in CH_4, CCl_4, CH_2Br_2 all is 4.

Along a period from left to right it increases from 1 to 7 with respect to hydrogen and from 1 to 4 and then decreases to 1 with respect to oxygen.

For the elements of a group it remains the same because the number of valence electrons (electrons of valence or outer shells) remains the same.

(b) Oxidation States

It is the residual charge left on an atom of a molecule when other atoms of the molecule are removed as ions. Its value can be zero, positive, negative or fractional. An element can have different oxidation states in different compounds *e.g.,* oxidation state of N in NO_2, NO, N_2O_3 and N_2O_5 are + 4, + 2, + 3 and + 5 respectively.

In case of alkali and alkaline earth metals it is fixed *i.e.,* + 1 and + 2 respectively.

It is generally variable for other elements. Higher *p*-block elements exhibit more stability for lower oxidation state due to inert pair effect. *e.g.,* Pb^{4+} is less stable than Pb^{2+}.

In case of *d*-block elements,

max. oxidation state = $(n-1)\, d\, e^-$ (unpaired) + $ns\, e^-$.

In general, the stability of the higher oxidation states is in the order

$$3d << 4d < 5d$$

(c) Chemical Reactivity

It is highest at the two extremes of a period and is lowest at the centre. This is because the elements present at left extreme of a period have the lowest ionisation enthalpy and that present at the right extreme have the highest electron affinity.

Highly reactive elements are always found in combined state.

In the groups, the reactivity of former elements (that present at left extreme) increases while that of latter decreases.

***Sample* Problem 11** *Which element among strontium, magnesium, potassium and lithium is most reactive?*

(a) *Magnesium* (b) *Potassium*
(c) *Lithium* (d) *Strontium*

Interpret (*b*) Potassium is the most reactive among the given metals as reactivity of metals decreases along a period and increases on moving down the group.

(d) Reducing and Oxidising Properties

Reducing agents provide electrons, thus metals act as good reducing agents. The *reducing power* of elements in the Periodic Table shows the following trend

→ Decrease (across the period)
↓ Reducing power of elements
Increase (down the group)

Oxidising agents accept electrons, thus non-metals are good oxidising agents. The *oxidising power* of elements shows following trend in the Periodic Table :

→ Increase (across the period)
↓ Oxidising power of elements
Decrease (down the group)

Thus, alkali metals are powerful reducing agents while halogens are powerful oxidising agents in the Periodic Table.

(e) Nature of Oxides

Metal oxides are basic *i.e,* form alkaline solutions when dissolved in water. Similarly, non-metal oxides are acidic while semi-metal oxides are amphoteric in nature. Thus, the basic character of oxides shows following trend in the Periodic Table.

→ Decreases (across the period)
↓ Basic nature of oxide
Increases (down the group)

Similarly, acidic nature of oxides shows the following trend

→ Increases (across the period)
↓ Acidic nature of oxides
Decreases (down the group)

The oxides CO, N_2O, NO and H_2O are neutral in nature. The oxides of Al, Zn, Sn, As and Sb along with metalloids are amphoteric in nature.

The acidic character of the oxides of a non-metal increases with increase in oxygen content in it, *e.g.,* $N_2O_3 < N_2O_5$; $SO_2 < SO_3$; $Cl_2O < Cl_2O_3 < Cl_2O_7$.

Non-metal oxides when dissolved in water form oxy-acids, thus, they are called *anhydrides* of the acid formed.

Sample Problem 12 *Which one of the following is the most acidic?*

(a) *Aluminium oxide*
(b) *Sodium oxide*
(c) *Magnesium oxide*
(d) *Calcium oxide*

Interpret (a) On moving from left to right in a period, acidic character of oxides increases. Thus, Al_2O_3 is the most acidic oxide among the given.

Table 8.2 **Summary of Variation of Periodic Properties**

S.No.	Periodic property	Variation	
		Along a period	Along a group
1.	Atomic radius	Decreases	Increases
2.	Ionic radius	Decreases	Increases
3.	Metallic nature	Decreases	Increases
4.	Reducing power	Decreases	Increases
5.	Basic nature of oxides	Decreases	Increases
6.	Electron gain enthalpy	Increases	Decreases
7.	Ionisation energy	Increases	Decreases
8.	Electronegativity	Increases	Decreases
9.	Acidic nature of oxide	Increases	Decreases

Some Other Properties of Elements

(a) Density

There is no regular trend in the variation of density in a group or period. *Density of osmium* (Os) *is the highest* (**d = 22.6** g/cc) *among all the known elements.* Lightest metal is lithium (d = 0.54 g/cc). *Density of* H_2 *is lowest among all the known elements.*

(b) Melting and Boiling Points

There is no regular trend in the variation of melting point and boiling point in a group or period. *Tungsten* (W) *has the highest melting poing among all the metals. Mercury has the lowest melting poing* (−38°C) *among all the metals.* Carbon in the form of diamond has highest melting point (3277°C) among all the known elements. Helium has lowest melting point (−270°C) among all the elements. In a period, inert gases have lowest melting point and boiling point

In a group, the melting and boiling points of metals usually decreases while that of non-metals increases.

(c) Atomic Volume

Volume occupied by one gram atom of an element in solid state is called its atomic volume.

Atomic volume = mass of one gram atom/density

Atomic volume of elements increases on moving down a group due to the presence of extra shell of electrons. On moving from left to right in a period atomic volume first decreases and becomes minimum in the middle and then again begins to increase.

On plotting a graph between atomic number of elements and their atomic volume, a curve is obtained in which alkali metals are present at peaks while elements of 'boron family' Ni, Ru and H etc., are present at troughs.

8.7 Elements Showing Highest and Lowest Properties

Many a times questions based on highest and lowest of some properites are seen in the examination. Here with we are given some elements showing highest and lowest properties.

Table 8.3 **Highest and Lowest of Some Properties**

Highest melting point	Carbon (diamond)
Highest EA	Chlorine
Highest electronegativity	F
Highest ionisation potential	He
Lowest ionisation potential	Cs
Highest density	Os
Lowest melting point	He
Lowest density	H_2
Lowest density among metals	Li
Highest melting point among metals	Tungsten
Smallest anion	H^-
Largest anion	I^-
Smallest cation	H^+
Largest cation	Cs^+

Check Point 3

1. In a group, all the elements have same valency. Is it true? Explain, why?
2. Alkali metals as well as halogens are highly reactive, however, the former occupy the left corner while the latter occupy the right corner. Explain, why?
3. The melting and boiling points of metals increase while that of non-metals decrease on moving down the group. Explain.
4. $\Delta_{eg}H$ of Cl is more negative than F why?

WORKED OUT Examples

Example 1 *An atom with atomic number 21 belongs to the category of*

(a) *d-block elements* (b) *s-block elements*
(c) *f-block elements* (d) *p-block elements*

Solution (*a*) The electronic configuration of the given element is

$$= 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^1$$

Since the last electron enters in *d*-block, its a *d*-block element.

Example 2 *The ionisation energy of* Li *is* 520 *kJ mol*$^{-1}$. *The amount of energy required to convert* 140 *mg of* Li *atoms into gaseous* Li$^+$ *ion, is*

(a) 10.4 *kJ* (b) 520 *kJ*
(c) 72.8 *kJ* (d) 3.71 *kJ*

Solution (*a*) Number of moles of $\text{Li} = \dfrac{\text{mass}}{\text{atomic mass}}$

$$= \frac{140 \times 10^{-3}}{7}$$

$$= 2 \times 10^{-2} \text{ mol}$$

$\because$ For the conversion of 1 mole atoms of Li into Li$^+$, the energy required $= 520$ kJ mol^{-1}

$\therefore$ For the conversion of 2×10^{-2} mole atoms of Li into Li$^+$ ions, the energy required will be $520 \times 2 \times 10^{-2}$

$$= 10.4 \text{ kJ}$$

Example 3 *Sodium can't exhibit* +2 *oxidation state because its second ionisation potential value is*

(a) *zero*
(b) *equal to first*
(c) *less than first*
(d) *much higher than the first*

Solution (*d*) IE$_2$ of Na is extremely high because after the removal of one electron, inert gas configuration is obtained. As a result sodium cannot show an oxidation state of +2.

Example 4 *The covalent radius of silicon is* 1.175 Å. *Calculate the electronegativity of silicon using Allred-Rochow method.*

(a) 1.73 (b) 3.80
(c) 2.94 (d) 4.28

Solution (*a*) Allred-Rochow equation is

$$x = 0.359 \times \frac{Z_{\text{eff}}}{r^2} + 0.744$$

Z_{eff} is calculated on the basis of Slater's rules taking all the electrons.

Electronic configuration of Si is $1s^2, 2s^2, 2p^6, 3s^2, 3p^2$

$$Z_{\text{eff}} = 14 - (0.35 \times 4 + 0.85 \times 8 + 2 \times 1) = 3.80$$

On putting values $x = 1.73$

Example 5 *The amount of energy when million atoms of iodine are completely converted into* I$^-$ *ions in the vapour state according to the equation*

$\text{I}(g) + e^- \longrightarrow \text{I}^-(g)$ *is* 4.9×10^{-13} J. *The electron gain enthalpy of iodine (in eV per atom) is*

(a) −295 (b) −3.06
(c) −6.45 (d) −622

Solution (*b*) Electron gain enthalpy per mol

$$= -\frac{4.9 \times 10^{-13} \times 6.023 \times 10^{23}}{10^6}$$

$$= -29.5 \times 10^4 \text{ J}$$

$$= -295 \text{ kJ}$$

$$= -\frac{295}{96.49} = -3.06$$

Example 6 *The* I^{st} *IE of* Li *is* 5.4 *eV and the electron gain enthalpy of* Cl *is* 3.6 *eV. If the following reaction,*

$$\text{Li}(g) + \text{Cl}(g) \longrightarrow \text{Li}^+ + \text{Cl}^-,$$

is carried out at such a low pressure that resulting ions do not combine with each other, the ΔH *of the reaction (in kcal mol*$^{-1}$*) is*

(a) 118.8 (b) 124.52
(c) 83.0 (d) 41.508

Solution (*d*) Given, $\text{Li}(g) \longrightarrow \text{Li}^+(g) + e^-$; $\Delta E_1 = 5.4$ eV

$$\text{Cl}(g) + e^- \longrightarrow \text{Cl}^-(g); \quad \Delta E_2 = -3.6 \text{ eV}$$

$$\Delta H = 5.4 - 3.6 = 1.8 \text{ eV}$$

$$= 1.8 \times 23.06 \text{ kcal mol}^{-1}$$

$$= 41.508 \text{ kcal mol}^{-1}$$

Example 7 *The number of chlorine atoms that can be ionised in the process* $Cl \longrightarrow Cl^{+} + e^{-}$*, by the energy liberated for the process* $Cl + e^{-} \longrightarrow Cl^{-}$ *for one Avogadro number of atoms is* [$IE = 13.0\,eV$, $\Delta e_g H = 3.60\,eV$]

(a) 2.17×10^{24} (b) 1.67×10^{23}

(c) 1.286×10^{22} (d) 6.023×10^{22}

Solution (*b*) Let *n* Cl atoms are ionised.

Thus, $6.02 \times 10^{23} \times \Delta e_g H = n \times \text{IE}$

$$n = \frac{6.02 \times 10^{23} \times 3.6}{13.0}$$

$$= 1.667 \times 10^{23}$$

Example 8 *For the following reaction,*

$$K(g) + F(g) \longrightarrow K^{+}(g) + F^{-}(g),$$

ΔH was calculated to be 19 kcal under conditions where the cations and anions were prevented by electrostatic separation from combining with each other. The IE of potassium is 4.3 *eV, the magnitude of* $\Delta e_g H$ *of* F *is*

(a) -4.3 (b) -0.82

(c) $+4.3$ (d) $+3.48$

Solution (*d*) $K(g) \longrightarrow K^{+}(g) + e^{-}$; IE = 4.3 eV

$$F(g) + e^{-} \longrightarrow F^{-}(g) \quad \Delta e_g H = -E \text{ eV}$$

$$\Delta H = \text{IE} + \Delta e_g H$$

$$\frac{19.0}{23.06}\text{ eV} = 4.3 - E$$

$$\therefore \qquad E = 4.3 - 0.82 = 3.48$$

Example 9 *The electronic configuration of four elements are*

(*i*) $[Xe]\,5s^1$ (*ii*) $[Xe]\,4f^{14}, 5d^1, 6s^2$

(*iii*) $[Ar]\,4s^2 4p^5$ (*iv*) $[Ar]\,3d^7, 4s^2$

Select the incorrect statement about these elements.

(a) (*i*) *is a strong reducing agent*

(b) (*ii*) *is a d-block element*

(c) (*iii*) *has high magnitude of* $\Delta e_g H$

(d) (*iv*) *exhibits variable oxidation states.*

Solution (*b*) (i) Since, in it the last electron enters in *s*-orbital, it is a *s*-block element and *s*-block elements are good reducing agents.

(ii) Since, the last electron enters in *f*-block, it is a *f*-block element (element of 4*f* series).

(iii) Electronic configuration reveals that it contains 7 electrons in its outer shell, so it is a halogen and halogens have high magnitude of $\Delta e_g H$.

(iv) The last electron enters in *d*-orbital, so it is a *d*-block element and variable oxidation states is an important feature of *d*-block elements.

Example 10 $\frac{N_0}{2}$ *atoms of* $X(g)$ *are converted into* $X^{+}(g)$ *by energy* ΔH_1 *and* $\frac{N_0}{2}$ *atoms of* $X(g)$ *are converted into* $X^{-}(g)$ *by energy* ΔH_2*. The* (*IE*) *and* (*EA*) *of* $X(g)$ *are respectively*

(a) $\frac{2\Delta H_1}{N_0}, \frac{2(\Delta H_2 - \Delta H_1)}{N_0}$ (b) $\frac{\Delta H_1}{N_0}, \frac{\Delta H_2}{N_0}$

(c) $\frac{2\Delta H_1}{N_0}, \frac{\Delta H_2}{N_0}$ (d) $\frac{2(\Delta H_2 - \Delta H_1)}{N_0}, \frac{\Delta H_2}{N_0}$

Solution (*a*) Let (IE) of $X(g) = I$ per atom and EA of $X(g) = -E$ per atom

(i) $X(g) \longrightarrow X^{+}(g) + e^{-}$

Energy required to ionise $\frac{N_0}{2}$ atoms of $X(g) = \frac{N_0 I}{2}$

$$\frac{N_0 I}{2} = \Delta H_1$$

$$I = \frac{2\Delta H_1}{N_0}$$

(ii) $X(g) \longrightarrow X^{+}(g) + e^{-}$ Energy $= \frac{N_0 I}{2}$ for $\frac{N_0 I}{2}$ atoms

$X(g)\ e^{-} \longrightarrow X^{-}(g)$ Energy $= -\frac{N_0 E}{2}$ of $\frac{N_0}{2}$ atoms

$$\frac{N_0 I}{2} - \frac{N_0 E}{2} = \Delta H_2$$

$$-\frac{N_0 E}{2} = \Delta H_2 - \Delta H_1$$

$$-E = \frac{2(\Delta H_2 - \Delta H_1)}{N_0}$$

Ionization energy (IE) $= \frac{2\Delta H_1}{N_0}$ atoms^{-1}

Electron affinity (EA) $= \frac{2(\Delta H_2 - \Delta H_1)}{N_0}$ atoms^{-1}

Start Practice for JEE Main

Round I (Topically Divided Problems)

Classification of Elements

1. Who developed the long form of the Periodic Table?

(a) Niels Bohr (b) Moseley

(c) Mendeleef (d) Lothar Meyer

2. The basis of keeping the elements in the groups of the Periodic Table is

(a) ionisation potential

(b) electronegativity

(c) electron affinity

(d) number of valence electrons

3. Which of the following pairs has both members of the same period of the Periodic Table?

(a) Na—Cl (b) Na—Ca

(c) Ca—Cl (d) Cl—Br

4. Write the atomic number of the element present in the third period and seventeenth group of the Periodic Table. **[NCERT]**

(a) 15 (b) 17

(c) 21 (d) 9

5. Which element do you think would have been named by Lawrence Berkeley laboratory? **[NCERT]**

(a) Berkelium (b) Lawrencium

(c) Both (a) and (b) (d) Seaborgium

6. Why do elements in the same group have similar physical and chemical properties? **[NCERT]**

(a) Because of same electronic configuration

(b) Because of same number of electrons

(c) Because of same number of protons

(d) Because of same valence electrons

7. The electronic configuration of gadolinium (Atomic number = 64) is **[NCERT Exemplar]**

(a) [Xe] $4f^3, 5d^5, 6s^2$ (b) [Xe] $4f^7, 5d^2, 6s^1$

(c) [Xe] $4f^7, 5d^1, 6s^2$ (d) [Xe] $4f^8, 5d^6, 6s^2$

8. The statement that is not correct for periodic classification of elements is **[NCERT Exemplar]**

(a) the properties of elements are periodic functions of their atomic numbers

(b) non-metallic elements are less in number than metallic elements

(c) for transition elements, the $3d$-orbitals are filled with electrons after $3p$-orbitals and before $4s$-orbitals

(d) the first ionisation enthalpies of elements generally increase with increase in atomic number as we go along a period

9. Which of the following is a metalloid?

(a) Sb (b) Mg

(c) Zn (d) Bi

10. Be resembles much with

(a) Li (b) Al

(c) Zn (d) Ra

11. An element with atomic number 20 will be placed in which period of the Periodic Table?

(a) 1 (b) 2

(c) 3 (d) 4

12. The position of the element having outer electronic configuration, ns^2np^4 for $n = 3$ is **[NCERT]**

(a) II period, fourth group

(b) III period, fourth group

(c) II period, 16 group

(d) III period, 16 group

13. Find the element having outer electronic configuration $(n-1)\,d^2ns^2$ for $n = 4$. **[NCERT]**

(a) Scandium

(b) Vanadium

(c) Titanium

(d) Tungsten

14. The element with outer shell configuration $(n-2)f^7(n-1)d^1ns^2$ for $n=6$ is [NCERT]
(a) uranium (b) gadolinium
(c) lead (d) niobium

15. The period number in the long form of the Periodic Table is equal to [NCERT Exemplar]
(a) magnetic quantum number of any element of the period
(b) atomic number of any element of the period
(c) maximum principal quantum number of any element of the period
(d) maximum azimuthal quantum number of any element of the period

16. The elements with atomic numbers 9, 17, 35, 53, 85 are all
(a) halogens (b) noble gases
(c) heavy metals (d) light metals

17. In which block does 106th element belong?
(a) s-block (b) p-block
(c) d-block (d) f-block

18. Which of the following electronic configurations in the outermost shell is characteristic of alkali metals?
(a) $ns^2p^6d^1$ (b) $(n-1)s^2p^6, ns^1$
(c) $(n-1)s^2p^6, ns^2p^1$ (d) $(n-1)s^2p^6d^{10}, ns^1$

19. Which one of the following belongs to representative group of elements in the Periodic Table?
(a) Aluminium (b) Chromium
(c) Argon (d) Lanthanum

20. In the modern Periodic Table, the period indicates the value of [NCERT]
(a) atomic number
(b) atomic mass
(c) principal quantum number
(d) azimuthal quantum number

21. Which of the following statements related to the modern Periodic Table is incorrect? [NCERT]
(a) The p-block has 6 columns, because a maximum of 6 electrons can occupy all the orbitals in a p-shell
(b) The d-block has 8 columns because a maximum of 8 electrons can occupy all the orbitals in a d-subshell
(c) Each block contains a number of columns equal to the number of electrons that can occupy that subshell
(d) The block indicates value of azimuthal quantum number (l) for the last subshell that received electrons in building up the electronic configuration

22. Which group of the Periodic Table does not contain only metals?
(a) IB (b) IA (c) IIA (d) IIIA

23. Which pair of atomic numbers represents s-block elements?
(a) 3, 12 (b) 6, 12
(c) 7, 15 (d) 9, 17

24. The tenth elements in the Periodic Table resembles with the
(a) first period (b) second period
(c) fourth period (d) ninth period

25. According to IUPAC nomenclature, a newly discovered element has been named as Uun. The atomic number of the element is
(a) 111 (b) 112
(c) 109 (d) 110

26. Mendeleef 's Periodic Table is upset by the fact that
(a) many elements have several isotopes
(b) noble gases do not form compounds
(c) some groups stand divided into two sub groups A and B
(d) atomic weights of elements are not always whole numbers

27. Variable valency in general, is exhibited by
(a) transition elements (b) gaseous elements
(c) non-metals (d) s-block elements

Atomic and Ionic Radii

28. In third row of the Periodic Table, the atomic radii from Na to Cl
(a) continuously decreases
(b) continuously increases
(c) remains constant
(d) increases but not continuously

29. The screening effect of d-electrons is
(a) equal to that of p-electrons
(b) more than that of p-electrons
(c) same as f-electrons
(d) less than p-electrons

30. Which of the following has largest ionic radius?
(a) Li^+ (b) K^+ (c) Na^+ (d) Cs^+

31. Which of the following ion is the smallest ion?
(a) O_2 (b) O_2^+ (c) O_2^- (d) O_2^{2-}

32. The order of screening effect of electrons of s, p, d and f orbitals of a given shell of an atom on its outer shell electrons is [NCERT]
(a) $s > p > d > f$ (b) $f > d > p > s$
(c) $p < d < s > f$ (d) $f > p > s > d$

33. Anything that influences the valence electrons will affect the chemistry of the element. Which one of the following factors does not affect the valence shell? **[NCERT]**

(a) Valence principal quantum number (n)
(b) Nuclear charge (Z)
(c) Nuclear mass
(d) Number of core electrons

34. Consider the following species

N^{3-}, O^{2-}, F^-, Na^+, Mg^{2+} and Al^{3+}

What is common in them? **[NCERT]**

(a) Number of electrons
(b) Number of valence electrons
(c) Number of protons
(d) All of the above

35. The correct order of increasing ionic radii is

(a) $Na^+ < Mg^{2+} < Al^{3+} < N^{3-} < O^{2-} < F^-$
(b) $Al^{3+} < Mg^{2+} < Na^+ < N^3 < O^{2-} < F^-$
(c) $Al^{3+} < Mg^{2+} < Na^+ < F^- < O^{2-} < N^{3-}$
(d) $F^- < O^{2-} < N^{3-} < Al^{3+} < Mg^{2+} < Na^+$

36. Which has the smallest size?

(a) Na^+ (b) Mg^{2+} (c) Al^{3+} (d) P^{5+}

37. Which of the following statements is correct?

(a) X^- ion is larger in size than X-atom
(b) X^+ ion is larger in size than X-atom
(c) X^+ ion is larger in size than X^- ion
(d) X^+ and X^- ions are equal in size

Ionisation Energy

38. Arrange the elements N, P, O and S in the order of increasing first ionisation enthalpy. **[NCERT]**

(a) P < S < O < N (b) S < P < O < N
(c) S < O < P < N (d) P < S < N < O

39. The correct increasing order of non-metallic character is **[NCERT]**

(a) P < S < O < N (b) S < P < O < N
(c) S < O < P < N (d) P < S < N < O

40. Among the elements B, Al, C and Si, element with the highest first ionisation enthalpy is **[NCERT]**

(a) B (b) Al (c) C (d) Si

41. As one moves along a given row in the Periodic Table, ionisation energy

(a) increases from left to right
(b) decreases from left to right
(c) first increases, then decreases
(d) remains the same

42. Ionisation potential is lowest for

(a) alkali metals (b) inert gas
(c) halogens (d) alkaline earth metals

43. The first ionisation energy of lithium will be

(a) greater than Be (b) less than Be
(c) equal to that of Na (d) equal to that of F

44. When the first ionisation energies are plotted against atomic number, the peaks are occupied by

(a) alkali metals (b) halogens
(c) transition metals (d) rare gases

45. The ionisation energy of nitrogen is larger than that of oxygen because of

(a) greater attraction of electrons by the nucleus
(b) the size of nitrogen atom being smaller
(c) the half-filled p-orbitals possess extra stability
(d) greater penetration effect

46. Highest energy will be absorbed to eject out the electron in the configuration

(a) $1s^2 2s^2 2p^1$ (b) $1s^2 2s^2 2p^3$
(c) $1s^2 2s^2 2p^2$ (d) $1s^2 2s^2 2p^4$

47. The correct order of ionisation energy for comparing carbon, nitrogen and oxygen is

(a) C < N > O (b) C > N < O
(c) C > N > O (d) C < N < O

48. Which of the following isoelectronic ions has lowest ionisation energy?

(a) Cl^- (b) Ca^{2+} (c) K^+ (d) S^{2-}

49. Which of the following relation is correct?

(a) I^{st} IE of C > I^{st} IE of B
(b) I^{st} IE of C < I^{st} IE of B
(c) II^{nd} IE of C > II^{nd} IE of B
(d) Both (b) and (c)

50. If the IP of Na is 5.48 eV, the ionisation potential of K will be

(a) same as that of Na (b) 4.34 eV
(c) 5.68 eV (d) 10.88 eV

51. The first ionisation energy of oxygen is less than that of nitrogen. Which of the following is the correct reason for this observation?

(a) Lesser effective nuclear charge of oxygen than nitrogen
(b) Lesser atomic size of oxygen than nitrogen
(c) Greater inter-electron repulsion between two electrons in the same p-orbital counter balances the increase in effective nuclear charge on moving from nitrogen to oxygen
(d) Greater effective nuclear charge of oxygen than nitrogen

52. Among the second period elements the actual ionisation enthalpies are in the order

$$\text{Li} < \text{B} < \text{Be} < \text{C} < \text{O} < \text{N} < \text{F} < \text{Ne}$$

Be has higher $\Delta_i H$ than B. This is because
(a) of the stable configuration of B from which electron has to be removed
(b) of the fact p orbital being larger attracted more towards nucleus
(c) $2s$ orbital is closer to nucleus as compared to $2p$ orbital
(d) $2p$ orbital is of higher stability than $2s$ orbital

53. O has lower $\Delta_i H$ than N and F because
(a) its size is smaller than F but larger than N
(b) F is smaller but N have stable configuration
(c) N is smaller and F have stable configuration
(d) its size is smaller than N but larger than F

Electron Affinity and Other Periodic Properties

54. Electron affinity is the
(a) energy released when an electron is added to an isolated atom in the gaseous state
(b) energy absorbed when an electron is added to an isolated atom in the gaseous state
(c) energy required to take out an electron from an isolated gaseous atom
(d) power of an atom to attract an electron to itself

55. Which of the following pairs show reverse properties on moving along a period from left to right and from top to down in a group?
(a) Nuclear charge and electron affinity
(b) Ionisation energy and electron affinity
(c) Atomic radius and electron affinity
(d) None of the above

56. Which of the following has highest electron affinity?
(a) N (b) O
(c) F (d) Cl

57. With respect to chlorine, hydrogen will be
(a) electropositive (b) electronegative
(c) neutral (d) None of these

58. Of the following elements, which one has the highest electronegativity?
(a) F (b) Cl
(c) Br (d) I

59. The values of electronegativity of atom A and B are 1.20 and 4.0 respectively. The percentage of ionic character of A–B bond is
(a) 58.3% (b) 48%
(c) 79.6% (d) 73.6%

60. Elements of which group form anions most readily?
(a) Halogens
(b) Alkali metals
(c) Oxygen family
(d) Nitrogen group

61. The halogen that most easily reduced is
(a) F_2 (b) Cl_2
(c) Br_2 (d) I_2

62. Which element has the lowest electronegativity?
(a) Li (b) F
(c) Cl (d) Fe

63. The elements X, Y, Z and T have the indicated electronic configurations. Starting with the innermost shell, which is the most metallic element?
(a) X = 2,8,4 (b) Y = 2,8,8
(c) Z = 2, 8, 8, 1 (d) T = 2, 8, 8, 7

64. The outermost electronic configuration of the most electronegative element is
(a) ns^2np^3 (b) ns^2np^4
(c) ns^2np^5 (d) ns^2np^6

65. Fluorine has low electron affinity than chlorine because of
(a) bigger radius of fluorine, less density
(b) smaller radius of fluorine, high density
(c) smaller radius of chlorine, high density
(d) smaller radius of chlorine, less density

66. The outermost configuration of the least reactive element is
(a) ns^2p^3 (b) ns^2p^4
(c) ns^2p^5 (d) ns^2p^6

67. Which one of the following process requiring absorption of energy?
(a) $Cl \longrightarrow Cl^-$ (b) $H \longrightarrow H^-$
(c) $O \longrightarrow O^{2-}$ (d) $F \longrightarrow F^-$

68. Among alkali metals which element do you expect to be least electronegative? **[NCERT]**
(a) K (b) Na
(c) Cs (d) Fr

69. The electron gain enthalpy of fluorine is less negative than that of chlorine because **[NCERT]**
(a) the added electron experience greater force of attraction from the other electron in case of F
(b) the added electron experience greater force of repulsion from the other electrons in case of F
(c) the size of F is smaller than Cl
(d) Both (b) and (c)

70. As we go from left to right in period two of the periodic table, gram atomic volume of the elements

(a) will change indefinitely
(b) decreases
(c) increase at a constant rate
(d) first increase then decrease

71. Metallic nature and basic nature of the oxides...... as we move along a period.

(a) increases
(b) decreases
(c) remains constant
(d) first increase then decreases

72. The metal having highest melting point is

(a) Cr
(b) Ag
(c) diamond
(d) W

73. Which of the following metals exhibits more than one oxidation state?

(a) Na
(b) Mg
(c) Al
(d) Fe

74. The maximum valency of an element with atomic number 7 is

(a) 2
(b) 3
(c) 4
(d) 5

75. The correct order of reactivity of halogens is

(a) F > Br > Cl > I
(b) F > Cl > Br > I
(c) I > Br > Cl > F
(d) Cl > I > Br > F

76. The correct order of increasing oxidising power is

(a) $F_2 < Cl_2 < Br_2 < I_2$
(b) $I_2 < F_2 < Cl_2 < Br_2$
(c) $Br_2 < I_2 < F_2 < Cl_2$
(d) $I_2 < Br_2 < Cl_2 < F_2$

77. Which of the following oxides is most basic?

(a) Na_2O
(b) SiO_2
(c) SO_2
(d) All are equally basic

Round II (Mixed Bag)

Only One Correct Option

1. The statement that is true for the long form of the Periodic Table is

(a) it reflects the sequence of filling the electrons in the order of sub-energy levels *s*, *p*, *d* and *f*
(b) it helps to predict the stable valency states of the elements
(c) it reflects trends in physical and chemical properties of the elements
(d) All of the above

2. The radii of F, F^-, O and O^{2-} are in the order of

(a) $F^- > O^{2-} > F > O$
(b) $F > F^- > O > O^{2-}$
(c) $O^{2-} > F^- > O > F$
(d) $F > O > F^- > O^{2-}$

3. Which of the following does not represent the correct order of the property indicated?

(a) $Sc^{3+} > Cr^{3+} > Fe^{3+} > Mn^{3+}$ — ionic radii
(b) Sc < Ti < Cr < Mn — density
(c) $Mn^{2+} > Ni^{2+} > Co^{2+} < Fe^{2+}$ — ionic radii
(d) FeO < CaO < MnO < CuO — basic nature

4. The first ionisation enthalpies for two isotopes of the same elements are **[NCERT]**

(a) same
(b) different
(c) some what different
(d) $IE_I = 2IE_{(\text{II isotope})}$

5. The size of isoelectronic species; F^-, Ne and Na^+ is affected by **[NCERT]**

(a) nuclear charge (Z)
(b) valence principal quantum number (n)
(c) electron-electron interaction in the outer orbitals
(d) none of the factors because their size is the same

6. Energy of an electron in the ground state of the hydrogen atom is -2.18×10^{-18} J. Calculate the ionisation enthalpy of atomic hydrogen in terms of J mol^{-1}. **[NCERT]**

(a) 2.18×10^{-18}
(b) 13.12×10^{5}
(c) 3.16×10^{-13}
(d) 2.21×10^{6}

7. The correct order of radii is

(a) N < Be < B
(b) $F^- < O^{2-} < N^{3-}$
(c) $Fe^{3+} < Fe^{2+} < Fe^{4+}$
(d) Na < Li < K

8. The correct order of ionic radius is

(a) $Ti^{4+} < Mn^{7+}$
(b) $^{35}Cl^- > {}^{37}Cl^-$
(c) $K^+ > Cl^-$
(d) $P^{3+} > P^{5+}$

9. The bond length of LiF will be

(a) equal to that of KF
(b) more than that of KF
(c) equal to that of NaF
(d) less than that of NaF

10. The ionic radius of 'Cr' is minimum in which of the following compounds?

(a) CrO_2
(b) K_2CrO_4
(c) CrF_3
(d) $CrCl_3$

11. The incorrect statement among the following is
- (a) the first ionisation potential of Al is less than the first ionisation potential of Mg
- (b) the second ionisation potential of Mg is greater than the second ionisation potential of Na
- (c) the first ionisation potential of Na is less than the first ionisation potential of Mg
- (d) the third ionisation potential of Mg is greater than that of Al

12. $A \rightarrow A^+ + e,\ E_1$ and $A^+ \rightarrow A^{2+} + e,\ E_2$. The energy required to pull out the two electrons are E_1 and E_2 respectively. The correct relationship between two energy would be

(a) $E_1 < E_2$ (b) $E_1 > E_2$
(c) $E_1 = E_2$ (d) $E_1 \neq E_2$

13. Which ionisation potential (IP) in the following equations involves the greatest amount of energy?

(a) $K^+ \longrightarrow K^{2+} + e^-$ (b) $Na \longrightarrow Na^+ + e^-$
(c) $C^{2+} \longrightarrow C^{3+} + e^-$ (d) $Ca^+ \longrightarrow Ca^{2+} + e^-$

14. The first four ionisation energy values of an element are 191, 578, 872 and 5962 kcal. The number of valence electrons in the element is

(a) 1 (b) 2 (c) 3 (d) 4

15. The I^{st} IEs of four consecutive elements present in the second the period of Periodic Table are 8.3, 11.3, 14.5 and 13.6 eV respectively. Which of these is the IE of nitrogen?

(a) 13.6 (b) 8.3
(c) 14.5 (d) 11.3

16. Which of the following transitions involves maximum amount of energy?

(a) $M^-(g) \longrightarrow M(g)$ (b) $M(g) \longrightarrow M^+(g)$
(c) $M^+(g) \longrightarrow M^{2+}(g)$ (d) $M^{2+}(g) \longrightarrow M^{3+}(g)$

17. The formation of the oxide ion, $O^{2-}(g)$, from oxygen atom requires first an exothermic and then an endothemic step as shown below.

$$O(g) + e^- \longrightarrow O^-(g)\,;\quad \Delta H^\ominus = -141\ \text{kJ mol}^{-1}$$
$$O^-(g) + e^- \longrightarrow O^{2-}(g)\,; \Delta H^\ominus = +780\ \text{kJ mol}^{-1}$$

Thus, process of formation of O^{2-} in gas phase is unfavourable even though O^{2-} is isoelectronic with neon. It is due to the fact that **[NCERT Exemplar]**
- (a) oxygen is more electronegative
- (b) addition of electron in oxygen results in larger size of the ion
- (c) electron repulsion outweighs the stability gained by achieving noble gas configuration
- (d) O^- ion has comparatively smaller size than oxygen atom

18. The electronic configuration of four elements are given below. Which element does not belong to the same family?

(a) $[Xe]\,4f^{14}5d^{10}6s^2$ (b) $[Kr]\,4d^{10}5s^2$
(c) $[Ne]\,3s^2 3p^5$ (d) $[Ar]\,3d^{10}4s^2$

19. Which of the following sequence correctly represents the decreasing acidic nature of oxides?
- (a) $Li_2O > BeO > CO_2 > N_2O_3 > B_2O_3$
- (b) $CO_2 > N_2O_3 > B_2O_3 > Li_2O > BeO$
- (c) $N_2O_3 > CO_2 > B_2O_3 > BeO > Li_2O$
- (d) $CO_2 > BeO > Li_2O > B_2O_3 > N_2O_3$

20. Which is not the correct order for the stated property?
- (a) Ba > Sr > Mg, atomic radius
- (b) F > O > N, first ionisation enthalpy
- (c) Cl > F > I, electron affinity
- (d) O > Se > Te, electronegativity

21. The electron affinity values (in kg mol^{-1}) of three halogens X, Y and Z are respectively –349, –333 and –325. Then X, Y and Z respectively, are

(a) F_2, Cl_2 and Br_2 (b) Cl_2, F_2 and Br_2
(c) Cl_2, Br_2 and F_2 (d) Br_2, Cl_2 and F_2

22. Which of the following has the highest second ionisation energy?

(a) Calcium (b) Chromium
(c) Iron (d) Cobalt

23. Electronic configuration of four elements A, B, C and D are given below

(A) $1s^2, 2s^2, 2p^6$ (B) $1s^2, 2s^2, 2p^4$
(C) $1s^2, 2s^2, 2p^6, 3s^1$ (D) $1s^2, 2s^2, 2p^5$

Which of the following is the correct order of increasing tendency to gain electron? **[NCERT Exemplar]**

(a) $A < C < B < D$ (b) $A < B < C < D$
(c) $D < B < C < A$ (d) $D < A < B < C$

24. Which one of the following arrangements represents the correct order of electron gain enthalpy (with negative sign) of the given atomic species?

(a) Cl < F < S < O (b) O < S < F < Cl
(c) S < O < Cl < F (d) F < Cl < O < S

25. In which one of the following pairs, the radius of the second species is greater than that of the first?

(a) Na, Mg (b) O^{2-}, N^{3-}
(c) Li^+, Be^{2+} (d) Ba^{2+}, Sr^{2+}

26. For d-block elements the first ionisation potential is of the order
- (a) Zn > Fe > Cu > Cr
- (b) Sc ≈ Ti < V ≈ Cr
- (c) Zn < Cu < Ni < Co
- (d) V > Cr > Mn > Fe

27. Match the correct atomic radius with the element.

	Element		Atomic radius (pm)
(A)	Be	(i)	74
(B)	C	(ii)	88
(C)	O	(iii)	111
(D)	B	(iv)	77
(E)	N	(v)	66

[NCERT Exemplar]

Codes

	A	B	C	D	E
(a)	(iii)	(iv)	(v)	(i)	(ii)
(b)	(iii)	(iv)	(v)	(ii)	(i)
(c)	(iv)	(iii)	(v)	(ii)	(i)
(d)	(v)	(iii)	(iv)	(i)	(ii)

28. Match the correct ionisation enthalpies and electron gain enthalpies of the following elements.

	Elements		ΔH_1	ΔH_2	$\Delta_{eg} H$
(A)	Most reactive non-metal	(i)	419	3051	– 45
(B)	Most reactive metal	(ii)	1681	3374	– 328
(C)	Least reactive element	(iii)	738	1451	– 40
(D)	Metal forming binary halide	(iv)	2372	5251	+ 48

[NCERT Exemplar]

Codes

	A	B	C	D		A	B	C	D
(a)	(ii)	(i)	(iv)	(iii)	(b)	(i)	(ii)	(iv)	(iii)
(c)	(i)	(iv)	(iii)	(iv)	(d)	(ii)	(i)	(iii)	(iv)

29. If Aufbau rule is not followed, K-19 will be placed in

(a) *s*-block
(b) *p*-block
(c) *d*-block
(d) *f*-block

30. Which of the following is correct order of increasing size?

(a) $Br^- > S^{2-} > Cl^- > Na^+ > Mg^{2+} > Be^{2+}$
(b) $Be^{2+} > Mg^{2+} > Na^+ > S^{2-} > Cl^- > Br^-$
(c) $S^{2-} > Cl^- > Br^- > Na^+ > Mg^{2+} > Be^{2+}$
(d) $Na^+ > Mg^{2+} > Be^{2+} > Br^- > Cl^- > S^{2-}$

31. Which is the correct order of ionic sizes?

(At. no. : Ce = 58, Sn = 50, Yb = 70 and Lu = 71)

(a) Ce > Sn > Yb > Lu
(b) Sn > Yb > Ce > Lu
(c) Sn > Ce > Yb > Lu
(d) Lu > Yb > Sn > Ce

32. In the isoelectronic species the ionic radii (Å) of N^{3-}, O^{2-} and F^- are respectively given by

(a) 1.71, 1.40, 1.36
(b) 1.71, 1.36, 1.40
(c) 1.36, 1.40, 1.71
(d) 1.36, 1.71, 1.40

33. The trivalent ion having largest size in lanthanide series is

(a) Ti
(b) Zr
(c) Hf
(d) La

34. A sudden large jump between the values of second and third ionisation energies of an element would be associated with the electronic configuration

(a) $1s^2, 2s^2, 2p^6, 3s^2$
(b) $1s^2, 2s^2, 2p^6, 3s^1$
(c) $1s^2, 2s^2, 2p^6, 3s^2, 3p^1$
(d) $1s^2, 2s^2, 2p^6, 3s^2, 3p^2$

35. The first ionisation potential (eV) of Be and B respectively are

(a) 8.29 eV, 8.29 eV
(b) 8.29 eV, 9.32 eV
(c) 9.32 eV, 9.32 eV
(d) 9.32 eV, 8.29 eV

36. The second electron affinity is zero for

(a) alkali metals
(b) halogens
(c) noble gases
(d) transition metal

37. A trend common to both group I and VII elements in the Periodic Table as atomic number increases is

(a) atomic radius increases
(b) oxidising power increases
(c) reactivity with water increases
(d) maximum valency increases

38. An element X which occurs in the first short period has an outer electronic structure $s^2 p^1$. What are the formula and acid-base character of its oxides?

(a) XO_3, basic
(b) X_2O_3, basic
(c) X_2O_3, amphoteric
(d) XO_2, acidic

More than One Correct Option

39. Which of the following pairs of species have nearly same size?

(a) Rb^+, O^{2-}
(b) Cl^-, Na^+
(c) Mg^{2+}, Na^+
(d) Li^+, Mg^{2+}

40. Which of the following statements is/are true?

(a) Metallic and covalent radii of potassium are 2.3 Å and 2.03 Å respectively
(b) Atomic and ionic radii of niobium and tantalum are almost same
(c) Ionisation energy is inversely proportional to the screening effect
(d) The first ionisation energies of Be and Mg are more than ionisation energies of B and Al respectively

41. Which of the following elements will gain one electron more readily in comparison to other elements of their group? [NCERT Exemplar]

(a) S (*g*)
(b) Na (*g*)
(c) O (*g*)
(d) Cl (*g*)

42. Which of the following statements are correct? **[NCERT Exemplar]**

(a) Helium has the highest first ionisation enthalpy in the Periodic Table
(b) Chlorine has less negative electron gain enthalpy than fluorine
(c) Mercury and bromine are liquids at room temperature
(d) In any period, atomic radius of alkali metal is the highest

43. Which of the following sets contain only isoelectronic ions? **[NCERT Exemplar]**

(a) $Zn^{2+}, Ca^{2+}, Ga^{3+}, Al^{3+}$ (b) $K^{+}, Ca^{2+}, Sc^{3+}, Cl^{-}$
(c) $P^{3-}, S^{2-}, Cl^{-}, K^{+}$ (d) Ti^{4+}, Ar, Cr^{3+}, V^{5+}

Assertion and Reason

Directions (Q. Nos. 44 to 48) *Each of these questions contains two statements : Statement* I *(Assertion) and Statement* II *(Reason). Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes* (*a*), (*b*), (*c*), (*d*) *given below :*

(a) Statement I is true; Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true; Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

44. **Statement I** Ionisation energy of nitrogen (7) is more than that of oxygen (8).

Statement II Half-filled *p*-orbitals in nitrogen ($2p^3$) are more stable.

45. **Statement I** Manganese has a less favourable electron affinity than its neighbours in either side.

Statement II The magnitude of an element's electron affinity depends on the element's valence shell electronic configuration.

46. **Statement I** Shielding effect increases as we go down the group.

Statement II More is the electrons in the penultimate shell, more is shielding.

47. **Statement I** Generally, ionisation enthalpy increases from left to right in a period.

Statement II When successive electrons are added to the orbitals in the same principal quantum level, the shielding effect of inner core of electrons does not increase very much to compensate for the increased attraction of the electron to the nucleus. **[NCERT Exemplar]**

48. **Statement I** Electron gain enthalpy becomes less negative as we go down a group.

Statement II Size of the atom increases on going down the group and the added electron would be farther from the nucleus. **[NCERT Exemplar]**

Comprehension Based Questions

Directions (Q.Nos. 49 to 51) In the modern Periodic Table, elements are arranged in order of increasing atomic numbers which is related to the electronic configuration. Depending upon the type of orbitals receiving the last electron, the elements in the Periodic Table have been divided into four block, *viz*, *s*, *p*, *d* and *f*. The modern Periodic Table consists of 7 periods and 18 groups. Each period begins with the filling of a new energy shell. In accordance with the Aufbau principle, the seven periods (1 to 7) have 2, 8, 8, 18, 18, 32 and 32 elements respectively. The seventh period is still incomplete. To avoid the Periodic Table being too long, the two series of *f*-block elements, called lanthanoids and actinoids are placed at the bottom of the main body of the Periodic Table.

49. Which of the elements whose atomic numbers are given below, cannot be accommodated in the present set up of the long form of the Periodic Table?

(a) 107 (b) 118 (c) 126 (d) 102

50. The electronic configuration of the element which is just above the element with atomic number 43 in the same group is **[NCERT Exemplar]**

(a) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^2$
(b) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^2, 4p^6$
(c) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6, 4s^2$
(d) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^7, 4s^2$

51. The elements with atomic numbers 35, 53 and 85 are all **[NCERT Exemplar]**

(a) noble gases (b) halogens
(c) heavy metals (d) light metals

Directions (Q.Nos. 52 and 53) Screening effect is the effect produced by intervening electrons between nucleus and valence electrons. They shield the nucleus from valence electron and hence, effective nuclear charge decreases. If there is less shielding effect, the effective nuclear charge decreases. Valence electrons are attracted by nucleus and repelled by other electrons.

Net attractive force on electron under consideration = $Z - S$ = (nuclear charge – screening effect)

It is the Slater's formula for screening constant.

If one electron is present in outermost orbit, there will be no screening in that orbital.

Each electron contributes 0.35 (total electrons minus 1) present in outermost shell.

In penultimate energy level, electrons contribute 0.85.

A contribution of 1.0 is from remaining electrons (present in last but one energy level)

52. The effective nuclear charge for 4*s* electrons of Zn will be
(a) 26.85 (b) 4.35 (c) 15.30 (d) 10

53. The atomic size of Ga and Al are almost same because
(a) of poor shielding effect of electrons in *d*-orbitals, due to which effective nuclear charge increases in gallium
(b) more shielding effect of *d*-electrons
(c) poor shielding effect of *f*-orbital in gallium
(d) high shielding effect of 3*s*, 3*p* and 3*d* electrons

Directions (Q.Nos. 54 to 56) Ionic radius is the effective distance from the nucleus of an ion up to which it has its influence on its electron cloud. A cation is always much smaller than the corresponding atom. Further, more the number of electrons removed, smaller will be the size of the resulting positive ion. For example $r_{Fe} > r_{Fe^{2+}} > r_{Fe^{3+}}$.

A cation formed by the loss of electrons may result in the complete disappearance of the outer shell and since, the remaining inner shells do not extend so far in space, the cation is much smaller than the metal atom. For example

$$\underset{(2,\,8,\,1)}{\text{Na}} \longrightarrow \underset{(2,\,8)}{\text{Na}^+}$$

In case of isoelectronic ions, the greater the nuclear charge, the greater is the attraction for electrons and smaller is ionic radius.

54. The size of the species Pb, Pb^{2+} and Pb^{4+} decreases as
(a) $Pb^{4+} > Pb^{2+} > Pb$ (b) $Pb > Pb^{2+} > Pb^{4+}$
(c) $Pb^{4+} > Pb > Pb^{2+}$ (d) $Pb^{2+} > Pb^{4+} > Pb$

55. The species which has the same number of electrons in the outermost as well as penultimate shell is
(a) F^- (b) Ca^{2+}
(c) O^{2-} (d) Mg^{2+}

56. Which out of the following has the largest size?
(a) Mg^{2+} (b) Na^+
(c) Rb^+ (d) Li^+

Directions (Q.Nos. 57 to 59)

The first ($\Delta_i H_1$) and the second ($\Delta_i H_2$) ionisation enthalpies (in kJ mol^{-1}) and the ($\Delta e_g H$) electron gain enthalpy (in kJ mol^{-1}) of a few elements are given below

Elements	ΔH_1	ΔH_2	$\Delta e_g H$
I	520	7300	– 60
II	419	3051	– 48
III	1681	3374	– 328
IV	1008	1846	– 295
V	2372	5251	+48
VI	738	1451	– 40

57. Which of the above elements is likely to be the least reactive element?
(a) I (b) V (c) VI (d) III

58. The metal which can form a stable binary halide of the formula MX_2(X = halogen) is
(a) V (b) VI (c) IV (d) I

59. The metal which can form a predominantly stable covalent halide of the formula MX (X = halogen) is
(a) I (b) II (c) III (d) IV

Previous Years' Questions

60. The increasing order of the ionic radii of the given isoelectronic species is [AIEEE 2012]
(a) $Cl^-, Ca^{2+}, K^+, S^{2-}$ (b) $S^{2-}, Cl^-, Ca^{2+}, K^+$
(c) $Ca^{2+}, K^+, Cl^-, S^{2-}$ (d) $K^+, S^{2-}, Ca^{2+}, Cl^+$

61. Which one of the following order presents the correct sequence of the increasing basic nature of the given oxides? [AIEEE 2011]
(a) $Al_2O_3 < MgO < Na_2O < K_2O$
(b) $MgO < K_2O < Al_2O_3 < Na_2O$
(c) $Na_2O < K_2O < MgO < Al_2O_3$
(d) $K_2O < Na_2O < Al_2O_3 < MgO$

62. The correct order of electron gain enthalpy with negative sign of F, Cl, Br and I, having atomic number 9, 17, 35 and 53 respectively, is [AIEEE 2011]
(a) I > Br > Cl > F (b) F > Cl > Br > I
(c) Cl > F > Br > I (d) Br > Cl > I > F

63. The correct sequence which shows decreasing order of the ionic radii of the elements is [AIEEE 2010]
(a) $Al^{3+} > Mg^{2+} > Na^+ > F^- > O^{2-}$
(b) $Na^+ > Mg^{2+} > Al^{3+} > O^{2-} > F^-$
(c) $Na^+ > F^- > Mg^{2+} > O^{2-} > Al^{3+}$
(d) $O^{2-} > F^- > Na^+ > Mg^{2+} > Al^{3+}$

64. The set representing the correct order of ionic radius is [AIEEE 2009]
(a) $Li^+ > Be^{2+} > Na^+ > Mg^{2+}$
(b) $Na^+ > Li^+ > Mg^{2+} > Be^{2+}$
(c) $Li^+ > Na^+ > Mg^{2+} > Be^{2+}$
(d) $Mg^{2+} > Be^{2+} > Li^+ > Na^+$

65. The charge/size ratio of a cation determines its polarising power. Which one of the following sequences represents the increasing order of the polarising power of the cationic species, K^+, Ca^{2+}, Mg^{2+}, Be^{2+}? **[AIEEE 2007]**

(a) $Mg^{2+} < Be^{2+} < K^+ < Ca^{2+}$
(b) $Be^{2+} < K^+ < Ca^{2+} < Mg^{2+}$
(c) $K^+ < Ca^{2+} < Mg^{2+} < Be^{2+}$
(d) $Ca^{2+} < Mg^{2+} < Be^{2+} < K^+$

66. Which one of the following sets of ions represents a collection of isoelectronic species? **[AIEEE 2006]**

(a) $K^+, Cl^-, Ca^{2+}, Sc^{3+}$ (b) $Ba^{2+}, Sr^{2+}, K^+, S^{2-}$
(c) $N^{3-}, O^{2-}, F^-, S^{2-}$ (d) $Li^+, Na^+, Mg^{2+}, Ca^{2+}$

67. The ionic mobility of alkali metal ions in aqueous solution is maximum for **[AIEEE 2006]**

(a) K^+ (b) Rb^+
(c) Li^+ (d) Na^+

68. The increasing order of the first ionisation enthalpies of the elements B, P, S and F (lowest first) is **[AIEEE 2006]**

(a) F < S < P < B
(b) P < S < B < F
(c) B < P < S < F
(d) B < S < P < F

69. Following statements regarding the periodic trends of chemical reactivity of the alkali metals and the halogens are given. Which of these statements give the correct picture? **[AIEEE 2006]**

(a) The reactivity decreases in the alkali metals but increases in the halogens with increase in atomic number down the group
(b) In both the alkali metals and the halogens, the chemical reactivity decreases with increase in atomic number down the group
(c) Chemical reactivity increases with increase in atomic number down the group in both the alkali metals and halogens
(d) In alkali metals the reactivity increases but in the halogens it decreases with increase in atomic number down the group

70. In which of the following arrangements the order is not according to the property indicated against it? **[AIEEE 2005]**

(a) Li < Na < K < Rb: Increasing metallic radius
(b) I < Br < F < Cl: Increasing electron gain enthalpy (with negative sign)
(c) B < C < N < O: Increasing first ionisation enthalpy
(d) $Al^{3+} < Mg^{2+} < Na^+ < F^-$: Increasing ionic size

71. Which one of the following ions has the highest value of ionic radius? **[AIEEE 2004]**

(a) Li^+ (b) B^{3+}
(c) O^{2-} (d) F^-

72. The formation of the oxide ion $O^{2-}(g)$ requires first an exothermic and then an endothermic step as shown below

$$O(g) + e^- = O^-(g)\,; \quad \Delta H^\circ = -142 \text{ kJ mol}^{-1}$$
$$O^-(g) + e^- = O^{2-}(g)\,; \Delta H^\circ = 844 \text{ kJ mol}^{-1}$$

This is because **[AIEEE 2004]**

(a) oxygen is more electronegative
(b) oxygen has high electron affinity
(c) O^- ion will tend to resist the addition of another electron
(d) O^- ion has comparatively larger size than oxygen atom

73. Among Al_2O_3, SiO_2, P_2O_3 and SO_2 the correct order of acid strength is **[AIEEE 2004[**

(a) $SO_2 < P_2O_3 < SiO_2 < Al_2O_3$
(b) $SiO_2 < SO_2 < Al_2O_3 < P_2O_3$
(c) $Al_2O_3 < SiO_2 < SO_2 < P_2O_3$
(d) $Al_2O_3 < SiO_2 < P_2O_3 < SO_2$

74. According to the periodic law of elements, the variation in properties of elements is related to their **[AIEEE 2003]**

(a) atomic masses
(b) nuclear masses
(c) atomic numbers
(d) nuclear neutron-proton number ratios

75. The radius of La^{3+} (atomic number : La = 57) is 1.06 Å. Which one of the following given values will be closest to the radius of Lu^{3+} (atomic number : Lu = 71)? **[AIEEE 2003]**

(a) 1.60 Å (b) 1.40 Å
(c) 1.06 Å (d) 0.85 Å

76. The atomic numbers of vanadium (V), chromium (Cr), manganese (Mn) and iron (Fe) are, respectively 23, 24, 25 and 26. Which one of these may be expected to have the highest second ionisation enthalpy? **[AIEEE 2003]**

(a) V (b) Cr (c) Mn (d) Fe

77. Ce^{3+}, La^{3+}, Pm^{3+} and Yb^{3+} have ionic radii in the increasing order as **[AIEEE 2002]**

(a) $La^{3+} < Ce^{3+} < Pm^{3+} < Yb^{3+}$
(b) $Yb^{3+} < Pm^{3+} < Ce^{3+} < La^{3+}$
(c) $La^{3+} = Ce^{3+} < Pm^{3+} < Yb^{3+}$
(d) $Yb^{3+} < Pm^{3+} < La^{3+} < Ce^{3+}$

Answers

Round I

1. (a)	**2.** (d)	**3.** (a)	**4.** (b)	**5.** (c)	**6.** (d)	**7.** (c)	**8.** (c)	**9.** (a)	**10.** (b)
11. (d)	**12.** (d)	**13.** (c)	**14.** (b)	**15.** (c)	**16.** (a)	**17.** (c)	**18.** (b)	**19.** (a)	**20.** (c)
21. (b)	**22.** (d)	**23.** (a)	**24.** (b)	**25.** (d)	**26.** (a)	**27.** (a)	**28.** (a)	**29.** (d)	**30.** (d)
31. (b)	**32.** (a)	**33.** (c)	**34.** (a)	**35.** (c)	**36.** (d)	**37.** (a)	**38.** (b)	**39.** (d)	**40.** (c)
41. (a)	**42.** (a)	**43.** (b)	**44.** (d)	**45.** (c)	**46.** (b)	**47.** (a)	**48.** (d)	**49.** (a)	**50.** (b)
51. (c)	**52.** (c)	**53.** (b)	**54.** (a)	**55.** (c)	**56.** (d)	**57.** (a)	**58.** (a)	**59.** (d)	**60.** (a)
61. (a)	**62.** (a)	**63.** (c)	**64.** (c)	**65.** (b)	**66.** (d)	**67.** (c)	**68.** (d)	**69.** (d)	**70.** (b)
71. (b)	**72.** (d)	**73.** (d)	**74.** (d)	**75.** (b)	**76.** (d)	**77.** (a)			

Round II

1. (c)	**2.** (c)	**3.** (a)	**4.** (a)	**5.** (a)	**6.** (b)	**7.** (b)	**8.** (d)	**9.** (d)	**10.** (b)
11. (b)	**12.** (a)	**13.** (a)	**14.** (c)	**15.** (c)	**16.** (d)	**17.** (c)	**18.** (c)	**19.** (c)	**20.** (b)
21. (b)	**22.** (b)	**23.** (a)	**24.** (b)	**25.** (b)	**26.** (a)	**27.** (b)	**28.** (a)	**29.** (c)	**30.** (a)
31. (c)	**32.** (a)	**33.** (d)	**34.** (a)	**35.** (d)	**36.** (b)	**37.** (a)	**38.** (c)	**39.** (a,d)	**40.** (a,b,c,d)
41. (a,d)	**42.** (a,c,d)	**43.** (b,c)	**44.** (a)	**45.** (b)	**46.** (a)	**47.** (b)	**48.** (a)	**49.** (c)	**50.** (a)
51. (b)	**52.** (a)	**53.** (a)	**54.** (b)	**55.** (b)	**56.** (c)	**57.** (b)	**58.** (b)	**59.** (a)	**60.** (c)
61. (a)	**62.** (c)	**63.** (d)	**64.** (b)	**65.** (c)	**66.** (a)	**67.** (b)	**68.** (d)	**69.** (d)	**70.** (c)
71. (c)	**72.** (c)	**73.** (d)	**74.** (c)	**75.** (d)	**76.** (b)	**77.** (b)			

the Guidance

Round I

3. Na—Cl Both belongs to III period.

4. General configuration for 17th group elements is ns^2np^5. In the third period, the principal quantum number for valence shell is three, so the electronic configuration of valence shell for the given element is $3s^2, 3p^5$. Third period starts from atomic number, $Z = 11$ and end at $Z = 18$. Hence, the atomic number of the given element is $10 + 7 = 17$.

5. Lawrencium $(Z = 103)$ and Berkelium $(Z = 97)$ were named by Lawrence Berkeley laboratory.

6. Same group elements have same number. of valence electrons therefore, have similar physical and chemical properties

8. In case of transition elements (or any elements), the order of filling of electrons in variou orbitals is $3p < 4s < 3d$

Thus, $3d$ orbital is filled when $4s$ orbital gets completely filled.

11. $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2$

Principal quantum number is 4, so it belongs to 4th period.

12. ns^2np^4 for $n = 3$

$n = 3$ means element belongs to third period. Since, last electron enters in the p-orbital, it belongs to p-block. For p-block elements, the group number $= 10 +$ valence shell electrons $= 10 + (2 + 4) = 16$

Hence, the element belongs to 16th group.

The complete electronic configuration of the element is as follows,

$$1s^2, 2s^2, 2p^6, 3s^2, 3p^4$$

Thus, the element is sulphur.

13. $(n-1)\,d^2\,ns^2$ for $n = 4$

$n = 4$ means the element belongs to fourth period. Since, last electron enters in d-orbital, the given element belongs to d-block. For d-block elements, group number = number of d-electrons + number of ns electrons $= 2 + 2 = 4$

Hence, the element belongs to 4th group.

The complete electronic configuration of the element is as follows,

$$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^2, 4s^2$$

Thus, the element is titanium.

14. $(n-2)\,f^7\,(n-1)\,d^1\,ns^2$ for $n = 6$

$n = 6$ means, the element belongs to sixth period.

Since, last electron enters in f-orbital, the given element belongs to f-block and all f-block elements are the members of third group. Hence, the element belongs to third group.

The complete configuration of the element is as follows,
$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{10},$
$5s^2, 5p^6, 4f^7, 5d^1, 6s^2$

Thus, the element is gadolinium (Gd).

15. Period number = Maximum n of any element (where , $n =$ principal quantum number)

16. These atomic numbers give the configuration ns^2np^5 which is of halogen group or VIIth group.

17. The electronic configuration of the element having atomic number 106 is $[Rn]_{86}, \ 7s^1, 5f^{14}, 6d^5$.

Since, the last electron enters in *d*-orbit, it is a *d*-block element. Its IUPAC name is unnilhexium (Unh).

20. In the modern Periodic Table, the period indicates the value of principal quantum number.

21. Statement (b) is incorrect. The correct statement (b) is; the *d*-block has 10 columns, because a maximum of 10 electrons can occupy all the orbitals in a *d*-subshell.
All other given statements are correct.

22. IIIA group contains both metals and non-metals.

23. $3 = 1s^2, 2s^1$
$12 = 1s^2, 2s^2, 2p^6, 3s^2$

Since, last electron enters in *s*-orbital, these are *s*-block elements.

24. Each period consists of a series of elements whose atoms have the same principal quantum number (n) of the outermost shell, *i.e.,* in second period, $n = 2$, this shell has four orbitals (one $2s$ and three $2p$) which can have eight electrons, hence second period contains 8 elements from atomic number 3 to 10.

26. Mendeleef failed to assign positions to isotopes on the basis of atomic mass according to his periodic law.

27. Variable valency is the characteristic feature of transition elements.

28. Since effective nuclear charge increases from left to right in a period thus, atomic radii decreases.

30. Ionic radii increases in a group.

31. Cation has small size than parent atom and anion has larger size than parent atom.

33. Nuclear mass (protons + neutrons) does not affect the valence shell, only protons, *i.e.,* nuclear charge affects the valence shell.

34. All the given species have same number of electrons ($10e^-$)

Therefore, all are isoelectronic.

35. The ionic radii of isoelectronic species decreases with increase in atomic number (as magnitude of the nuclear charge increases with increase in atomic number). Therefore, their ionic radii increase in the order
Isoelectronic ions $= Al^{3+} < Mg^{2+} < Na^+ < F^- < O^{2-} < N^{3-}$
Atomic number, $Z = 13 \quad 12 \quad 11 \quad 9 \quad 8 \quad 7$

36. As the nuclear charge per electron is maximum in P^{5+}. therefore, its size is smallest.

38.

Period	Group 15	Group 16
2nd period	N	O
3rd period	P	S

Ionisation enthalpy of nitrogen ($_7N = 1s^2, 2s^2, 2p^3$) is greater than oxygen ($_8O = 1s^2, 2s^2, 2p^4$) due to extra stable exactly half-filled $2p$-orbitals. Similarly, ionisation enthalpy of phosphorus ($_{15}P = 1s^2, 2s^2, 2p^6, 3s^2, 3p^3$) is greater than sulphur ($_{16}S = 1s^2, 2s^2, 2p^6, 3s^2, 3p^4$).

On moving down the group, ionisation enthalpy decreases with increasing atomic size. So, the order is
$S < P < O < N \rightarrow$ First ionisation enthalpy increases.

39. Non-metallic character across a period (left to right) increases but on moving down the group it decreases. So, the order is
$P < S < N < O \rightarrow$ Non-metallic character increases.

40.

Period	Group 13	Group 14
2nd period	Boron	Carbon
3rd period	Aluminium	Silicon

Ionisation enthalpy increases along a period (as we move from left to right in a period) with decrease in atomic size and decreases down the group with increase in atomic size. Hence, carbon has the highest first ionisation enthalpy.

47. Nitrogen has more ionisation potential than carbon and oxygen because its outermost orbit is half-filled. So the order is $C < N > O$.

48. S^{2-} has the largest size and hence, has the lowest ionisation energy.

49. $_6C \longrightarrow 1s^2, 2s^2, 2p^2$
$_5B \longrightarrow 1s^2, 2s^2, 2p^1$

In first case IE_1 of $C > IE_1$ of B. Since, carbon is smaller than B in size. But $IE_2(B) > IE_2(C)$ because electron are paired as well as present in inner *s*-orbital whereas for carbon it will be still in $2p$-orbital and in unpaired state.

50. Ionisation potential decreases down the group.

51. The electronic configuration of nitrogen is

$$_7N = 1s^2, 2s^2, 2p^3$$

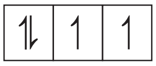
$$2p^3 \quad \underbrace{\boxed{\uparrow \mid \uparrow \mid \uparrow}}_{\text{half-filled } p\text{-orbital}}$$

Due to the presence of half-filled *p*-orbitals a large amount of energy is required to remove an electron from nitrogen. Hence, first ionisation energy of nitrogen is greater than that of oxygen.

The electronic configuration of oxygen is

$$_8O = 1s^2,\ 2p^2,\ 2p^4$$

$2p^4$



The other reason for the greater IP of nitrogen is that in oxygen, there is a greater inter-electronic repulsions between the electrons present in the same *p*-orbital which counter balance the increase in effective nuclear charge from nitrogen to oxygen.

52. Be has higher $\Delta_i H$ (ionisation enthalpy) than boron. In both the cases, the electron to be removed belongs to the same principal shell. In $_4Be = (1s^2,\ 2s^2)$, it is 2*s*-electron while in boron $_5B = (1s^2, 2s^2, 2p^1)$ it is 2*p*-electron. The penetration of a 2*s*-electron to the nucleus is more than that of a 2*p*-electron. It means 2*s*-electrons are more strongly attracted by the nucleus than 2*p*-electrons. Therefore, higher amount of energy is required to remove a 2*s*-electron than a 2*p*-electron. Hence, Be has higher $\Delta_i H$ than B.

53. O has lower $\Delta_i H$ than N and F

$$_7N = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1;$$
$$_8O = 1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1;$$
$$_9F = 1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^1$$

Across a period, ionisation enthalpy increases as we move from left to right due to decrease in atomic size. But $\Delta_i H$ of nitrogen is greater than oxygen. It is becasue of the more stable electronic configuration (exactly half filled orbitals are more stable) of nitrogen, so it is difficult to remove an electron from nitrogen than from oxygen. That's why oxygen has lower ionisation enthalpy than nitrogen and fluorine.

56. The electron affinities of some of the elements of second period (*i.e.*, N, O, F, etc.) are however, lower than the corresponding elements (*i.e.*, P, S, Cl, etc.) of the third period. This is due to the reason that the elements of second period have the smallest atomic size amongst the elements in their respective groups. As a result, there are considerable electron-electron repulsion within the atom itself and hence, the additional electron is not accepted with the same ease as is the case with the remaining elements in the same group.

58. F has the highest electronegativity because of its smallest size.

59. If the EN difference is 1.9, then bond is 50% ionic. The difference in electronegativity is 2.8, therefore, percentage ionic character due to EN difference of 2.8 is

$$\frac{2.8}{1.9} \times 50 = 73.6\%$$

61. Fluorine being most electronegative atom, has a high tendency to gain electron. Thus, it readily forms anions.

62. $_3Li - 1s^2,\ 2s^1$ donates one electron easily.

63. $Z = 2, 8, 8, 1$. Because it would donate electron more easily.

64. Halogens are most electronegative. Their general configuration is ns^2np^5.

65. Fluorine has low EA than chlorine because of smaller size of fluorine and compact 2*p*-orbital where interelectronic repulsion is more.

67. Second electron affinity of oxygen is endothermic and greater than first electron affinity, which is exothermic.

68. On moving down the group, electronegativity decreases because atomic size increases. Fr has the largest size, therefore it is least electronegative.

69. Electron gain enthalpy of F is less negative than that of Cl because when an electron is added to F, the added electron goes to the smaller $n = 2$ quantum level and suffers repulsion from other electrons present in this level. In case of Cl, the added electron goes to the larger $n = 3$ quantum level and suffers much less repulsion from other electrons.

74. Valency is according to valence shell configuration which here is $1s^2, 2s^2, 2p^3$, *i.e.*, 5.

75. Fluorine is more reactive than chlorine, bromine and iodine.

76. Oxidising power decreases in a group.

77. In a period, from left to right basic character of oxides decreases, thus Na_2O is most basic.

Round II

1. Periodic Table reflects trends in physical and chemical properties of the elements.

2. Atomic radius decreases on going from left to right in a period. Thus, size of O > F. As O^{2-} and F^- are isoelectronic, therefore, size of $O^{2-} > F^-$.

3. $Sc^{3+} > Cr^{3+} > Fe^{3+} > Mn^{3+}$, the correct order is $Cr^{3+} > Mn^{3+} > Fe^{3+} > Sc^{3+}$.

4. First ionisation enthalpies of two isotopes of the same element are expected to be same because ionisation enthalpy depends upon the electronic configuration and effective nuclear charge. Isotopes of an element have same electronic configuration and thus, the same nuclear charge.

5. The size of isoelectronic species; F^-, Ne and Na^+ is affected by nuclear charge (Z). With increase in nuclear charge (atomic number), the size of the isoelectronic species decreases.

6. Ionisation energy is the amount of energy required to remove the electron from the ground state (E_1) to infinity (E_∞).

$$E_1 = -2.18 \times 10^{-18}\ \text{J}$$
$$E_\infty = 0$$

$$\Delta E = E_{\infty} - E_1 = 0 - (-\,2.18 \times 10^{-18}\ \text{J})$$
$$= 2.18 \times 10^{-18}\ \text{J}$$

Ionisation enthalpy per hydrogen atom $= 2.18 \times 10^{-18}$ J

$\therefore$ Ionisation enthalpy per mole of hydrogen atoms

$$= 2.18 \times 10^{-18} \times 6.022 \times 10^{23}\ \text{Jmol}^{-1}$$
$$= 13.12 \times 10^{5}\ \text{J mol}^{-1}$$

Note Energy of an electron at infinity = 0.

7. Ionic radii decreases significantly from left to right in a period among representative elements.

8. Ionic radius $\propto \dfrac{1}{Z_{\text{eff}}}$

Since, P^{5+} has higher Z_{eff} as compared to P^{3+}, it has smaller ionic radii.

9. Down the group, size of atom increases. Therefore, bond length of LiF is less than that of NaF.

10. In K_2CrO_4, the oxidation state of Cr is $+6$. Therefore, Cr has the minimum radius in K_2CrO_4.

11. IE (II) of Na is higher than that of Mg because in case of Na, the second e^- has to be removed from the noble gas core while in case of Mg removal of second e^- gives a noble gas core.

Mg has high first ionisation potential than Na because of its stable ns^2 configuration.

12. $E_1 < E_2$, because second IE is greater than first IE.

13. $K^+ \longrightarrow K^{2+} + e^-$. Since, electron is to be removed from stable configuration.

14. Since, the IVth IE is very high, *i.e.*, electron is to be removed from stable configuration, thus it has 3 valence electrons.

15. Generally in a period, IE increases but nitrogen due to the presence of half-filled *p*-subshell (stable configuration) has higher IE as compared to its consecutive elements. Thus, the IE of nitrogen is 14.5.

16. $M^{2+} \longrightarrow M^{3+}$, after the removal of $2e^-$, the nuclear charge per electron increases due to which high energy is required to remove $3e^-$.

17. Although O^{2-} has noble gas configuration but its formation is unfavourable because here, the electronic repulsion outweigh the stability gained by achieving inert gas configuration.

18. In order to belong with the same family, the outer configuration must be the same. Thus, element with $[\text{Ne}]\,3s^2 3p^5$ configuration belongs to a different family.

19. On passing from left to right in a period, acidic character of the normal oxides of the element goes on increasing with increase in electronegativity. Thus, the correct order is

$$N_2O_3 > CO_2 > B_2O_3 > BeO > Li_2O$$

20. On moving along a period, ionisation enthalpy increases. Thus, the order of ionisation enthalpy should be as follows :

$$F > O > N$$

But N has half-filled configuration, therefore it is more stable than O and has higher ionisation enthalpy.

21. Generally electron affinity decreases on moving down a group but Cl_2 has higher electron affinity than F_2 due to its larger size as compared to F. Thus, chlorine has the highest electron affinity value.

So, the correct order of electron affinity will be

$$Cl_2 > F_2 > Br_2$$

22. $\text{Cr}(24) = [\text{Ar}]_{18}\ 3d^5, 4s^1$

Chromium after losing one electron gain stable configuration due to the presence of half-filled *d*-orbitals, therefore its second ionisation enthalpy is highest.

23. Element with *A*, *B* and *D* configuration belong to second period. *D* being a halogen (*i.e.,* because of its smaller size in the period) has the highest ΔH_e among the given followed by *B*. *A* is an inert gas, so ΔH_e is zero or negative. Thus, the correct order of ΔH_e is $A < C < B < D$.

24. The correct order of electron gain enthalpy is

$$O < S < F < Cl$$

Element	O	S	F	Cl
Electron gain enthalpy (in eV)	1.48	2.07	3.45	3.61

25. O^{2-} and N^{3-} both are isoelectronic but differ in the charge possessed by them. As the negative charge increases, the electrons are held less and less tightly by the nucleus, therefore, radius increases from O^{2-} to N^{3-}.

26. The ionisation energy increases with increase in atomic number in a period. The trend is irregular among *d*-block elements.

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
IE° (kJ/mol)	631	656	650	652	717	762	758	736	745	905

Hence, correct order is Zn > Fe > Cu > Cr.

27. All the given elements are of same period and along a period atomic radii decreases because effective nuclear charge increases. Thus, the order of atomic radii is

$$O < N < C < B < Be$$

or Be = 111, O = 66, C = 77, B = 88, N = 74.

28. (ii) is the most reactive non-metal because of its higher IE and $\Delta_{eg}H$.

(i) is the most reactive metal because of its lowest Ist IE. [There is a larger difference in IE_1 and IE_2 in case of (i)]

(iv) is a least reactive element because of its high IEs and positive $\Delta_{eg}H$.

(iii) is a bivalent metal because of less difference in ΔH_1 and ΔH_2.

29. If Aufbau rule is not followed then 19th electron in K enters in $3d$ sub-shell, not in $4s$.

30. Size $\propto \dfrac{1}{Z_{\text{eff}} \text{ or nuclear charge}}$

Thus, the correct order of size is

$$\text{Br}^- > \text{S}^{2-} > \text{Cl}^- > \text{Na}^+ > \text{Mg}^{2+} > \text{Be}^{2+}$$

31. $\text{Ce}_{58} = [\text{Xe}]\, 4f^2\, 5d^0\, 6s^2$

$\text{Sn}_{50} = [\text{Kr}]\, 4d^{10}\, 5s^2\, 5p^2,$

$\text{Yb}_{70} = [\text{Xe}]\, 4f^{14}\, 6s^2$

$\text{Lu}_{71} = [\text{Xe}]\, 4f^{14}\, 5d^1\, 6s^2$

Among lanthanoids size reduces from La to Lu thus, the order of size is Ce > Yb > Lu. Size of Sn is greater than Ce.

32. As the negative charge increases, effective nuclear charge decreases, thus size increases. Thus, the order of ionic radii is

$$\text{F}^- < \text{O}^{2-} < \text{N}^{3-}, 1.36 < 1.40 < 1.71$$

33. In lanthanide series, size decreases from La to Lu due to lanthanide contraction. Thus, La is largest among lanthanides.

34. $1s^2, 2s^2, 2p^6, 3s^2$ configuration after losing two electrons acquire noble gas configuration, thus a large amount of energy is required to remove a third electron *i.e.,* there is a large jump between the values of second and third IEs.

35. First IP of Be > B because of stable ns^2 configuration.

36. Halogens (ns^2np^5) after getting one electron occupy ns^2np^6 configuration, thus have EA_2 zero.

37. For both group I and VII elements, atomic radii increases on moving down the group.

38. The outer electronic configuration = s^2p^1

Thus, valency $= 2 + 1 = 3$

Therefore, the formula of the oxide is X_2O_3.

Since, it is an oxide of III group element, its nature is amphoteric.

39. Li and Mg show diagonal relationship, thus have same size. Rb^+ and O^{2-} also have similar size.

40. (a) $r_{\text{metallic}} > r_{\text{covalent}}$ because covalent bond formation involves the overlapping of orbitals.

(b) Due to lanthanide contraction.

(c) If screening effect increases, the valence shell electron get loosely bound. Hence, ionisation energy decreases.

(d) Be and Mg have ns^2 configuration, *i.e.,* stable configuration, thus have higher IE.

41. Cl and S due to less electronic repulsion, gain one electron more readily in comparison to other elements of their group.

42. Cl has more negative electron gain enthalpy than fluorine. All other given statements are correct.

43. $\text{K}^+ = 19 - 1 = 18, \quad \text{P}^{3-} = 15 + 3 = 18$

$\text{Ca}^{2+} = 20 - 2 = 18, \quad \text{S}^{2-} = 16 + 2 = 18$

$\text{Sc}^{3+} = 21 - 3 = 18, \quad \text{Cl}^- = 17 + 1 = 18$

$\text{Cl}^- = 17 + 1 = 18, \quad \text{K}^+ = 19 - 1 = 18$

So the only sets $\text{K}^+, \text{Ca}^{2+}, \text{Sc}^{3+}, \text{Cl}^-$ and $\text{P}^{3-}, \text{S}^{2-}, \text{Cl}^-, \text{K}^+$ contain isoelectronic ions.

44. Symmetrical configuration (half-filled) is stable. Oxygen also gains half-filled configuration by losing an electron.

45. ${}_{25}\text{Mn} = 3d^5, 4s^2; \quad {}_{24}\text{Cr} = 3d^5, 4s^1; \quad {}_{26}\text{Fe} = 3d^6, 4s^2$

Electron affinity of an element depends upon electronic configuration.

46. The phenomenon in which the penultimate shell, *i.e.,* $(n-1)$ electrons act as shield in between nucleus and valence shell electrons thereby reducing the effective nuclear charge is known as shielding effect.

47. Both the statements are correct but statement II is not a correct explanation for I as IE increases along a period because effective nuclear charge increases and atomic size decreases.

48. Electron gain enthalpy becomes less as we go down a group size of the atom increases. This is because in group screening effect increase on going downward and the added electron would be a farther from the nucleus.

49. The long form of the Periodic Table contain element with atomic numbers 1 to 118.

50. The element which is just above the element with atomic number 43 in the same group is Mn(at. no. = 25).

Electronic configuration $= 1s^2, 2s^2, 2p^6, 3s^2\, 3p^6, 3d^5, 4s^2$

51. All the halogens have seven electrons ($ns^2\, np^5$) in their outermost shell.

The elements with atomic numbers 35, 53 and 85 are all halogen because the element with atomic number 35, 53 and 85 have seven electrons ($ns^2\, np^5$) in their outermost shell.

52. $\text{Zn} = (1s^2)\, (2s^2, 2p^6)\, (3s^2, 3p^6)\, (3d^{10})\, (4s^2)$

$S = 18 \times 1 + 10 \times 0.85 + 1 \times 0.35 = 26.85$

53. $\text{Al}_{13} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^1$

$\text{Ga}_{31} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^1$

Electronic configuration reveals that extra 3*d* electron are present in case of Ga which have lower shielding tendency and hence, Z_{eff} is more. Because of this atomic size decreases and becomes almost equal to Al.

54. Higher is the positive charge, smaller is the size of the atom.

55. Ca^{2+} has the electronic configuration 2, 8, 8 but $\text{Mg}^{2+}, \text{O}^{2-}$ and F^- are all isoelectronic with the configuration 2, 8.

56. Down the group size increases with increase in nuclear charge. Then, Rb^+ is largest among the given.

57. The least reactive element is element (V) because it has highest $\Delta_i H_1$ (first ionisation enthalpy) and positive electron gain enthalpy ($\Delta_{eg} H$). The element (V) is an inert gas because inert gases have positive electron gain enthalpy. The given values for element (V) match with He.

58. The metal which can form a stable binary halide of the formula MX_2 is element (VI). Element VI is alkaline earth metal because it has low $\Delta_i H_1$ but higher than that of alkali metals. Moreover, the difference between $\Delta_i H_1$ and $\Delta_i H_2$ is very less. The given values for element VI match with Mg.

59. Element I has low $\Delta_i H_1$ but a very high $\Delta_i H_2$. It has less negative electron gain enthalpy. So, element (I) is alkali metal. The given values for element I match with Li. Lithium forms predominantly stable covalent halide of the formula MX.

60. For isoelectronic species, $r_n \propto \frac{1}{Z}$

Species	Z	Electrons
Cl^-	17	18
Ca^{2+}	20	18
K^+	19	18
S^{2-}	16	18

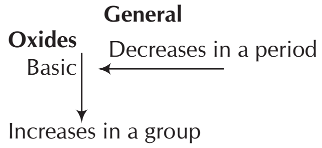
Thus, ionic size is in order

$$Ca^{2+} < K^+ < Cl^- < S^{2-}$$

61. Oxides when dissolved in water form hydroxides.

$$Na_2O + H_2O \longrightarrow 2NaOH$$
$$MgO + H_2O \longrightarrow Mg(OH)_2$$
$$Al_2O_3 + 3H_2O \longrightarrow 2Al(OH)_3$$

Smaller the size of cation, larger the charge, greater the polarising power of cation, hence greater the covalent character, hence smaller the basic nature.



Charge $Al^{3+} > Mg^{2+} > Na^+ = K^+$

Size $Al^{3+} < Mg^{2+} < Na^+ < K^+$

Polarising power $Al^{3+} > Mg^{2+} > Na^+ > K^+$

Basic nature of oxides

$$Al_2O_3 < MgO < Na_2O < K_2O$$

62. As we go down the group in Periodic Table, atomic size increases, force of attraction for the added electron decreases, hence electron gain enthalpy decreases.

$$X(g) + e^- \longrightarrow X^-(g)$$

Actual order is $Cl > F > Br > I$

The fact that fluorine has a less electron gain enthalpy than chlorine seems to be due to the relatively greater effectiveness of $2p$-electron in the small F-atom to repel the additional electron entering the atom than do $3p$-electrons in the larger Cl-atom.

63. $O^{2-}, F^-, Na^+, Mg^{2+}$ and Al^{3+} are isoelectronic species and higher the nuclear charge, smaller the size of isoelectronic species.

64. The ionic radius in general increases on moving top to bottom and further decreases on moving from left to right. So, the correct order is

$$\underset{0.98\,Å}{Na^+} > \underset{0.68\,Å}{Li^+} > \underset{0.65\,Å}{Mg^{2+}} > Be^{2+}$$

65. Higher the charge/size ratio, more is the polarising power.

$\therefore$ $K^+ < Ca^{2+} < Mg^{2+} < Be^{2+}$

66. Isoelectronic means having same number of electrons, $K^+, Cl^-, Ca^{2+}, Sc^{3+}$ (all are having 18 electrons).

67. Li^+ is having largest hydrated ionic size while Rb^+ is having smallest.

Smaller the size, greater the mobility.

68. Examine the positions in Periodic Table

B C N O F
P S

Phosphorus is having stable half-filled configuration.

Hence, order is B < S < P < F.

69. In alkali metal reactivity increases down the group as electropositivity increases, but for halogens F_2 is more reactive as on moving down molecular stability increases.

70. (a) Metallic radii increases in a group from top to bottom.

Thus, Li < Na < K < Rb is true.

(b) Electron gain enthalpy of Cl > F and decreases along a group.

Thus, I < Br < F < Cl is true.

(c) Ionisation enthalpy increases along a period from left to right but due to the presence of half-filled orbitals in N, ionisation enthalpy of N > O.

Thus, B < C < N < O is incorrect.

71. All the ions belong to same period, thus for them cations will be smaller than anions. Now, O^{2-} and F^- are isoelectronic and $r_n \propto \frac{1}{Z}$. Thus, ionic radius of $O^{2-}\ (Z = 8) > F^-\ (Z = 9)$

72. $O^-(g) + e^- \longrightarrow O^{2-}(g);\ \Delta H^\circ = 844\ \text{kJ mol}^{-1}$.

This process is unfavourable in the gas phase because the resulting increase in electron-electron repulsion overweighs the stability gained by achieving the noble gas configuration.

73. While moving along a group from top to bottom, acidic nature of oxides decreases and along a period from left to right, acidic nature increases.

$$\begin{array}{ccccc} & Al & Si & P & S \\ Z & 13 & 14 & 15 & 16 \\ & Al_2O_3 & SiO_2 & P_2O_3 & SO_2 \\ \multicolumn{5}{c}{\xrightarrow{\hspace{6cm}}} \\ & \text{amphoteric} & \text{acidic} & \text{max.} & \text{acidic} \end{array}$$

Thus, $Al_2O_3 < SiO_2 < P_2O_3 < SO_2$

74. According to periodic law, all physical and chemical properties of elements are periodic function of their atomic number.

75. Due to lanthanide contraction there occurs net decrease in size. Only 0.85Å is smaller one.

76. $Fe^+\ (26) = [Ar]\,3d^6, 4s^1$

$Mn^+\ (25) = [Ar]\,3d^5\ 4s^1$

$V^+ (23) = [Ar]\,3d^2\ 4s^2$

$Cr^+\ (24) = [Ar]\,3d^5\ 4s^0$

(By first IP)

The electronic configuration of Cr^+ is most stable, hence formation of Cr^{2+} by second IP requires maximum enthalpy.

77. r_n (radius) $\propto \frac{1}{Z}$

9 Hydrogen

JEE Main MILESTONE

- Occurrence of Hydrogen
- Position of Hydrogen in the Periodic Table
- Isotopes, Allotropes and Molecular forms of Hydrogen
- Dihydrogen or Hydrogen Gas
- Different Atomic forms of Hydrogen
- Water
- Heavy Water or Deuterium Oxide (D_2O)
- Hydrogen Peroxide (H_2O_2)
- Hydrides

9.1 Occurrence of Hydrogen

Hydrogen is the most abundant element in the universes (70% of universe's total mass). However, it does not occur in the earth's atmosphere in its free form because of the absence of enough gravitational pull to hold the lighter hydrogen molecules but forms 90% of Sun's atmosphere. The giant planets Jupiter and Saturn consist mostly of hydrogen.

9.2 Position of Hydrogen in the Periodic Table

Hydrogen consists of 1 proton in its nucleus with 1 planetary electron present in the s-orbital of K-shell or first orbital. *Neutron is absent in its nucleus.* Thus, its electronic configuration is $1s^1$. This configuration is responsible for dual nature of hydrogen, *i.e.,* behaviour like an electropositive element (or alkali metals) and as an electronegative element (or halogens).

Due to its resemblance with alkali metals as well as halogens, its position is uncertain in the Periodic Table.

Hydrogen, the lightest element, is the first member of the Periodic Table. It was first isolated by an english chemist and physicist ***Henry Cavendish*** *but the name hydrogen was given by* ***Lavoisier*** *due to its water producing nature.*

(a) Resemblance with Alkali Metals

Hydrogen shows following resemblance with alkali metals

1. All (including hydrogen) have similar outermost electronic configuration, *i.e.,* ns^1.

H—$1s^1$

Li—$1s^2, 2s^1$

Na—$1s^2, 2s^2 2p^6, 3s^1$

K—$1s^2, 2s^2 2p^6, 3s^2, 3p^6, 4s^1$

Rb—$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6, 5s^1$

Cs—$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10}, 5s^2 5p^6, 6s^1$

2. All of them are strongly electropositive, *i.e.,* have tendency to lose solitary electron of their outermost shell and to change into unipositive ions.
3. Normal valency of all is 1.
4. All form stable oxides (like H_2O, Na_2O, K_2O etc.) and peroxides (like H_2O_2, Na_2O_2 etc).
5. All are good reducing agents due to their high electropositive character.

(b) Resemblance with Halogens

Hydrogen shows following similarities with halogens.

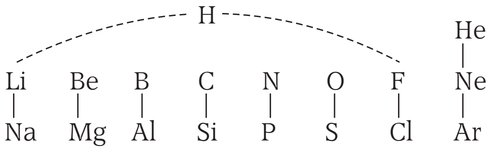
1. Hydrogen, like halogens, have the tendency to gain an electron, thus change to H^- ion (hydride ion) and acquire the stable configuration ($1s^2$).
2. Ionisation energy of hydrogen is 313 kcal. Halogens also show the ionisation energy of same order, *i.e.,* fluorine = 402 kcal; chlorine = 300 kcal; bromine = 273 kcal; iodine = 241 kcal.
3. In its molecular state, hydrogen (H_2) is a gas. Similarly among halogens F_2 and Cl_2 are gases; Br_2 is volatile liquid and I_2 is a volatile solid.
4. All of them have **diatomic configuration** in their molecular state.
5. Hydrogen in organic compounds can be replaced by halogens.

(c) Dissimilarities with Halogens

Hydrogen and halogens also have some points of differences

1. Hydrogen has much smaller tendency to form H^- ions as compared to halogens.
2. Electron affinity of hydrogen (17.3 kcal/mol) is much smaller than that of halogens (more than 70 kcal/mol).

It is, therefore, suggested that hydrogen be alloted a separate position and not grouped with either alkali metals or halogens. Thomson assigned a separate independent position to hydrogen on the top of the Periodic Table as shown below.



This does not disturb the symmetry of the table and there is no violation of periodic law.

In some respects, hydrogen also resembles carbon of the group IV, since both have a half-filled shell of electrons.

H 1 (half of first shell maximum capacity of 2 electrons)

C 2, 4 (half of second shell maximum capacity of 8 electrons).

There are a number of similarities between hydrogen and organometallic compounds since the group CH_3— and H— both have one remaining valency. Thus, the position of hydrogen is not fixed and hydrogen is best treated as a group on its own. Hydrogen is sometimes referred as a **'roque element'.**

However, on the basis of its electronic configuration ($1s^1$) hydrogen is placed above lithium in the first group of Bohr's Periodic Table *but still, it is not considered as the member of that group.*

9.3 Isotopes, Allotropes and Molecular forms of Hydrogen

Hydrogen exists in several forms that are described below one by one.

Isotopes

There are three known isotopes of hydrogen, each possessing an atomic number 1 and atomic mases 1, 2 and 3 respectively. These are named as protium, (^1H) deuterium (^2H or D) and tritium (^3H or T).

The most common is the ordinary hydrogen, usually called **protium** with atomic mass 1.008123. It consists of one proton in the nucleus and an electron revolving around it. This isotope constitutes 99.984 per cent of the total hydrogen available in nature.

The second isotope of hydrogen is called **heavy hydrogen** or **deuterium**. It consists of one proton and one neutron in the nucleus and an electron revolving around it. Its atomic mass is 2.0142. It constitutes only 0.016 per cent of the total hydrogen occurring in nature. It is represented by the symbol D or $_1^2H$.

The third isotope of hydrogen is called **tritium.** It consists of one proton and two neutrons in the nucleus and an electron revolving around it. Its atomic mass is 3.0170. It constitutes only 1×10^{-15} per cent of the total natural hydrogen. This isotope is unstable and exhibits radioactivity.

Allotropes

Ortho hydrogen (o-H_2) and *para* hydrogen (p-H_2); similarly *ortho* and *para* deuterium (o and p-D_2) and *ortho* and *para* tritium (o and p-T_2).

The *ortho* isomer shows *parallel spins* while *para* isomer shows *opposite spins or antiparallel spins of protons.*

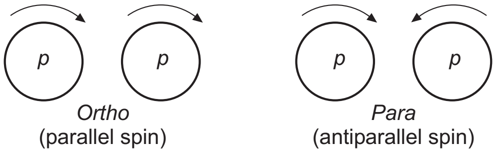


Fig. 9.1 *Ortho* and *para* hydrogen

The two forms differ in their physical properties like specific heat, thermal conductivity, boiling point, etc., but show similar chemical properties. Both the forms are interconvertible.

Para form has lower energy and at absolute zero, the gas contains 100% *para* form. Due to their interconvertible nature as the temperature rises, *para* form starts converting into *ortho* form. At room temperature, these are in dynamic equilibrium with equilibrium mixture containing 75% *ortho* form and 25% *para* form. On decreasing the temperature, quantity of *para* form increases in the solution. Thus, it is clear that *para hydrogen is favoured at lower temperature.*

Its three times more presence at room temperature suggests that *ortho* hydrogen is more stable than *para* hydrogen at room temperature. *Ortho* and *para* interconversion is a slower process in the absence of catalyst. The suitable catalyst include activated charcoal, atomic hydrogen, metals, *e.g.,* like Fe, Ni, Pt, W, etc., along with paramagnetic substances like O_2, NO, NO_2, Co^{2+}, Cr_2O_3 etc.

Molecular Forms

Due to its high reactivity protium or hydrogen combines with its own atoms or with the atoms of isotopes and exists in molecular forms as $^1H_2$ (dihydrogen), $^2H_2$ or D_2 (dideuterium), $^3H_2$ or T_2 (ditritium), along with HD, HT, DT etc.

Sample **Problem 1** *What is the mass ratio of isotopes of hydrogen?* **[NCERT]**

(*a*) 1:1:1
(*b*) 1 : 2 :1
(*c*) 1 : 2 : 3
(*d*) 1 : 3 : 2

Interpret (*c*) Protium (H^1), deuterium (H^2) and tritium (H^3) are three isotopes of hydrogen. Thus, their mass ratio is 1 : 2 : 3.

9.4 Dihydrogen or Hydrogen Gas

Being highly reactive, hydrogen always exists in its diatomic form, called the dihydrogen or simply the hydrogen.

Hot Spot 1

GENERAL METHODS of Preparation of Dihydrogen

Analysis of previous years' examination papers reveals that the preparation of hydrogen is an important topic of this chapter and generally question from this topic can be seen in JEE Main AIEEE examination. The level of the question is moderate.

(a) Laboratory Method

In laboratory, dihydrogen is produced by the reaction of Zn with dilute H_2SO_4 as,

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2\uparrow$$

Actual changes takes place here are,

$$Zn \longrightarrow Zn^{2+} + 2e^-$$
$$H_2SO_4 \longrightarrow H^+ + HSO_4^-$$
$$2H^+ + 2e^- \longrightarrow 2H \longrightarrow H_2\uparrow$$

(b) By the Electrolysis of Water

In the electrolysis method, water is electrolysed as

$$\underset{\text{(containing small amount of acid or alkali)}}{\text{Water}} \xrightleftharpoons[\text{using suitable electrodes}]{\text{Electrolysed}} \underset{\text{cathode}}{H_2\uparrow} + \underset{\text{anode}}{O_2\uparrow}$$

At cathode Hydrogen gas is liberated due to discharge of H^+ ions as,

$$2H^+ + 2e^- \longrightarrow 2H \longrightarrow H_2\uparrow$$

At anode Hydroxyl ions are discharged to give O_2 gas as,

$$2(OH)^- \longrightarrow H_2O + 2e^- + O$$
$$O + O \longrightarrow O_2\uparrow$$

Case I Suppose the hydrolysis is carried out in acidic medium (*e.g.*, in the presence of H_2SO_4) then at anode, SO_4^{2-} ions are not discharged (although present in much larger quantity) due to very high discharge potential of these ions as compared to that of OH^- ions.

Case II Similarly, if hydrolysis is carried out in the alkaline medium (*e.g.*, in the presence of KOH) then at cathode, K^+ ions are not discharged (although present in much large quantity) due to very high discharge potential of K^+ ions as compared to that of H^+ ion.

(c) By the Electrolysis of Barium Hydroxide Solution

Pure dihydrogen is prepared by the electrolysis of a warm concentrated solution of $Ba(OH)_2$ in hard glass U-tube with Ni electrodes. Here, H_2 is liberated at cathode and O_2 is liberated at anode. The H_2 liberated is passed over heated Pt gauze to remove O_2 as an impurity which is converted into H_2O. This H_2O is removed by passing the gas over solid KOH and P_2O_5. The H_2 gas formed is finally readsorbed over Pd foil. From here, it can be recovered whenever required by heating it to dull red heat.

For the above process $Ba(OH)_2$ *is preferred over* NaOH, *because, if any* CO_2 *is absorbed in the process,* $BaCO_3$ *is produced which being insoluble, settles down at the bottom and does not interfere with the process, while* Na_2CO_3 *(formed if we use* NaOH*) is soluble in water and may interfere in the process.*

(d) From Active and Moderately Active Metals

Active metals when reacts with water or any other protic solution, evolve hydrogen. Alkali metals are most active for this reaction. The reaction is violent in almost each case when we use any of the alkali metal for the purpose (least reactive is the Li and reactivity increases as we move down the group). Large amount of heat is given in the reaction and very often H_2 evolved catches fire.

However, not all the metals give this reaction. Among *s*-block elements, **Be does not react with water** (hot or cold) to evolve H_2, Mg reacts only with hot water (steam) while rest of the other members react with cold water in non-violent manner. Zn and Fe are even less reactive, they decompose water only when superheated steam is led over them at high temperature.

$$3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2\uparrow$$

Most other elements are far less reactive to displace H_2 from water. The process involves release of electrons by these metals which is taken up by H^+ present in the solution. The H^+ is then converted in atomic hydrogen. This atomic hydrogen combines with other similar atom to form molecular hydrogen.

Besides above written metals, elements like Sn and Al also give similar type of reactions but not with water. They give such type of reactions with dilute acid solutions.

Certain metals like Zn, Sn, Al react with alkali to evolve H_2 as,

$$2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2\uparrow$$
$$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2\uparrow$$
$$Sn + 2NaOH + H_2O \longrightarrow Na_2SnO_3 + 2H_2\uparrow$$

(e) From Ionic Hydrides

The ionic hydrides of **alkali and alkaline earth metals** also evolve H_2 on reaction with water as,

$$CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2\uparrow$$

Industrial Methods of Preparation of Dihydrogen

Besides the above written processes, the industrial preparation of dihydrogen involve following processes

(a) Electrolysis

In the **electrolysis process**, dihydrogen is produced by the electrolysis of water containing 15-20% H_2SO_4. Here also, H_2 is liberated at cathode while O_2 is liberated at anode.

(b) Bosch Process

In the **Bosch process,** dihydrogen is prepared through the reaction of water vapours (steam) by carbon as

$$\underset{\substack{\text{coke}\\ \text{at 400–660°C}}}{C} + \underset{\substack{\text{superheated}\\ \text{steam}}}{H_2O} \longrightarrow \underset{\boxed{\substack{\text{water gas}\\ \text{or } syn \text{ gas}}}}{CO + H_2}$$

$$\Big\downarrow \text{ Reacts with steam again in the presence of catalyst, usually a mixture of Fe, Cr and Co.}$$

$$CO_2 + H_2$$

The CO_2 is removed either by washing under pressure of 25–30 atmosphere or by reacting with KOH (alkali).

(c) Lane Process

In the *Lane process*, dihydrogen is produced as

$$\underset{\substack{\text{heated to}\\ \text{900°C}}}{3Fe} + \underset{\substack{\text{superheated}\\ \text{steam}}}{4H_2O} \longrightarrow Fe_3O_4 + 4H_2\uparrow$$

$$\Big\downarrow \text{ CO is passed over it}$$

$$\text{reduces to Fe}$$

(d) From Nelson or Castner Kellner Process

H_2 is also produced in **Nelson** or **Castner Kellner cell** by the electrolysis of brine solution (*aq* NaCl) in them.

(e) From Petrochemicals

Presently near about 77% of the industrial hydrogen is produced from petrochemicals *e.g.,* 18% from coal, 4% from electrolysis of brine solution and 1% from other sources.

Caution Point *H_2 and CO_2 can be easily separated from each other by bubbling the gaseous mixture through water in which CO_2 is fairly soluble and H_2 is virtually insoluble.*

$$H_2O + CO_2 \longrightarrow H_2CO_3$$

Sample Problem 2 *In the method of bulk preparation of hydrogen by electrolytic method, the role of electrolyte is* **[NCERT]**

(*a*) *decrease the boiling point of water*
(*b*) *increase the boiling point of water*
(*c*) *increase the ionisation of water*
(*d*) *increase the charge carrying particles in water*

Interpret (*d*) Electrolysis of acidified **water** using platinum electrodes gives hydrogen.

$$2H_2O(l) \xrightarrow[\text{Traces of acid/base}]{\text{Electrolysis}} 2H_2(g) + O_2(g)$$

The role of an electrolyte is to make water conducting by increasing the number of charge carrying particles, *i.e.,* ions.

Sample Problem 3 *Which of the following reactions increases the production of dihydrogen from synthesis gas?* **[NCERT Exemplar]**

(*a*) $CH_4(g) + H_2O(g) \xrightarrow[\text{Ni}]{1270\text{ K}} CO(g) + 3H_2(g)$

(*b*) $C(s) + H_2O(g) \xrightarrow{1270\text{ K}} CO(g) + H_2(g)$

(*c*) $CO(g) + H_2O(g) \xrightarrow[\text{Catalyst}]{673\text{ K}} CO_2(g) + H_2(g)$

(*d*) $C_2H_6 + 2H_2O \xrightarrow[\text{Ni}]{1270\text{ K}} 2CO + 5H_2$

Interpret (*c*) The process of producing *syn* gas or synthesis gas from coal is called 'coal gasification'.

$$\underset{\text{coal}}{C(s)} + \underset{\text{steam}}{H_2O(g)} \xrightarrow[\text{Ni}]{1270\text{ K}} \underbrace{CO(g) + H_2(g)}_{syn\text{ gas}}$$

The production of hydrogen can be increased by reacting carbon monoxide of the *syn* gas with steam in the presence of iron chromate as catalyst at 673 K.

$$CO(g) + H_2O(g) \xrightarrow{FeCrO_4,\ 673\text{ K}} CO_2(g) + H_2(g)$$

CO_2 is removed by scrubbing with a solution of sodium arsenite.

Physical and Chemical Properties of Dihydrogen

Various characteristics exhibited by dihydrogen or hydrogen gas are as follows

(a) Physical Properties

Hydrogen is a colourless, odourless, tasteless diatomic ($C_p/C_V = 1.40$) gas. It is the **lightest element known** (density = 0.0695 g/cc). Being non-polar H_2 molecules, have very weak intermolecular forces. Due to which its melting point and boiling point are very low. Its critical temperature is –236.9°. It can be liquefied at −252.8° and solidifies at −259.8°. Metals like Ni, Pt, Pd, Fe, Au, etc., can adsorb or occlude large volumes of H_2 gas at different temperatures (Pd can occlude 1000 times of its own volume).

The bonding forces within the H_2 molecule are exceptionally strong and hence, it is thermally stable.

(b) Reaction with Non-metals

On combination with non-metals (like O_2, N_2, F_2, Cl_2, Br_2, etc.), it forms covalent compounds (like H_2O, NH_3, HX etc.) at higher temperatures. However, it remains unreactive with above written elements at ordinary (room) temperatures because at ordinary temperatures, H_2 exists in molecular state in which atoms have stable He structure. To be converted into atomic hydrogen either high temperature (700–800°C) or a catalyst (like Ni, Pt, Pd, etc., which bring down the temperature to about 250°) is required after which H_2 molecules dissociate into atoms. These atoms then combine with non-metals to form requisite product.

(c) Reaction with Metals

On combination with metals (like Li, Na, K, Cs, Ca etc.), electrovalent hydrides are formed. These are good reducing agents and are infact good sources of H_2. The hydrides so formed can conduct electricity in fused or molten state and possess high melting points.

(d) Reducing Property

H_2 has the property to reduce the oxides of less electropositive elements, *e.g.,*

$$CuO + H_2 \longrightarrow Cu + H_2O$$

Similarly, $$Fe_3O_4 + 4H_2 \longrightarrow 3Fe + 4H_2O$$

Certain chlorides also get reduced as

$$2AgCl + H_2 \longrightarrow 2Ag + 2HCl$$

However, hydrogen does not have the ability to reduce the oxides of alkali metals and alkaline earth metals.

Uses of Dihydrogen

The important uses of dihydrogen are as follows :

1. Manufacture of NH_3 by Haber's process.
2. Manufacture of hydrocarbons and their derivatives.
3. Manufacture of HCl, metal hydrides etc.
4. Reduction of heavy metal oxides to metals in metallurgical processes.
5. In oxy-hydrogen and oxy-atomic hydrogen torches for cutting and welding.
6. Besides, dihydrogen is also used as rocket fuel, in bubble chambers as liquid hydrogen for the study of high energy particles and in fuel cells. Remember that *dihydrogen is considered as very good fuel as it does not cause any pollution and produces greater energy per unit mass of fuel as compared to gasoline or other fuels.*

9.5 Different Atomic forms of Hydrogen

The hydrogen can also be

Nascent Hydrogen (H)

It is the hydrogen produced in contact with the substance to be reduced. *Its sources are*

1. **Metal + protic solution,** *e.g.,* Zn/acid, Sn/acid, Na + alcohol, Zn/Cu couple + water or alcohol, Zn—Hg/HCl etc.
2. **Complex metal hydrides,** *e.g.,* $LiAlH_4$, $NaAlH_4$, $NaBH_4$ dibal-H (di *iso*butyl aluminium hydride) etc.
3. **Acidulated water** (by its electrolysis)

However, pratical existence of nascent hydrogen is not proven.

Active H is much more reactive because hydrogen at the moment of its formation is more reactive than the ordinary H_2 gas. For example, when ordinary hydrogen is passed through acidified potassium permanganate solution or ferric chloride solution, neither of them is reduced. However, when zinc pieces are added, both get reduced.

$$\begin{tikzcd} \text{Ordinary Hydrogen} \arrow[r] & \underset{\text{Purple coloured solution}}{KMnO_4/H_2SO_4} \arrow[r] \arrow[d, "\begin{array}{l}+\text{ Zn pieces}\\(Zn + \text{dil. } H_2SO_4 \rightarrow \text{Hydrogen liberated})\end{array}"] & \text{No change in colour as reduction does not occur} \\ & \begin{array}{c}\text{Decolourisation occurs,}\\ \textit{i.e.,}\text{ liberated hydrogen}\\ \text{reduces acidified } KMnO_4\end{array} & \end{tikzcd}$$

It is believed that a part of energy liberated in the reaction producing hydrogen become associated with hydrogen molecules and thus, make them hyper active.

Atomic Hydrogen

When hydrogen is passed through an electric arc established between two tungsten filaments, hydrogen is dissociated into atoms. This form of hydrogen is known as atomic hydrogen.

$$H_2 \underset{}{\overset{\text{Electric arc}}{\rightleftharpoons}} 2H - 104.5\,\text{kcal}$$

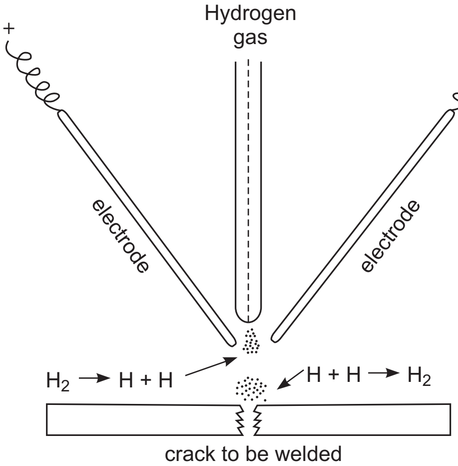


Fig. 9.2 Atomic hydrogen welding torch

The life period of atomic hydrogen is 0.3 s. It readily returns to ordinary form. This conversion is highly exothermic and used for welding purposes.

The important reactions of active hydrogen are

1. Reaction with non-metals like S, P, As, Sb and Bi etc., at ordinary (room) temperature to form hydrides, with O_2 (at very low temperature) to form H_2O_2. However, it does not combine with N_2.
2. Reaction with metals like Li, Na, Ca etc., at room temperature to form hydrides. It combines with metals like Ag and Hg at even very low temperature (– 180°C) to form their hydrides as

$$Ag + H \xrightarrow{-180^\circ C} AgH$$

$$Hg + H \xrightarrow{-180^\circ C} HgH$$

3. It is more powerful reducing agent as
   (i) It reduces oxides, chlorides and sulphides of certain metals like Cu, Hg, Ag, Bi etc., at ordinary (room) temperatures as

$$CuS + 2H \longrightarrow H_2S + Cu$$
$$CuO + 2H \longrightarrow Cu + H_2O$$
$$AgCl + H \longrightarrow Ag + HCl$$

   (ii) It reduces CO_2 and CO as

$$CO_2 + 2H \longrightarrow HCOOH$$

and $$CO + 2H \longrightarrow HCHO$$

   (iii) It reduces P_2O_5 as

$$P_2O_5 + 16H \longrightarrow 2PH_3 + 5H_2O$$

   (iv) It reduces alkali metal salts, *e.g.,* nitrates, amides and cyanides to free metals as

$$NaNO_3 + H \longrightarrow Na + HNO_3$$
$$NaNH_2 + H \longrightarrow Na + NH_3$$
$$NaCN + H \longrightarrow Na + HCN$$

   However, it does not affect the sulphates and halides of alkali metals.

4. Atomic hydrogen makes hydrogenation process more easier and at lower temperature than molecular hydrogen in organic compounds.

Active Hydrogen (H_3)

When steam of H_2 is subjected to silent electric discharge (at ordinary temperature), active hydrogen is produced. It is denoted by H_3 and have a half-life of 1/3rd of a second. It shows great chemical activity, *e.g.,* combines directly with Pb and S at ordinary temperature to form hydrides. Similarly, it reduces CuO to Cu at ordinary temperature.

Check Point 1

1. Why does hydrogen occur in diatomic form rather than in a monoatomic form under normal conditions?
2. Pure dihydrogen is not prepared by the electrolysis of NaOH. Explain, why?
3. Why is dihydrogen not preferred in balloons these days?
4. Dihydrogen combines with non-metals only at high temperature. Explain, why?
5. Hydrogen is evolved when an active or moderately active metal reacts with acid but not in case of less active metal. Explain.
6. How does the atomic hydrogen or oxy-hydrogen torch function for cutting and welding purposes? Explain.

[NCERT]

9.6 Water

Water is very essential for the existence of life. It constitutes about three fourth of earth's surface and two third of human body. *Its high importance is because of its ability to dissolve large number of substances.*

Although it is most often perceived as a liquid at normal atmospheric pressure, water exists as a solid below 0°C and as a gas above 100°C. The terms ice and steam are used to described the solid and gaseous states of water. Water occurs in the following natural forms

(i) **Rain water** It is the purest of natural waters. Usually, the first few showers of rain are not very pure as it absorbs atmospheric gases, but afterwards the rain water can be quite pure.

(ii) **Sea water** It is an impure water. It contains about 3.5 per cent of dissolved substances out of which 2.5 per cent is sodium chloride. This water is not fit for drinking purposes.

(iii) **Surface water** It includes streams, rivers and lakes is most important source of water for all purposes. It contains many soluble impurities and near cities gets contaminated with refuse and sewage.

The estimated world's water supply by oceans and in land seas is 97.34%, by polar ice and glaciers is 2.04 and by rivers is only 0.0001% of the total.

Purification of Drinking Water

The purification of water, needed for drinking purposes in towns and cities, requires two major operations (i) removal of the suspended impurities and (ii) destroying the bacteria. The removal of suspended materials is achieved by filteration through large filter beds made of layers of sand and gravel. The addition of aluminium sulphate helps in the coagulation of colloidal particles. Various methods are used for destroying bacteria such as aeration, chlorination, ozonisation, etc.

Structure of Water

H_2O is a bent molecule in gas phase with bond angle of 104.5° C and OH bond length of 95.7 pm. It is highly polar due to the presence of highly electronegative atom like oxygen in it.

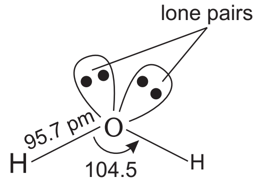


Fig. 9.3 Structure of H_2O in the gas phase

H_2O *in its solid form (ice) is less dense than its liquid form due to which an ice cube can float on water.* It is because in ice, each H_2O molecule is surrounded by three H_2O molecules in hexagonal honey comb manner as shown in the Fig. 9.4.

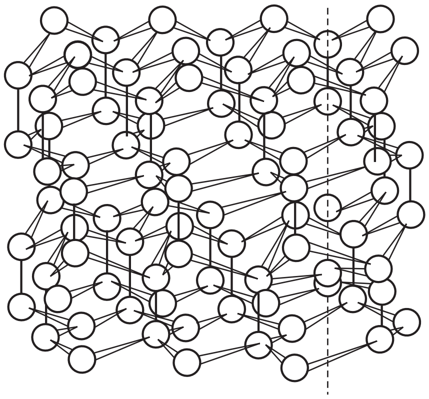


Fig. 9.4 Structure of H_2O in solid form (ice); (only O atoms are shown)

This arrangement gives rise to an open-cage like structure. There are evidently a number of 'holes' or open spaces. In such a structure lesser number of molecules are packed per mL. When ice melts a large number of hydrogen bonds are broken. The molecules, therefore, move into the holes or open spaces and come closer to each other than they were in solid state. This results sharp increase in the density. Thus, *ice has lower density than water and there is contraction in volume. The contraction continues from* 0°*C to* 4°*C* as the hydrogen bonds are broken progressively. Thus, *the density of water is maximum at* 4°*C*.

Physical Properties of Water

Water is a colourless, volatile liquid with many unusual properties. Some of the physical properties of water and heavy water (D_2O) are tabulated below.

Table 9.1 **Properties of Water and Heavy Water**

S. No.	Property	H_2O	D_2O
1.	Melting point	273 K	276.8 K
2.	Boiling point	373 K	374.4 K
3.	Temperature of maximum density	276.98 K	284.2 K
4.	Dielectric constant	78.39 K	78.06 K

Due to its high dielectric constant and polar nature, water is an excellent solvent for polar and ionic substances.

The peculiar properties of water in its condense phases (liquid and solid) are due to the presence of extensive hydrogen bonding between water molecules. Some of these properties include abnormally high freezing point, boiling point, heat of vaporisation, heat of fusion as compared to hydrides of other elements of same group.

Besides, *high specific heat, thermal conductivity and high heat capacity are the properties which are responsible for making water a vital content of our life.*

Chemical Properties of Water

The chemical characteristics exhibited by water are as follows

(a) Nature

Water is neutral in nature with pH 7. In pure water $[H^+] = [OH^-] = 10^{-7}$ at 25°C. Water undergoes self-ionisation (autoprotolysis) and hence, amphoteric in nature.

(b) Decomposition

Water containing either alkali or acid when electrolysed gets decomposed into H_2 and O_2.

$$2H_2O \longrightarrow 2H_2 + O_2$$

When heated at 2500°C, it breaks up into hydrogen and oxygen to a small extent (4%).

(c) Reaction with Metals

It reacts with active metals and evolves hydrogen. The reaction is highly exothermic in the case of alkali and alkaline earth metals and the hydrogen evolved catch fire.

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

$$Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2$$

It is decomposed by metals like Zn, Mg, Fe, etc., when steam is passed over hot metals.

$$Zn + H_2O \longrightarrow ZnO + H_2$$

$$3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2$$

$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$$

Pb and Cu decompose water only at a white heat. Ag, Au, Hg and Pt metals do not decompose water.

(d) Reaction with Non-metals

Fluorine decomposed cold water.

$$\left.\begin{array}{l} 2F_2 + 2H_2O \longrightarrow 2H_2F_2 + O_2 \\ 3F_2 + 3H_2O \longrightarrow 3H_2F_2 + O_3 \end{array}\right\} \text{Ozonised oxygen}$$

Chlorine decomposes cold water forming HCl and HClO.

$$Cl_2 + H_2O \longrightarrow HCl + \underset{\text{hypochlorous acid}}{HClO}$$

However, in the presence of sunlight only HCl is formed with liberation of oxygen.

$$2Cl_2 + 2H_2O \xrightarrow{\text{Sunlight}} 4HCl + O_2$$

(e) Hydrolysis

Many salts specially the salts of strong bases with weak acids, weak bases with strong acids and weak bases with weak acids undergo hydrolysis with water.

$$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$$

$$CH_3COONH_4 + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

$$FeSO_4 + 2H_2O \rightleftharpoons Fe(OH)_2 + H_2SO_4$$

However, salts of strong acid and strong base are not hydrolysed with water.

Some salts on hydrolysis form oxy compounds.

$$BiCl_3 + H_2O \longrightarrow \underset{\text{bismuth oxychloride}}{BiOCl} + 2HCl$$

$$SbCl_3 + H_2O \longrightarrow \underset{\text{antimony oxychloride}}{SbOCl} + 2HCl$$

Halides of non-metals are decomposed by water.

$$PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$$

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

$$SO_2Cl_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl$$

$$SiCl_4 + 3H_2O \longrightarrow H_2SiO_3 + 4HCl$$

(f) Reaction with Hydrides, Carbides, Nitrides and Phosphides

Water decomposes these compounds with the evolution of hydrogen, acetylene (or methane), ammonia, phosphine gas respectively.

$$CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2$$

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$

(g) Water in Associated Forms

The association of water is essentially of 5 types namely **coordinated water** (or water of crystallisation as found in $CuSO_4 \cdot 5H_2O$), *hydrogen bonded water, lattice water, zeolitic water and clathrate water.*

Zeolites have SiO_4 and AlO_4 tetrahedrons, linked together in a three dimensional open structure in which 4 or 6 membered rings predominates. The open structure permits the formation of channels and cavities in which water and other smaller molecules like NH_3, CO_2, C_2H_5OH etc., can be trapped.

Clathrate (Latin clathratus = enclosed or protected by crossbars or graftings) is a substance in which one component, **the host molecule,** crystallises with an open structure that contains holes or channels in which atoms or molecules of appropriate size like H_2O, NH_3, CO_2, inert gases, etc., can be trapped easily.

Tests of Water

1. A drop of water when added to anhydrous copper sulphate, changes its colour from white to blue.
2. Water reacts with CaC_2 to evolve acetylene which burns with bright flame.

Sample Problem 4 *Which of the following reaction involves hydration?* **[NCERT]**

(a) $PbS(s) + H_2O_2(aq) \longrightarrow$

(b) $CaO(s) + H_2O(g) \longrightarrow$

(c) $AlCl_3(g) + H_2O(l) \longrightarrow$

(d) $Ca_3N_2(s) + H_2O(l) \longrightarrow$

Interpret (*d*) Addition of water is called hydration.

(a) $PbS(s) + 4H_2O_2(aq) \longrightarrow PbSO_4(s) + 4H_2O(l)$ (Redox reaction)

(b) $CaO(s) + H_2O(g) \longrightarrow Ca(OH)_2(aq)$ (Hydrolysis reaction)

(c) $AlCl_3(g) + 6H_2O(l) \longrightarrow [Al(OH_2)_6]^{3+}(aq) + 3Cl^-(aq)$ (Hydrogen reaction)

(d) $Ca_3N_2(s) + 6H_2O(l) \longrightarrow 3Ca(OH)_2(aq) + 2NH_3(aq)$ (Hydrolysis reaction)

Among the given reactions, water is added only with $AlCl_3$ so it is an example for hydration reaction.

Sample Problem 5 *Give reasons lakes freeze from top towards bottom.* **[NCERT]**

Interpret Density of ice is less than that of liquid water. During severe winter, the temperature of lake water keeps on decreasing. Since, cold water is heavier, therefore, it moves towards bottom of the lake and warm water from the bottom moves towards surface. This process continues. The density of water is maximum at 277 K. Therefore, any further decrease in temperature of the surface water will decrease the density. The temperature of surface water keeps on decreasing and ultimately it freezes. Thus, the ice layer at lower temperature floats over the water below it. Due to this freezing of water into ice takes place continuously from top towards bottom.

Hard and Soft Water

Water can be soft or hard depending upon the nature of substances dissolved in it. **Hard water** on one hand contains bicarbonates, chlorides and sulphates of Ca and Mg while **soft water** is free from all such impurities. In hard water, soap does not leather as sodium sterate changes to corresponding Ca or Mg salt which precipitates out as,

$$2C_{17}H_{35}COONa + Ca^{2+}/Mg^{2+} \longrightarrow (C_{17}H_{35}COO)_2Ca/Mg + 2Na^+$$

Soft water, on the other hand, readily lathers with the soap.

The hardness of water may be temporary or permanent. The **temporary hardness** is due to the presence of bicarbonates of Ca and Mg while **permanent hardness** is due to the soluble sulphates and chlorides of Ca and Mg. The former one can be removed by

(a) Boiling

Through boiling soluble bicarbonates change to insoluble carbonates and get precipitated as

$$M(HCO_3)_2 \overset{\Delta}{\rightleftharpoons} MCO_3\downarrow + H_2O + CO_2\uparrow$$

here, M = Mg or Ca

(b) Clark's Process

In this process, addition of calculated quantity of lime causes precipitation of $CaCO_3$ as

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + 2H_2O$$

or $$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + Mg(OH)_2 + 2H_2O$$

Permanent hardness on the other hand can be removed by following methods.

(a) By Treatment with Na_2CO_3

$$CaSO_4 + Na_2CO_3 \rightleftharpoons CaCO_3\downarrow + Na_2SO_4$$

$$MgCl_2 + Na_2CO_3 \rightleftharpoons MgCO_3\downarrow + 2NaCl$$

(b) Using Calgon

Calgon is chemically sodium polymetaphosphate (or sodium hexa metaphosphate). The Ca^{2+} and Mg^{2+} ions present in hard water react with calgon to form soluble complexes as

$$\underset{\text{(from hard water)}}{2M^{2+}} + Na_2[Na_4(PO_3)_6] \longrightarrow \underset{\text{soluble}}{Na_2[M_2(PO_3)_6]} + 4Na^+$$

(here, $M^{2+} = Mg^{2+}$ or Ca^{2+})

The complexes, so obtained, do not cause hinderance in the lather formation.

(c) Using Permutit (Ion exchange method)

When hard water is treated with permutit (also called zeolite or hydrated sodium aluminium silicate, $Na_2Al_2Si_2O_8\cdot xH_2O$), the cations present in hard water are exchanged with Na^+ ions.

$$\underset{\text{sodium zeolite}}{Na_2Z} + \underset{\text{(from hard water)}}{MCl_2} \longrightarrow MZ + 2\,NaCl$$

(here, M = Ca or Mg)

In this process, zeolite gets exhausted because of its conversion into Ca and Mg salt. When 10% NaCl solution is percolated through it, the exhausted resin gets regenerated.

(d) Ion Exchange Resins

Ion exchange resins are the most popular water softners these days. The cation exchanger are granular insoluble organic acid resin having giant molecules with $—SO_3H$ or —COOH group while the anion exchanger contains giant organic molecules with basic groups derived from amines. Ion exchange resins remove all soluble minerals from water. The hard water is first passed through a bed of cation exchanger, which removes the cations like Na^+, Mg^{2+}, Ca^{2+} and others by exchanging with H^+ ions.

$$\underset{\text{resin}}{2RH} + Ca^{2+} \longrightarrow (R)_2Ca + 2H^+$$

The water coming from cation exchanger is acidic on account of free H^+ ions. This water is then passed through another bed containing anion exchanger. This exchanger removes anions like Cl^-, SO_4^{2-}, NO_3^- by exchanging with OH^- ions.

$$\underset{\text{resin}}{R—NH_3OH} + Cl^- \longrightarrow R—NH_3Cl + OH^-$$

The OH^- ions neutralise the H^+ ions.

$$H^+ + OH^- \rightleftharpoons H_2O$$

This process gives distilled water and can be used in laboratories.

The cation exchanger is regenerated by the action of an acid and the anion exchanger is regenerated by using an alkali solution.

Disadvantages of Hard Water

Hard water cannot be used

(i) for domestic purposes as it spoils the utensils lustre, result in scale formation and require a large amount of soap.

(ii) for boiler as it results in the formation of scales and bubbles, corroids the boiler surface.

(iii) in industries like dyeing, printing, textiles, sugar etc., as plenty of water is required.

Degree of Hardness

It is the measure of quantity of Ca and/or Mg salts in a certain volume of water and is defined as the number of parts by mass of $CaCO_3$ (equivalent to various Ca and Mg salts) present in a million parts by mass of water. It is measured in ppm.

Sample **Problem 6** *One litre of a water sample contains 1 mg of* $CaCl_2$ *and 1 mg of* $MgCl_2$*. The total hardness in terms of parts of* $CaCO_3$ *per* 10^6 *parts of water by mass is*

(a) 0.9 *ppm* (b) 1.05 *ppm*
(c) 1.95 *ppm* (d) 0.15 *ppm*

Interpret (c) 111 g of $CaCl_2 \equiv 100$ g of $CaCO_3$

$$1 \text{ mg of } CaCl_2 = \frac{100}{111} \times 1 \text{ mg of } CaCO_3 = 0.9 \text{ mg } CaCO_3$$

$$95 \text{ g of } MgCl_2 \equiv 100 \text{ g of } CaCO_3$$

$$1 \text{ mg of } MgCl_2 = \frac{100}{95} \times 1 \text{ mg } CaCO_3 = 1.05 \text{ mg of } CaCO_3$$

Thus, 1 L sample contains

$$= 0.9 + 1.05$$
$$= 1.95 \text{ mg of } CaCO_3$$
$$= 1.95 \text{ ppm}$$

9.7 Heavy Water or Deuterium Oxide (D_2O)

The credit for the discovery of heavy water goes of **Urey** who first proved that ordinary water contains one part of heavy water in 6000 parts of it. **Lewis** and **Donald,** in 1933, were able to isolate Few millilitres of pure D_2O by continuous electrolysis of water containing alkali.

Preparation

Heavy water (D_2O) is obtained mainly by the multistage electrolysis of ordinary water as shown by Washburn and Urey. It is also obtained by fractional distillation of ordinary water or by fractional freezing.

Physical Properties

Heavy water is a colourless, odourless and tasteless mobile liquid. Nearly all the physical constants are higher for heavy water than the corresponding values for ordinary water.

Chemical Properties

It gives all the reactions that are given by ordinary water but with a slower rate. This is called **isotopic effect.** *e.g.*,

$$2Na + 2D_2O \longrightarrow 2NaOD + D_2$$
$$SO_2 + D_2O \longrightarrow D_2SO_3$$
$$CaC_2 + 2D_2O \longrightarrow Ca(OD)_2 + C_2D_2$$

It also reacts with a number of compounds containing labile hydrogen atoms, where H-atom is partially or completely replaced by D-atom as,

$$NaOH + D_2O \rightleftharpoons NaOD + HOD$$
$$HCl(aq) + D_2O \rightleftharpoons DCl + HOD$$
$$NH_4Cl + 4D_2O \rightleftharpoons ND_4Cl + 4HOD$$

(If the compound contains ionic (polar) hydrogen atoms, the exchange reactions take place more readily in comparison to compounds containing non-ionic hydrogen).

Heavy water like ordinary water may be associated with salts as water of crystallisation, giving deutero-hydrate, *e.g.,* $Na_2SO_4 \cdot 10D_2O$, $CuSO_4 \cdot 5D_2O$, $MgSO_4 \cdot 7H_2O$, etc.

Biological and Physiological Effects

It has been established that heavy water of high concentration retards the growth of plants and animals. Pure heavy water kills small fishes, tadpoles and mice, when fed on with it.

Taylor has shown that heavy water has germicide and bactericide properties. Water containing small quantity of D_2O acts as a tonic and stimulates vegetable growth. Certain moulds have been found to develop better in heavy water in comparison to ordinary water.

Uses

Heavy water is used as a moderator in nuclear reactors, in the study of mechanisms of chemical reactions involving hydrogen and its compounds etc. It is also used for the preparation of deuterium.

9.8 Hydrogen Peroxide (H_2O_2)

It was discovered by the French chemist, **L.J. Thenard,** in 1818, by the action of sulphuric acid on barium peroxide. Initially it was named **oxygenated water.**

It occurs in traces in air, rain, snow, some natural waters and juices of certain plants.

General Methods of Preparation

Following methods are used to prepare H_2O_2 *in laboratory.*

(a) By the Action of Dilute HCl on Anhydrous BaO_2

Thenard, a French scientist, prepared H_2O_2 accidentally in 1818 by the action of dil HCl on BaO_2 (barium peroxide) while he was trying to evolve some new methods for the preparation of water. He called it as **oxygenated water,** *i.e.,* the water with more oxygen.

$$BaO_2 + 2HCl \longrightarrow BaCl_2 + H_2O_2$$

(b) By the Action of Dilute H_2SO_4 on Anhydrous Na_2O_2

While preparing H_2O_2 through dil H_2SO_4 and Na_2O_2, the later is added slowly to ice cold 20% H_2SO_4. On cooling crystals of $Na_2SO_4 \cdot 10H_2O$ separate out from H_2O_2. These are filtered off while some impurity, as Na_2SO_4, remains present in H_2O_2. The reaction proceed as,

$$Na_2O_2 + \text{dil } H_2SO_4 (20\%) \longrightarrow Na_2SO_4 + H_2O_2$$

(c) By the Action of Dilute H_3PO_4 on Hydrated BaO_2

A bit modified form of the above written process mixed with the application of Thenard's reaction is used more commonly for the preparation of H_2O_2 in laboratory. Here, *hydrated* BaO_2 *is used instead of anhydrous* BaO_2 (because $BaSO_4$ formed as the by-product of reaction, forms a layer on BaO_2, thus preventing further reaction but with hydrated BaO_2 such a problem does not arise).

Secondly, the H_2SO_4 *used, catalyses the decomposition of* H_2O_2 *also, hence comparatively weaker acids like* H_3PO_4 *and* H_2CO_3 *etc., are used in the place of* H_2SO_4.

$$3BaO_2 + 2H_3PO_4 \longrightarrow \underset{\text{ppt.}}{Ba_3(PO_4)_2} + 3H_2O_2$$

Insoluble barium phosphate is filtered off. The filtrate consists of hydrogen peroxide.

The barium phosphate is decomposed by dilute sulphuric acid.

$$Ba_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 3BaSO_4 + 2H_3PO_4$$

$BaSO_4$ is removed by filtration and orthophosphoric acid is used again.

(d) Merck's Process

H_2O_2 can be obtained by passing a current of CO_2 through a cold pasty solution of barium peroxide in water.

$$BaO_2 + CO_2 + H_2O \longrightarrow BaCO_3 + H_2O_2$$

Barium carbonate being insoluble is filtered off.

Industrial Preparation of H_2O_2

Following methods are used for the industrial preparation of H_2O_2.

(a) By the Electrolysis of H_2SO_4 or NH_4HSO_4 at a High Current Density

The **electrolysis of 50% H_2SO_4** is done at 0°C using Pt electrodes. Here, perdisulphuric acid ($H_2S_2O_8$) is formed at anode as,

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

At **cathode** (reduction) $2H^+ + 2e^- \longrightarrow 2H \longrightarrow H_2$

At **anode** (oxidation) $2HSO_4^- \longrightarrow H_2S_2O_8 + 2e^-$

This $H_2S_2O_8$ on hydrolysis gives H_2O_2 which is separated by distillation under reduced pressure.

When $(NH_4)_2SO_4$ and H_2SO_4 are mixed in 1 : 1 ratio, NH_4HSO_4 is formed, which is electrolysed to give ammonium persulphate by using Pt electrodes at 0°C.

$$2NH_4HSO_4 \rightleftharpoons 2H^+ + 2NH_4SO_4^-$$

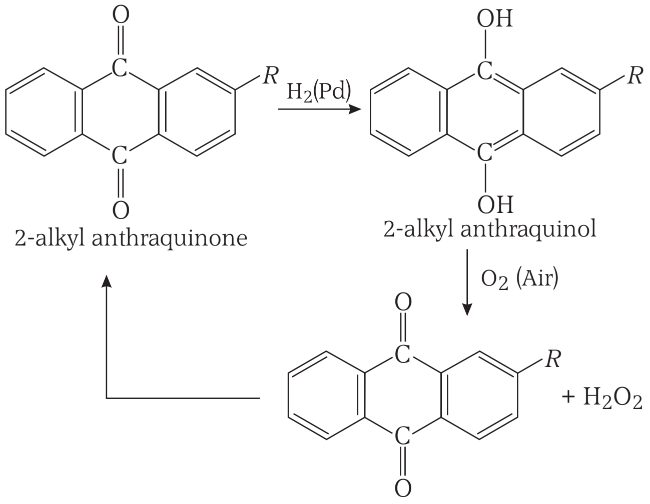
At **cathode** (reduction) $2H^+ + 2e^- \longrightarrow 2H \longrightarrow H_2$

At **anode** (oxidation) $2NH_4SO_4^- \longrightarrow (NH_4)_2S_2O_8 + 2e^-$

The ammonium persulphate so formed is hydrolysed by heating with water at low pressure (43 mm of Hg) resulting in H_2O_2.

(b) By the Auto-oxidation of 2-alkyl Anthraquinol

2-alkyl anthraquinol is oxidised as



The reaction is carried out in a mixture of organic solvents, *e.g.*, ester/hydrocarbon or octanol/methyl naphthalene. The solvent must

1. dissolve quinol and quinone,
2. resist oxidation,
3. be immiscible with water.

Concentration of H_2O_2 Solution

Hydrogen peroxide obtained by the above methods is always in the form of dilute aqueous solution. The concentration of this solution is difficult due to explosive nature of hydrogen peroxide. It is done by using the following steps.

Step I The dilute solution is concentrated on a water bath at 60–70°C. By this the 30% solution is obtained.

Step II The obtained 30% solution is distilled at 35–40°C under reduced pressure of about 15 mm. Repeated distillation gives 90% H_2O_2.

Step III Further concentration is achieved by cooling 90% solution with the help of solid CO_2 and ether both till crystallisation occurs. The crystals are washed, separated, melted and refrozen to obtain 99% pure H_2O_2.

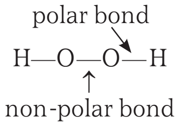
Storage of H_2O_2

H_2O_2 gets easily decomposed in the presence of metals, rough surfaces, sunlight, dust particles, glass and alkali. Thus, it is stored in vessels of pure aluminium or in stone jars in dark. Concentrated solutions of hydrogen peroxide are stored these days in polythene bottles kept in refrigerators. Small amounts of stabilizers such as orthophosphoric acid, acetanilide or sodium stannate are also added to the solutions to be stored to prevent its decomposition.

Physical Properties of H_2O_2

The important physical properties of H_2O_2 *are as follows*

1. It is light blue in pure anhydrous form, odourless, syrupy liquid, produces blisters on skin and soluble in water, alcohol and ether.
2. Its boiling point is 152°C and freezing point is −0.89°C. The further increase in the boiling point of H_2O_2 in comparison with water is due to the reason that here intermolecular hydrogen bonding is even more stronger than water.
3. Density of H_2O_2 at 0°C is 1.45 g/cc and dielectric constant is 93.7.
4. H_2O_2 molecule is diamagnetic, polar and its dipole moment is 2.1 D.
5. It has both **polar** and **non-polar bonds** as



Chemical Properties of H_2O_2

H_2O_2 *exhibits following chemical properties*

(a) Decomposition

H_2O_2 decomposes on heating. It is an unstable liquid. Finely divided Fe, Cu, Au, Pt, MnO_2, metal ions like Cu^{2+}, Ni^{2+} and traces of base act as **positive catalyst** (destabilisers) for its decomposition while H_3PO_4, $C_6H_5NHCOCH_3$ (acetanilide), C_2H_5OH, glycerol, etc., act as **negative catalyst** (stabilisers) for its decomposition.

(b) Nature

H_2O_2 is acidic in nature but its aqueous solution is neutral towards litmus. It dissociates in water to give hydronium ion as,

$$H_2O_2 + H_2O \longrightarrow H_3O^+ + HO_2^- \quad (K_a = 1.4 \times 10^{-12} \text{ at } 298\text{ K})$$

Value of its dissociation constant suggests that its aqueous solution is more acidic than water (for water $K_w = 10^{-14}$ at 298 K).

The acidic nature of H_2O_2 is confirmed by its reactions with **alkalies and carbonates.** In these reactions, corresponding peroxides are formed.

$$H_2O_2 + 2NaOH \longrightarrow Na_2O_2 + 2H_2O$$
$$H_2O_2 + Ba(OH)_2 \longrightarrow BaO_2 + 2H_2O$$
$$H_2O_2 + Na_2CO_3 \longrightarrow Na_2O_2 + CO_2 + H_2O$$

Formation of H_2O *and* CO_2 *in the last reaction instead of* H_2CO_3 *suggests that* H_2O_2 *is even stronger acid than* H_2CO_3.

(c) Oxidising Property

H_2O_2 is a strong oxidising agent. It accepts the electron easily and itself gets reduced in alkaline as well as acidic medium as,

$$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O \qquad (E° = +1.77\ V)$$
$$HO_2^- + H_2O + 2e^- \longrightarrow 3OH^- \qquad (E° = +0.87\ V)$$

Thus, in acidic medium, H_2O_2 is reduced into H_2O and in alkaline medium into OH^-. In both the cases oxidation number of oxygen decreases. Here, the important point to be remember is that **in alkaline solution these reactions are generally faster.**

Some examples of oxidising reactions are

(i) Lead sulphide (PbS) is oxidised into $PbSO_4$,

$$PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$$

(ii) KNO_2 is oxidised into KNO_3,

$$KNO_2 + H_2O_2 \longrightarrow KNO_3 + H_2O$$

(iii) Na_2SO_3 is oxidised into Na_2SO_4,

$$Na_2SO_3 + H_2O_2 \longrightarrow Na_2SO_4 + H_2O$$

(iv) Sodium arsenite (Na_3AsO_3) is oxidised into sodium arsenate,

$$Na_3AsO_3 + H_2O_2 \longrightarrow Na_3AsO_4 + H_2O$$

(v) Hydrogen sulphide is oxidised into sulphur,

$$H_2S + H_2O_2 \longrightarrow 2H_2O + S$$

(vi) Ferrous sulphate is oxidised into ferric sulphate,

$$2FeSO_4 + H_2SO_4 + H_2O_2 \longrightarrow Fe_2(SO_4)_3 + 2H_2O$$

(vii) KI is oxidised into I_2,

$$2KI + H_2SO_4 + H_2O_2 \longrightarrow K_2SO_4 + 2H_2O + I_2$$

(viii) Formaldehyde (HCHO) is oxidised into formic acid,

$$HCHO + H_2O_2 \longrightarrow HCOOH + H_2O$$

(ix) Potassium ferrocyanide is oxidised into potassium ferricyanide,

$$2K_4[Fe(CN)_6] + H_2SO_4 + H_2O_2 \longrightarrow 2K_3[Fe(CN)_6] + K_2SO_4 + 2H_2O$$

(x) In the presence of $FeSO_4$ benzene is oxidised into phenol,

$$C_6H_6 + H_2O_2 \xrightarrow{FeSO_4} C_6H_5OH + H_2O$$

(xi) Hg is oxidised into HgO,

$$Hg + H_2O_2 \longrightarrow HgO + H_2O$$

(xii) In alkaline medium, it oxidises manganese sulphate (a manganeous salt) to manganese dioxide.

$$MnSO_4 + H_2O_2 + 2NaOH \longrightarrow MnO_2 + Na_2SO_4 + 2H_2O$$
$$\text{or} \qquad Mn^{2+} + H_2O_2 \longrightarrow Mn^{4+} + 2OH^-$$

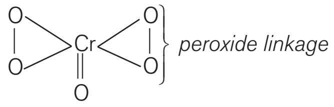
(xiii) It dissolves the chromic hydroxide precipitate present in NaOH solution forming a yellow solution of sodium chromate.

$$\begin{array}{rcl} [H_2O_2 & \longrightarrow & H_2O + O] \times 3 \\ 2Cr(OH)_3 + 4NaOH + 3O & \longrightarrow & 2Na_2CrO_4 + 5H_2O \\ \hline 2Cr(OH)_3 + 4NaOH + 3H_2O_2 & \longrightarrow & 2Na_2CrO_4 + 8H_2O \end{array}$$

Caution Point *When cold* H_2O_2 *is added in cold mixture of* $K_2Cr_2O_7$ *and conc.* H_2SO_4 (*i.e.,* $K_2Cr_2O_7$ *in acidic medium*), *a blue solution of blue perchromate is obtained as,*

$$K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + H_2Cr_2O_7$$
$$H_2Cr_2O_7 + 4H_2O_2 \longrightarrow \underset{\text{blue perchromate}}{2CrO_5} + 5H_2O$$

The structure for blue perchromate is



Because of the presence of two peroxide linkages, the oxidation state of Cr *in* CrO_5 *is* +6, *not* +10.

(d) Reducing Property

Due to electron donating property of H_2O_2, it also acts as a reducing agent in acidic as well as in alkaline medium and proceeds as

$$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$$
$$H_2O_2 + 2OH^- \longrightarrow 2H_2O + O_2 + 2e^-$$

Some important examples in which H_2O_2 acts as a reducing agent are

(i) Silver oxide (Ag_2O) is reduced to Ag,

$$Ag_2O + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$$

(ii) Lead dioxide (PbO_2) is reduced to PbO,

$$PbO_2 + H_2O_2 \longrightarrow PbO + H_2O + O_2$$

(iii) Cl_2 is reduced to HCl,

$$Cl_2 + H_2O_2 \longrightarrow 2HCl + O_2$$

(iv) Gold oxide is reduced to gold,

$$Au_2O + H_2O_2 \longrightarrow 2Au + H_2O + O_2$$

(v) In acid medium, MnO_2 is reduced to $MnSO_4$,

$$MnO_2 + H_2SO_4 + H_2O_2 \longrightarrow MnSO_4 + 2H_2O + O_2$$

(vi) Acidified $KMnO_4$ is reduced by H_2O_2. Pink colour of $KMnO_4$ disappears.

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

(vii) In alkaline medium, potassium ferricyanide is reduced to potassium ferrocyanide,

$$2K_3[Fe(CN)_6] + 2KOH + H_2O_2 \longrightarrow 2K_4[Fe(CN)_6] + 2H_2O + O_2$$

(e) Reaction with Ozone

H_2O_2 on reaction with O_3 shows the following reaction,

$$H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$$

i.e., both reduce each other.

(f) Bleaching Property

H_2O_2 also exhibits bleaching property. This property is due to the nascent oxygen which it liberates on decomposition.

$$H_2O_2 \longrightarrow H_2O + [O]$$

The nascent oxygen combines with the colouring matter, which in turn, gets oxidised.

$$\text{Colouring matter} + [O] \longrightarrow \text{colourless matter}$$

It bleaches delicate materials like silk, cotton, wool, hair, feather, ivory etc.

(g) Addition Reactions

H_2O_2 reacts with alkenes to give respective glycols.

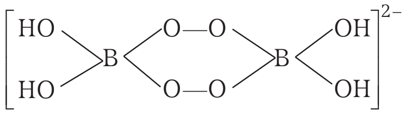
$$\underset{\text{ethene}}{CH_2{=}CH_2} + H_2O_2 \longrightarrow \underset{\text{ethylene glycol}}{CH_2OH—CH_2OH}$$

Uses of H_2O_2

1. H_2O_2 is *germicide* and antiseptic. It is used for washing cuts, wounds, teeth, ears, etc., and in gargles under the name **perhydrol.** (30% solution of H_2O_2)
2. It prevents the purification of milk, liquor etc.
3. Its dilute solution is used in the bleaching of cotton, wool, silk, hair, ivory, paper, pulp etc.
4. Old oil paintings turn black with time due to the formation of black PbS. Hydrogen peroxide oxidises black PbS into white $PbSO_4$ and thus, restore their colour.
5. It is used as an oxidising agent as well as reducing agent.
6. It is used to produce sodium peroxoborate. $Na_2B_2(O_2)_2(OH)_4$. In hexahydrate state, it used as a brightner in washing powders.

   $$2NaBO_2 + 2H_2O_2 + 6H_2O \longrightarrow Na_2[(OH)_2B(O—O)_2B(OH)_2]6H_2O$$

   Structure of preoxoborate ion may be given as



7. It is used as a laboratory reagent in the test of Ti^{4+}, Cr^{3+} and V^{5+} ions.
8. It is used as propellant for rockets, torpedoes, etc., and as a fuel. As a propellant it is used to oxidise alcohol, petrol, hydrazine etc.

   $$N_2H_4 + 2H_2O_2 \longrightarrow N_2 + 4H_2O$$

9. H_2O_2 is used as **antichlor** to remove Cl_2 etc., present in a solution.

Strength of H_2O_2

Strength of H_2O_2 solution may be represented in several ways such as **g/L, mol/L, normality, ppm** (mg/L), volume etc. Some important one among them are

(a) Concentration as Volume

It is equal to the volume of O_2 obtained at STP by decomposing one volume H_2O_2 solution. If the strength of H_2O_2 solution is 20 volume, this means that 1 cc H_2O_2 solution on decomposition gives 20 cc O_2 at STP or 1 L H_2O_2 solution on heating gives 20 L O_2 at STP.

(b) Concentration as Percentage

It is equal to the gram of H_2O_2 present in 100 mL of H_2O_2 solution. Thus, if the strength of a H_2O_2 solution is 8%, this means that 8 g of H_2O_2 is present in its 100 mL solution.

(c) Concentration as Normality

Strength of H_2O_2 as normality is calculated with the help of equivalent weight of H_2O_2 (17) as,

Normality of H_2O_2 solution

$$= \frac{\text{strength of } H_2O_2 \text{ solution in g/L}}{\text{equivalent wt. of } H_2O_2}$$

Conversion of One Concentration Term into Another

Concentration of H_2O_2 is expressed in terms of "volume of O_2." We know that **"10 volume H_2O_2" means that 1 mL of H_2O_2 at NTP gives 10 mL O_2 gas.** These values can be changed into other concentration terms like density, g L^{-1}, normality and molarity as

$$\underset{?}{\underset{68\text{ g}}{2H_2O_2}} \longrightarrow 2H_2O + \underset{x\text{ mL}}{\underset{1\text{ mol}}{O_2}} \quad (22400 \text{ mL at NTP})$$

22400 mL O_2 is obtained from H_2O_2 = 68 g (at NTP)

x mL O_2 gas will be obtained from H_2O_2

$$= \frac{68}{22400} \times x \text{ g (at NTP)}$$

This amount is in 1 mL H_2O_2 (by definition).

Thus, $$1 \text{ mL } H_2O_2 = \frac{68}{22400} \times x \text{ g}$$

$$\text{Density} = \frac{68}{22400} x \text{ g/mL}$$

$$\text{Conc. in g/L} = \frac{68}{22400} x \times 1000$$

$$\text{g/L conc.} = \frac{680x}{224} \text{ g/L}$$

$$\text{Normality } (N) = \frac{\text{conc. in g/L}}{\text{equivalent wt.}} = \frac{680x}{224} \times \frac{1}{17}$$

$$\therefore \quad N = \frac{x}{5.6}$$

$$\text{Molarity } (M) = \frac{\text{conc. in g/L}}{\text{mol. wt.}} = \frac{680x}{224} \times \frac{1}{34}$$

$$\therefore \quad M = \frac{x}{11.2}$$

Sample Problem 7 *The volume strength of* 1.6 *N* H_2O_2 *solution is*

(a) 3.57 (b) 8.96
(c) 9.57 (d) 5.45

Interpret (b) Strength = normality × eq. wt.

$= 1.6 \times 17$ g/L

$\because$ 68 g of H_2O_2 at NTP gives $O_2 = 22400$ mL

$\therefore$ 1.6×17 g H_2O_2 at NTP will give O_2

$$= \frac{22400}{68} \times 1.6 \times 17 \text{ mL}$$

$$= 8960 \text{ mL}$$

But 1.6×17 g H_2O_2 is present in 1000 mL of H_2O_2 solution.

Hence, 1000 mL of H_2O_2 solution will give O_2 (at NTP) = 8960 mL

$\therefore$ 1 mL of H_2O_2 solution will give $O_2 = \frac{8960}{1000}$

$= 8.96$ mL O_2

Hence, the volume strength of 1.6 N H_2O_2 is 8.96 volume.

Sample Problem 8 *5 mL of* H_2O_2 *solution liberates* 0.508 *g of* I_2 *from an acidified* KI *solution. The strength of* H_2O_2 *solution in terms of volume strength at STP will be*

(a) 4.48 (b) 5.6
(c) 9.96 (d) 8.20

Interpret (a) Let the normality of $H_2O_2 = N$

$$\text{Equivalents of } H_2O_2 = \frac{5N}{1000} = \frac{N}{200}$$

$$\text{Equivalents of } I_2 = \frac{0.508}{127}$$

$$\frac{N}{200} = \frac{0.508}{127}$$

$$N = 0.8 \text{ N } H_2O_2$$

If volume strength = x

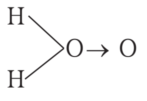
then, $$N = \frac{x}{5.6}$$

$$x = N \times 5.6$$

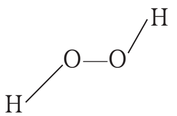
$$= 0.8 \times 5.6 = 4.48 \text{ V}$$

Structure of H_2O_2

Following two structures have been suggested for hydrogen peroxide.



Kingzett's formula



Baeyer's formula

(a) Evidence in Favour of Kingzett's Structure

H_2O_2 is an oxidising agent. Reaction in which H_2O_2 acts as an oxidant, one oxygen atom per H_2O_2 molecule is decreased. Thus, this structure explains the instability of one of the oxygen atom.

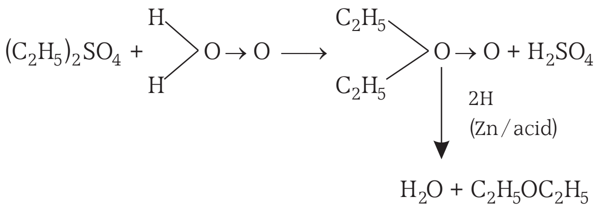
(b) Evidence in Favour of Baeyer's Structure

1. H_2O_2 is a weak dibasic acid. It has two —OH groups. Therefore, it forms two series of salts such as $NaHO_2$ and Na_2O_2.
2. Ethylene glycol is formed by the action of H_2O_2 on ethylene. This confirms the presence of two —OH groups in H_2O_2.
3. H_2O_2 reacts with ethyl sulphate. Diethyl peroxide is formed. This on reduction gives ethyl alcohol. From this reaction, it is concluded that O—O bond is present in H_2O_2 and one H-atom is bonded to each atom.

$$\text{H—O—O—H} + (C_2H_5)_2SO_4 \longrightarrow C_2H_5\text{—O—O—}C_2H_5 + H_2SO_4$$

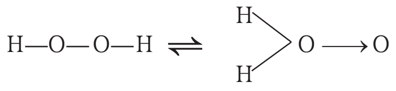
$$C_2H_5\text{—O—O—}C_2H_5 \xrightarrow{2H(Zn/acid)} 2C_2H_5OH$$

If we take Kingzett's structure as the real structure of H_2O_2 then the product for the above reaction should be diethyl ether and not alcohol. As a matter of fact, H_2O_2 gives diethyl ether also as the product for above reaction, *i.e.*,



$$(C_2H_5)_2SO_4 + H_2O \rightarrow O \longrightarrow (C_2H_5)_2O \rightarrow O + H_2SO_4 \xrightarrow{2H\,(Zn/acid)} H_2O + C_2H_5OC_2H_5$$

Formation of ethyl alcohol as well as diethyl ether as the product of the above reaction supports the view that H_2O_2 infact contains both the type of molecules in equilibrium as the tautomeric mixture. In other words, we can say that Kingzett and Baeyer's formulae are infact tautomeric forms of each other.



$$\text{H—O—O—H} \rightleftharpoons H_2O \longrightarrow O$$

4. H_2O_2 (one molecule) reacts with two molecules of chlorosulphonic acid to give perdisulphuric acid. This confirms the O—O bond in H_2O_2.

$$HSO_3\ \boxed{Cl + H}\text{—O—O—}\boxed{H + Cl}\,SO_3H \longrightarrow$$
$$HSO_3\text{—O—O—}SO_3H + 2HCl$$

5. X-ray study confirms the presence of O—O bond in peroxides such as Na_2O_2, BaO_2, etc.

   Dipole moment of H_2O_2 is 2.1 D. This shows that all the four atoms in H_2O_2 are not in one plane.

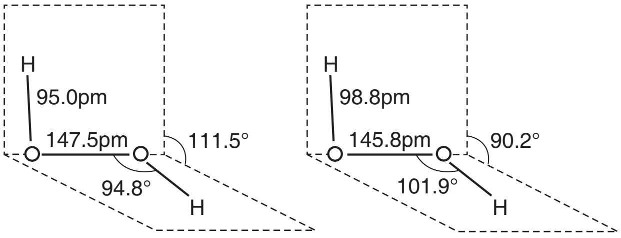
   X-ray studies shows that H_2O_2 is non-polar molecule. H_2O_2 molecule may be pictured as lying on the spine of a book open at an angle of 94.8°. One hydrogen atom is placed on each cover. The two oxygen atoms are present along the axis of the spin of the book. The H—O bonds make an angle of 94.8° with the O—O bond.

   O—O bond length = 1.49 Å

   O—H bond length = 0.97 Å

   O—O—H angle = 94.8°

   For H_2O_2 in solid phase, the dihedral angle between two planes is different and the length of O—H bond is different as shown in the figure.



(a) Gas phase (b) Solid phase

Fig. 9.5 (a) H_2O_2 structure (gas phase), dihedral angle 115.5°, (b) H_2O_2 (solid phase at 110 K). The dihedral angle is reduced to

9.9 Hydrides

The compounds of hydrogen in which hydrogen is suppose to be present as H^- are called **hydrides.** The oxidation state of H in these compounds is –1.

Based upon their physical and chemical properties, hydrides are of the following three types

1. Ionic or Salt Like Hydrides

These are the compounds of hydrogen with most of the *s*-block elements. These are formed by transfer of electrons from metal to hydrogen atom. These are white crystalline solids, have ionic lattices, high boiling and melting points and behave as salts. They can conduct electricity only in fused or molten state. *Their density is higher than that of metals.* Their aqueous solutions are strongly alkaline. These hydrides are famous for complex formation and are used as good reducing agents, *e.g.,*

$$LiH + AlH_3 \longrightarrow Li(AlH_4)$$
$$NaH + BH_3 \longrightarrow Na(BH_4)$$

2. Molecular or Covalent Hydrides

These are the compounds of hydrogen with *p*-block elements. Their bonds are mostly covalent in character (in some cases partly covalent and partly ionic character *e.g.,* HF). These have molecular lattices, soft in texture, with low melting point and boiling point and low electrical conductivity. Acidic character in these hydrides increases while moving left to right in a period, *e.g.,*

$NH_3 \longrightarrow$ base, $H_2O \longrightarrow$ neutral,

$HF \longrightarrow$ acid $PH_3 \longrightarrow$ weak base,

$H_2S \longrightarrow$ weak acid, $HCl \longrightarrow$ strong acid

The molecular hydrides are named with the suffix-ane *e.g.,* phosphane (PH_3); oxidane (H_2O); azane (NH_3) etc., and are of following three types

(i) **Electron deficient hydrides** with elements of 13 group, which normally behave as Lewis acid, *e.g.,* B_2H_6.

(ii) **Electron precise hydrides** with elements of 14 group, *e.g.,* CH_4.

(iii) **Electron rich hydrides** with elements of 15, 16 and 17 group, *e.g.,* H_2O, NH_3, HF etc. Here, the excess electron is being present as lone pair ($NH_3 \rightarrow 1$ lone pair; $H_2O \rightarrow 2$ lone pairs; $HF \rightarrow 3$ lone pairs). The presence of lone pair and highly electronegative elements like O, N and F results in hydrogen bond formation. Presence of hydrogen bonds leads to high boiling points, high permittivities and aggregation in such compounds.

3. Metallic or Interstitial Hydrides

These are formed by the reaction of *d*- and *f*-block metals with hydrogen. These are non-stoichiometric hydrides and show electric conduction.

These hydrides are generally formed by the

(i) transition metals of group 3, 4, 5 of *d*-block;

(ii) Cr metals of group 6 and

(iii) *f*-block elements.

It may be noted that elements of group 7, 8, 9 *of d-block do not form hydrides at all.* This inability of metal of group 7, 8, 9 of the Periodic Table to form hydrides is referred to as *hydride gap* of *d*-block.

In these compounds, H atoms are supposed to occupy interstitial position in the metal lattices. Some scientists consider these compounds as simply solid solutions of hydrogen. The composition of these hydrides may not correspond to simple whole number ratio and therefore, they are also called non-stoichiometric hydrides. Their composition is also found to vary with the conditions of temperature and pressure. Some examples of interestitial hydrides of elements of group 3 to 5 are ScH_2, YH_2, YH_3, LiH_3,

CrH, TiH_2, ZrH_2 HfH_2, VH, NbH, NbH_2, TaH etc.

Check Point 2

1. Can phosphorus with outer configuration $3s^2 3p^3$ form PH_5?
2. Explain, temporary hard water becomes soft on boiling.
3. Saline hydrides when react with water, produce fire violently. Can we use CO_2 to extinguish this fire?
4. Density of ice is lower than water although the density of solid is higher than liquid. Explain, why?
5. Why use of hydrated BaO_2 is preferred during the preparation of H_2O_2?

Hydrogen as a Fuel

Hydrogen has been considered as one of the alternate sources of energy because.

1. It is environmentally clean, giving only water as a combustion product.
2. The heat of combustion of hydrogen per gram is higher than any other fuel as tabulated below :

$$H_2(g) + \left(\frac{1}{2}\right) O_2(g) \longrightarrow H_2O(l); \ \Delta H^\circ = -284 \text{ kJ mol}^{-1}$$

Table 9.2 **Energy Released by the Combustion of Some Substances**

Substance	Energy released (kJ/g)
Hydrogen [combustion product $H_2O(l)$]	142
Gasoline	48
Crude petroleum	43
Typical animal fat	38
Coal	29.3
Charcoal	29
Paper	20
Wood or dung	15

Hydrogen could replace coal and oil as major sources of energy. Our energy needs can be met by gaseous, liquid and solid hydrogen. For heating homes, gaseous hydrogen could be conveyed through underground pipes while liquid hydrogen could be shipped by truck or rail in large vacuum insulated tanks. Automobiles might be powered by solid hydrogen in the form of solid interstitial hydrides. Prototype cars have already been built with their engines modified to run on hydrogen.

Since hydrogen is not a naturally occurring energy source like coal, natural gas etc., cheaper ways of producing hydrogen must be discovered. Direct methods of hydrogen production are very costly. For example, decomposing water with electricity is too expensive but if future methods for generating electricity prove economical, the ocean provide an inexhaustible source of starting material.

If we succeed in developing economically feasible methods for producing hydrogen cheaply and in large quantities, we still face significant problems in **storing** and **transporting** it. In case hydrogen is to be stored and transported in its gaseous state, large, heavy-walled metal cylindrical will be required, *i.e.,* it will be a costly affair. To save space, gases are converted to the liquid state under high pressure as in the case of "bottled gas." But hydrogen must be cooled to −253°C before it liquefies. Thus, keeping hydrogen in liquid state requires low temperatures and high costs.

A number of attempts have been made to tackle the problem of storing H_2. One of these, proposed recently, involves absorbing gaseous H_2 on a solid, such as activated carbon, An another approach involves reacting the H_2 with certain metals to produce compounds called hydrides, which are relatively stable solid that have a reasonably high storage capacity. For example, when 10 litres of H_2 gas at 25°C and 1 atmosphere react with lithium metal, the resulting LiH occupies a mere 4.3 mL.

$$Li(s) + \frac{1}{2} H_2(g) \longrightarrow LiH(s)$$

When such hydrides are reacted with water, they produce H_2, which can be burned.

$$LiH(s) + H_2O(l) \longrightarrow H_2(g) + LiOH(aq)$$

Some of the interstitial hydrides can be made suitable storage compounds for hydrogen. The reactions that form these hydrides are usually reversible; so hydrogen gas can be obtained simply by reducing the pressure above the metal. Fuel cell is an important device where hydrogen and oxygen gases are used as fuels.

WORKED OUT Examples

Example 1 *In which of the properties listed below hydrogen does not show similarity with halogens?*

I. Nature of the oxide
II. Electropositive character
III. Combination with alkali metals
IV. Atomicity

(a) I *and* II (b) III *and* IV
(c) II *only* (d) I *and* III

Solution (a) Hydrogen forms a neutral oxide, *i.e.*, H_2O (water) while the oxide of halogens *i.e.*, HCl, HI, HBr, are acidic. Hydrogen atom is electropositive in nature also while halogens are mostly electronegative in nature.

Example 2 *Mass percentage of deuterium in heavy water is*

(a) *same as that of protium in water*
(b) 11.1
(c) 20.0
(d) *cannot be predicted*

Solution (c) The formula of heavy water is D_2O, *i.e.*, molecular mass = 20

$$\% \text{ of deuterium} = \frac{4}{20} \times 100 = 20$$

Example 3 *In which reaction, hydrogen peroxide neither acts as an oxidising agent nor as a reducing agent?*

(a) $PbS + H_2O_2 \longrightarrow$
(b) $SO_3^- + H_2O_2 \longrightarrow$
(c) $PbO_2 + H_2O_2 \longrightarrow$
(d) $Na_2CO_3 + H_2O_2 \longrightarrow$

Solution (d) H_2O_2 neither acts as an oxidising agent nor as a reducing agent, when reacts with Na_2CO_3 because there is neither gain nor loss of electrons in this reaction.

$$Na_2CO_3 + H_2O_2 \longrightarrow Na_2O_2 + CO_2 + H_2O$$

Example 4 *Given sample of water has degree of hardness equal to 40 ppm. If the entire hardness is due to* $MgSO_4$, *the amount of* $MgSO_4$ *present per kg of water is*

(a) 24 *g* (b) 24 *mg*
(c) 48 *g* (d) 48 *mg*

Solution (d) Degree of hardness of H_2O is 40 ppm,

i.e., 10^6 g of water contains $CaCO_3 = 40$ g

Since, 1 mole of $CaCO_3$ = 1 mole of $MgSO_4$

$\therefore$ 100 g of $CaCO_3$ = 120 g of $MgSO_4$

$$\therefore\ 10^6 \text{ g of water contains } MgSO_4 = \frac{40 \times 120}{100} = 48 \text{ g}$$

Example 5 *Hydrogen peroxide solution (20 mL) reacts quantitatively with a solution of* $KMnO_4$ *(20 mL) acidified with dilute* H_2SO_4. *The same volume of the* $KMnO_4$ *solution is just decolourised by 10 mL of* $MnSO_4$ *in neutral medium simultaneously forming a dark brown precipitate of hydrated* MnO_2. *The brown ppt is dissolved in 10 mL of 0.2 M sodium oxalate under boiling condition in the presence of dilute* H_2SO_4. *The molarity of* H_2O_2 *is*

(a) 0.4 *m* (b) 0.2 *m*
(c) 0.1 *m* (d) 0.02 *m*

Solution (c)

$$\begin{aligned} 2KMnO_4 + 3H_2SO_4 &\longrightarrow K_2SO_4 + 2MnSO_4 \\ &\qquad + 3H_2O + 5[O] \\ [H_2O_2 + [O] &\longrightarrow H_2O + O_2] \times 5 \\ \hline 2KMnO_4 + 3H_2SO_4 + 5H_2O_2 &\longrightarrow K_2SO_4 + 2MnSO_4 \\ &\qquad + 8H_2O + 5O_2 \downarrow \end{aligned}$$

$$\begin{aligned} 3MnSO_4 + 2KMnO_4 + (x+2)H_2O &\longrightarrow \underset{\text{brown ppt.}}{5MnO_2 \cdot xH_2O \downarrow} \\ &\qquad + K_2SO_4 + 2H_2SO_4 \end{aligned}$$

$$\begin{aligned} MnO_2 \cdot xH_2O + Na_2C_2O_4 + 2H_2SO_4 &\longrightarrow MnSO_4 + Na_2SO_4 \\ &\qquad + (x+2)H_2O + 2CO_2 \end{aligned}$$

Millimoles of $Na_2C_2O_4 = 10 \times 0.2 = 2$

Meq. of $Na_2C_2O_4 = 4$ ($\because$ meq. = 2 × millimoles)

Meq. of $MnO_2 \cdot xH_2O$ formed = 4

Meq. of $MnO_2 \cdot xH_2O$ = meq. of $KMnO_4 = 4$

Meq. of $KMnO_4$ = meq. of $H_2O_2 = 4$

Meq. of $H_2O_2 = 4$

Millimoles of $H_2O_2 = 2$ $\left(\frac{\text{Meq.}}{2} = \text{Millimoles for } H_2O_2\right)$

$\therefore$ Moles of H_2O_2 in 20 mL of solution $= 2 \times 10^{-3}$

$$\text{Molarity of solution} = \frac{2 \times 10^{-3}}{20} \times 1000 \text{ M} = 0.1 \text{ M}$$

Start **Practice** *for* JEE Main

Round I (Topically Divided Problems)

Hydrogen and its Different Forms

1. Which pair does not show hydrogen isotopes?
(a) *Ortho* hydrogen and *para* hydrogen
(b) Protium and deuterium
(c) Deuterium and tritium
(d) Tritium and protium

2. The sum of protons, electrons and neutrons in the heaviest isotope of hydrogen is
(a) 3 (b) 5 (c) 4 (d) 6

3. The adsorption of hydrogen by metals is called
(a) adsorption (b) occlusion
(c) hydrogenation (d) dehydrogenation

4. Hydrogen resembles halogens in many respects for which several factor are responsible. Of the following factors which one is the most important in this respect? **[NCERT Exemplar]**
(a) Its tendency to lose an electron to form a cation
(b) Its tendency to gain a single electron in its valence shell to attain stable electronic configuration
(c) Its low negative electron gain enthalpy value
(d) Its small size

5. Why does H^+ ion always get associated with other atoms or molecules? **[NCERT Exemplar]**
(a) Ionisation enthlapy of hydrogen resembles that of alkali metals
(b) Its reactivity is similar to halogens
(c) It resembles both alkali metals and halogens
(d) Loss of an electron from hydrogen atom results in a nucleus of very small size as compared to other atoms or ions. Due to small size it cannot exist free

6. Radioactive elements emit α, β and γ rays and are characterised by their half-lives. The radioactive isotope of hydrogen is **[NCERT Exemplar]**
(a) protium (b) deuterium
(c) tritium (d) hydronium

7. Under what conditions of temperature and pressure, the formation of atomic hydrogen from molecular hydrogen will be favoured more?
(a) High temperature and low pressure
(b) Low temperature and low pressure
(c) High temperature and high pressure
(d) Low temperature and high pressure

8. Which of the following reactions is an example of use of water gas in the synthesis of other compounds? **[NCERT Exemplar]**

(a) $CH_4(g) + H_2O(g) \xrightarrow[Ni]{1270\text{ K}} CO(g) + H_2(g)$

(b) $CO(g) + H_2O(g) \xrightarrow[\text{Catalyst}]{673\text{ K}} CO_2(g) + H_2(g)$

(c) $C_nH_{2n+2} + nH_2O(g) \xrightarrow[Ni]{1270\text{ K}} nCO + (2n+1)\,H_2$

(d) $CO(g) + 2H_2(g) \xrightarrow[\text{Catalyst}]{\text{Cobalt}} CH_3OH(l)$

9. Which is the poorest reducing agent?
(a) Atomic hydrogen
(b) Nascent hydrogen
(c) Dihydrogen
(d) All have same reducing strength

Water and Heavy Water

10. Heavy water is
(a) water at 0°C
(b) water containing Fe, Cr, Mn
(c) D_2O
(d) water obtained after a number of distillations

11. Heavy water is used in atomic reactor as
(a) moderator
(b) coolant
(c) both moderator and coolant
(d) neither coolant nor moderator

12. Permutit is the technical name given to
(a) aluminates of calcium and sodium
(b) hydrated silicate of aluminium and sodium
(c) silicates of calcium and magnesium
(d) silicates of calcium and sodium

13. Demineralised water is obtained by **[NCERT]**
(a) boiling (b) treating with calgon
(c) ion-exchange resins (d) All of these

14. If same mass of liquid water and a piece of ice is taken, then why is the density of ice less than that of liquid water? **[NCERT Exemplar]**
(a) Because ice is a solid
(b) Because molecules of ice are closely packed
(c) Because vacant spaces are present in the crystal lattice
(d) The given statement is wrong

15. Which of the following statements do not define the characteristic property of water "water is a universal solvent".?
(a) It has high liquid range
(b) It has very low dielectric constant
(c) It can dissolve maximum number of compounds
(d) None of the above

16. The boiling point of water is high because
(a) water molecule is linear
(b) water molecule is not linear
(c) water molecules possess covalent bond between H and O
(d) water molecules associate due to H-bonding

17. When two ice cubes are pressed over each other they unite to form one cube. Which of the following forces are responsible to hold them together?
(a) Ionic interaction
(b) van der Waals' forces
(c) Covalent interaction
(d) Hydrogen bond formation

18. When zeolite which is hydrated sodium aluminium silicate is treated with hard water, the sodium ions are exchanged with
(a) H^+ ions
(b) Mg^{2+} ion
(c) Ca^{2+} ion
(d) Both Ca^{2+} and Mg^{2+}

19. In the reactions of water with F_2, water acts as **[NCERT]**
(a) oxidant (b) reductant
(c) Both (a) and (b) (d) None of these

20. Deionised water is obtained by passing hard water through
(a) anion exchanger
(b) zeolite
(c) cation exchanger
(d) Both anion and cation exchanger

21. Which of the following ions will cause hardness in water sample? **[NCERT Exemplar]**
(a) Ca^{2+} (b) Na^+ (c) Cl^- (d) K^+

22. Which of the following compounds is used for water softening? **[NCERT Exemplar]**
(a) $Ca_3(PO_4)_2$ (b) Na_3PO_4
(c) $Na_6P_6O_{18}$ (d) Na_2HPO_4

Hydrogen Peroxide

23. Hydrogen peroxide is obtained by the electrolysis of …… . **[NCERT Exemplar]**
(a) water (b) sulphuric acid
(c) hydrochloric acid (d) fused sodium peroxide

24. In laboratory, H_2O_2 is prepared by
(a) cold $H_2SO_4 + BaO_2$ (b) $HCl + BaO_2$
(c) conc. $H_2SO_4 + Na_2O_2$ (d) $H_2 + O_2$

25. The H—O—O bond angle in H_2O_2 is
(a) 107.28° (b) 97° (c) 104.5° (d) 109.28°

26. H_2O_2 is manufactured these days
(a) by burning hydrogen in excess of oxygen
(b) by the action of H_2O_2 on BaO_2
(c) by the action of H_2SO_4 on Na_2O_2
(d) by electrolysis of 50% H_2SO_4

27. Hydrogen peroxide is …… . **[NCERT Exemplar]**
(a) an oxidising agent
(b) a reducing agent
(c) Both an oxidising and a reducing agent
(d) neither oxidising nor reducing agent

28. The oxide that gives H_2O_2 on treatment with dilute H_2SO_4 is **[NCERT Exemplar]**
(a) PbO_2 (b) $BaO_2 \cdot 8H_2O + O_2$
(c) MnO_2 (d) TiO_2

29. When sodium peroxide is treated with dilute sulphuric acid, we get **[NCERT Exemplar]**
(a) sodium sulphate and water
(b) sodium sulphate and oxygen
(c) sodium sulphate, hydrogen and oxygen
(d) sodium sulphate and hydrogen peroxide

30. The volume strength of 1.5 N H_2O_2 solution is
(a) 16.8 L (b) 8.4 L
(c) 4.2 L (d) 5.2 L

31. The strength of 5 volume H_2O_2 is [**NCERT** Exemplar]

(a) 15 (b) 1.5 (c) 150 (d) 0.15

32. Phosphoric acids is preferred over sulphuric acid in preparing hydrogen peroxide from peroxides because [**NCERT** Exemplar]

(a) H_2SO_4 acts as a reducing agent
(b) H_2SO_4 gives $BaSO_4$ which is difficult to separate
(c) H_2SO_4 acts as catalyst
(d) Both (b) and (c)

Hydrides

33. Non-stoichiometric hydrides are

(a) hydrides of all *d*-block elements
(b) deficient in hydrogen
(c) the hydrides having hydrogen atom in interstitial sites
(d) Both (b) and (c)

34. Which of the following hydrides is electron precise hydride? [**NCERT** Exemplar]

(a) B_2H_6 (b) NH_3 (c) H_2O (d) CH_4

35. Elements of which of the following group(s) of Periodic Table do not form hydrides? [**NCERT** Exemplar]

(a) Groups 7, 8, 9 (b) Group 13
(c) Group 15, 16, 17 (d) Group 14

36. Only one element of …… forms hydride [**NCERT** Exemplar]

(a) Group 6 (b) Group 7
(c) Group 8 (d) Group 9

37. When electric current is passed through an ionic hydride in the molten state,

(a) hydrogen is liberated at the cathode
(b) hydrogen is liberated at the anode
(c) hydride ion migrates towards cathode
(d) no reaction takes place

38. The characteristics of an electron deficient hydride with respect to its structure and chemical reactions is [**NCERT**]

(a) these behave as Lewis acids
(b) these reacts with metals as well as non-metals
(c) these have trigonal planar shape
(d) All of the above

39. Saline hydrides are known to react with water violently producing fire. The fire cannot be extinguished by CO_2 because [**NCERT**]

(a) CO_2 is lighter than the gas evolved
(b) CO_2 is heavier than the gas evolved
(c) CO_2 gets reduced by the evolved gas
(d) CO_2 gets oxidised by the evolved gas

40. Metallic hydrides are useful for hydrogen storage because [**NCERT**]

(a) they reacts with hydrogen and form stable compound
(b) they absorb H-atoms
(c) they adsorb H-atoms
(d) they form unstable compounds with hydrogen

Round II (Mixed Bag)

Only One Correct Option

1. Which of the following reactions produces hydrogen?

(a) $H_2S_4O_8 + H_2O$
(b) $BaO + HCl$
(c) $Mg + H_2O$
(d) $Na_2O_2 + 2HCl$

2. Which of the following metals evolves hydrogen on reacting with cold dilute HNO_3?

(a) Fe (b) Cu
(c) Al (d) Mg

3. Which of the following is not true?

(a) D_2O freezes at lower temperature than H_2O
(b) Reaction between H_2 and Cl_2 is much faster than D_2 and Cl_2
(c) Ordinary water electrolysed more rapidly than D_2O
(d) Bond dissociation energy of D_2 is greater than H_2

4. The reagent commonly used to determine hardness of water titrimetrically is

(a) oxalic acid
(b) sodium thiosulphate
(c) sodium citrate
(d) disodium salt of EDTA

5. Polyphosphates are used as water softening agents because they

(a) form soluble complexes with anionic species
(b) precipitate anionic species
(c) precipitate cationic species
(d) form soluble complexes with cationic species

6. An element reacts with hydrogen to form a compound *A*, which on treatment of water liberates hydrogen gas. The element can be

(a) chlorine (b) selenium
(c) calcium (d) nitrogen

7. Which one of the following is used for reviving the exhausted 'permutit'?

(a) HCl solution (b) 10% $CaCl_2$ solution
(c) 10% $MgCl_2$ solution (d) 10% NaCl solution

8. What is formed when calcium carbide reacts with heavy water?

(a) C_2D_2 (b) CaD_2
(c) CaD_2O (d) CD_2

9. Steam is passed over red hot carbon and the gaseous products cooled and passed first through a solution of alkali, then through ammoniacal cuprous chloride and then through water. What is finally collected?

(a) CO_2
(b) A mixture of hydrocarbons
(c) $CO + H_2$
(d) H_2

10. Which of the following statements about H_2O_2 is not true?

(a) H_2O_2 is used to clean oil paintings
(b) H_2O_2 acts as oxidising as well as reducing agent
(c) Two hydroxyl groups in H_2O_2 lie in the same plane
(d) It retains same structure in liquid and solid form

11. The volume strength of perhydrol is

(a) 20 (b) 30
(c) 100 (d) 10

12. Which of the following equations depict the oxidising nature of H_2O_2? **[NCERT Exemplar]**

(a) $2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$
(b) $2Fe^{3+} + 2H^+ + H_2O_2 \longrightarrow 2Fe^{2+} + 2H_2O + O_2$
(c) $2I^- + 2H^+ + H_2O_2 \longrightarrow I_2 + 2H_2O$
(d) $KIO_4 + H_2O_2 \longrightarrow KIO_3 + H_2O + O_2$

13. Out of the following metals which will give H_2 on reaction with NaOH

I : Zn II : Mg
III : Al IV : Si

(a) I, II, III, IV
(b) I, III, IV
(c) II, IV
(d) I, III

14. In the absence of hydrogen bonding, boiling point of water would have been

(a) 100°C (b) 0°C
(c) −100°C (d) 373°C

15. H_2 gas is liberated at cathode and anode both by electrolysis of the following aqueous solutions except in

(a) NaH (b) HCOONa
(c) NaCl (d) LiH

16. Which is true statement?

(a) The layer of ice on the surface of river in the winter acts as a thermal insulator between the water below and the air above
(b) The fish and other marine organisms are enabled to survive long periods of freezing weather due to the fact that ice is lighter than water
(c) Both (a) and (b) are correct
(d) None of the above

17. H_2O_2 can be obtained when following reacts with H_2SO_4 except with

(a) PbO_2 (b) BaO_2 (c) Na_2O_2 (d) SrO_2

18. The increasing order of bond dissociation energy in **[NCERT]**

(a) $H—H < D—D < F—F$ (b) $F—F < H—H < D—D$
(c) $F—F < D—D < H—H$ (d) $D—D < F—F < H—H$

19. The increasing order of reducing property of NaH, MgH_2 and H_2O is **[NCERT]**

(a) $NaH < H_2O < MgH_2$ (b) $MgH_2 < H_2O < NaH$
(c) $H_2O < MgH_2 < NaH$ (d) $NaH < MgH_2 < H_2O$

20. Arrange CaH_2, BeH_2 and TiH_2 in the order of increasing electrical conductance. **[NCERT]**

(a) $BeH_2 < CaH_2 < TiH_2$ (b) $TiH_2 < CaH_2 < BeH_2$
(c) $BeH_2 < TiH_2 < CaH_2$ (d) $TiH_2 < BeH_2 < CaH_2$

21. Consider the reactions,

(A) $H_2O_2 + 2HI \longrightarrow I_2 + 2H_2O$
(B) $HOCl + H_2O_2 \longrightarrow H_3O^+ + Cl^- + O_2$

Which of the following statements is correct about H_2O_2 with reference to these reactions? Hydrogen peroxide is …… . **[NCERT Exemplar]**

(a) an oxidising agent in both (A) and (B)
(b) an oxidising agent in (A) and reducing agent in (B)
(c) an reducing agent in (A) and oxidising agent in (B)
(c) a reducing agent in both (A) and (B)

More than One Correct Option

22. H_2O_2 is "5.6 volume", then

(a) it is 1.7% weight by volume
(b) it is 1 N
(c) it is 1 M
(d) it is 5.6 M

23. Which of the following statement(s) is/are correct in the case of heavy water? **[NCERT Exemplar]**

(a) Heavy water is used as a moderator in nuclear reactor
(b) Heavy water is more effective as solvent than ordinary water
(c) Heavy water is more associated than ordinary water
(d) Heavy water has lower boiling point than ordinary water

24. Which of the following statements about hydrogen are correct? [**NCERT** Exemplar]

(a) Hydrogen has three isotopes of which protium is the most common
(b) Hydrogen never acts as cation in ionic salts
(c) Hydrogen ion H^+, exists freely in solution
(d) Dihydrogen does not acts as a reducing agent

25. Some of the properties of water are described below. Which of them is/are not correct? [**NCERT** Exemplar]

(a) Water is known to be a universal solvent
(b) Hydrogen bonding is present to a large extent in liquid water
(c) There is no hydrogen bonding in the frozen state of water
(d) Frozen water is heavier than liquid water

26. Select the correct statement(s) about lime light

(a) Oxy-hydrogen flame
(b) Used in welding
(c) Temperature of lime light is sufficient to melt even platinum
(d) Produced in an endothermic reaction

27. Which of the following substances catalyses the rate of *ortho-para* conversions?

(a) NO (b) NO_2 (c) O_2 (d) Co^{2+}

Assertion and Reason

Directions (Q. Nos. 28 to 32) *Each of these questions contains two statements : Statement* I (*Assertion*) *and Statement* II (*Reason*). *Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes* (*a*), (*b*), (*c*), (*d*) *given below :*

(a) Statement I is true; Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true; Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

28. **Statement I** Permanent hardness of water is removed by treatment with washing soda.

Statement II Washing soda reacts with soluble magnesium and calcium sulphate to form insoluble carbonates. [**NCERT** Exemplar]

29. **Statement I** Some metals like platinum and palladium, can be used as storage media for hydrogen.

Statement II Platinum and palladium can adsorb large volumes of hydrogen. [**NCERT** Exemplar]

30. **Statement I** When blood is added to a solution of H_2O_2, the solution bubbles furiously.

Statement II Catalase (an enzyme) present in blood decomposes H_2O_2 and produces bubbles of O_2.

31. **Statement I** In space crafts H_2 gas is used in fuel cells for generating electrical energy and for providing clean drinking water to the astronauts.

Statement II A fuel cell may have an alkaline or acidic electrolyte.

32. **Statement I** Drinking of heavy water (D_2O) mixed water (H_2O) could prove fatal.

Statement II There is slower rate of transfer of D^+ compared with that of H^+ ion in acid-base reactions involved in enzyme catalysis.

Comprehension Based Questions

Directions (Q. Nos. 33 to 35) Depletion of resources of fossil fuels will at some future time make hydrogen, either for use directly by combustion and electrochemically in fuel cells or indirectly *via* hydrogenation of coal, the major alternative to nuclear energy; hence, arises the current interest in the so-called hydrogen economy.
A thermochemical cycle for hydrogen production involves at least one element that can exist in two different oxidation states.

$$2H_2O \longrightarrow 2H_2 + O_2$$

33. Production of H_2 from H_2O requires a net input of energy that would come from

(a) nuclear source
(b) solar source
(c) Both (a) and (b)
(d) None of the above

34. In the above thermochemical cycle, $FeCl_2$ is one of the catalyst involved and thus regenerated at the end of the reaction, after formed into

(a) $FeCl_3$, FeO, Fe_2O_3
(b) $FeCl_3$, Fe_2O_3, Fe_3O_4
(c) $FeCl_3$, FeO
(d) $FeCl_3$, Fe_3O_4

35. H_2 is produced in the following thermochemical reaction

(a) $FeCl_2 + H_2O \longrightarrow$
(b) $Fe_3O_4 + Cl_2 + HCl \longrightarrow$
(c) $FeO + H_2O \longrightarrow$
(d) $FeCl_3 + H_2O \longrightarrow$

Directions (Q. Nos. 36 and 37) Research scholar *A* added zinc pieces into aqueous $FeCl_3$ solution and performed some experiments with resultant solution. Research scholar *B* passed H_2 gas into aqueous $FeCl_3$ solution and performed some experiments with resultant solution."

36. Yellow coloured $FeCl_3$ solution changed to light green (appeared as colourless) in the experiment of

(a) *A* (b) *B*
(c) Both (a) and (b) (d) None of these

37. Select the correct statements.

(a) Zn pieces liberate nascent hydrogen on reaction with acidic solution of $FeCl_3$
(b) $FeCl_3$ solution is reduced to $FeCl_2$ in the experiments of *A* and *B* both
(c) Blue colour complex is formed in both the experiments on reaction with $K_4[Fe(CN)_6]$
(d) All of the above

Previous Years' Questions

38. Very pure hydrogen (99.9) can be made by which of the following processes? **[AIEEE 2010]**

(a) Reaction of methane with steam
(b) Mixing natural hydrocarbons of high molecular weight
(c) Electrolysis of water
(d) Reaction of salts like hydrides with water

39. In context with the industrial preparation of hydrogen from water gas $(CO + H_2)$, which of the following is the correct statement? **[AIEEE 2008]**

(a) CO and H_2 are fractionally separated using differences in their densities
(b) CO is removed by absorption in aqueous Cu_2Cl_2 solution
(c) H_2 is removed through occlusion with Pd
(d) CO is oxidised to CO_2 with steam in the presence of a catalyst followed by absorption of CO_2 in alkali

40. Which one of the following processes will produce hard water? **[AIEEE 2003]**

(a) Saturation of water with $CaCO_3$
(b) Saturation of water with $MgCO_3$
(c) Saturation of water with $CaSO_4$
(d) Addition of Na_2SO_4 to water

Answers

Round I

1. (a)	**2.** (c)	**3.** (b)	**4.** (b)	**5.** (d)	**6.** (c)	**7.** (a)	**8.** (d)	**9.** (c)	**10.** (c)
11. (c)	**12.** (b)	**13.** (c)	**14.** (c)	**15.** (b)	**16.** (d)	**17.** (d)	**18.** (d)	**19.** (b)	**20.** (d)
21. (a)	**22.** (c)	**23.** (b)	**24.** (a)	**25.** (b)	**26.** (d)	**27.** (c)	**28.** (b)	**29.** (c)	**30.** (b)
31. (b)	**32.** (c)	**33.** (d)	**34.** (c)	**35.** (a)	**36.** (a)	**37.** (b)	**38.** (d)	**39.** (c)	**40.** (c)

Round II

1. (c)	**2.** (d)	**3.** (a)	**4.** (d)	**5.** (d)	**6.** (c)	**7.** (d)	**8.** (a)	**9.** (d)	**10.** (c)
11. (c)	**12.** (c)	**13.** (b)	**14.** (c)	**15.** (c)	**16.** (c)	**17.** (a)	**18.** (b)	**19.** (c)	**20.** (a)
21. (b)	**22.** (a,b)	**23.** (b,d)	**24.** (a,b)	**25.** (c,d)	**26.** (a,b,c)	**27.** (a,b,c,d)	**28.** (a)	**29.** (a)	**30.** (a)
31. (b)	**32.** (a)	**33.** (c)	**34.** (d)	**35.** (a)	**36.** (a)	**37.** (a)	**38.** (d)	**39.** (d)	**40.** (c)

the Guidance

Round I

1. *Ortho* and *para* hydrogen show different spin in a hydrogen molecule, hence, these are not the isotopes.

2. $_1H^3$ has 3 nucleons (1 proton + 2 neutrons) and one electron, so sum of these is $3 + 1 = 4$.

4. Hydrogen like halogen accept an electron readily to achieve nearest inert gas configuration.

7. $H_2 \longrightarrow H + H, \ \Delta H = +\text{ve}$

This reaction is favoured by low pressure and high temperature.

9. Because dihydrogen is less reactive.

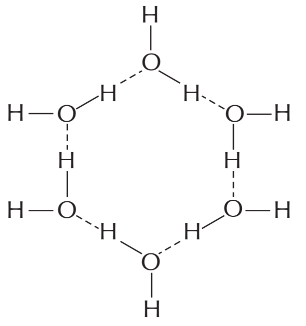
11. Heavy water is used as a moderator to slow down the speed of fast moving neutrons and also as a coolant.

12. It is $Na_2Al_2Si_2O_8 \cdot xH_2O$.

13. Water which is free from all soluble minerals salts is called demineralised water. Demineralised water is obtained by passing water successively through a cation exchange and an anion exchange resins. In cation exchanger, Ca^{2+}, Mg^{2+}, Na^+ and other cations present in water are removed by exchanging them with H^+ ions while in anion exchanger, Cl^-, HCO_3^-, SO_4^{2-}, etc., present in water are removed by exchanging them with OH^- ions.

$$\underset{\text{(released in cation exchanger)}}{H^+} + \underset{\text{(released in anion exchanger)}}{OH^-} \longrightarrow H_2O$$

14. In ice, molecules of H_2O are not packed so closely as in liquid water. There exists vacant spaces in the crystal lattice. This results in larger volume and lower density (density = mass/volume).



Hexagonal honey comb structure of ice

15. Water has high dielectric constant, *i.e.*, 82, high liquid range and can dissolve maximum number of compounds. That's why it is used as universal solvent.

19. Fluorine being more electronegative removes oxygen from water and itself gets reduced to fluoride ion.

$$\underset{\text{oxidant}}{2F_2(g)} + \underset{\text{reductant}}{2H_2O(l)} \longrightarrow O_2(g) + 4H^+(aq) + 4F^-(aq)$$

$$\underset{\text{oxidant}}{3F_2(g)} + \underset{\text{reductant}}{3H_2O(l)} \longrightarrow O_3(g) + 6H^+(aq) + 6F^-(aq)$$

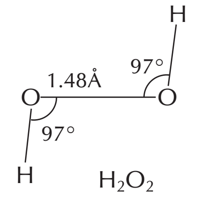
In these reactions, water acts as a reducing agent and hence itself gets oxidised to either oxygen or ozone. Fluorine acts as an oxidising agent and hence is itself gets reduced to F^- ion.

20. Deionised or demineralised water is obtained by passing hard water through both cation and anion exchangers one after the other.

21. Bicarbonates, chlorides and sulphates of Ca and Mg are responsible for the hardness of water.

24. $H_2SO_4 + BaO_2 \longrightarrow BaSO_4 + H_2O_2$

25.



26. Electrolysis of 50% sulphuric acid gives per disulphuric acid ($H_2S_2O_8$) which on distillation yields 30% solution of hydrogen peroxide.

29. $Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$

30. Volume strength $= 5.6 \times \text{normality}$

$$= 5.6 \times 1.5 = 8.4 \text{ L}$$

31. 5 volumes H_2O_2 solution means that 1 L of 5 volumes H_2O_2 solution on decomposition produces 5 L of O_2 at NTP.

$$\underset{2 \times 34 \text{ g}}{2H_2O_2} \longrightarrow 2H_2O + \underset{22.7 \text{ L at NTP}}{O_2}$$

22.7 L O_2 at NTP will be obtained from $H_2O_2 = 68$ g

$\therefore$ 5 L of O_2 at NTP will be obtained from $H_2O_2 = \dfrac{68 \times 5}{22.7}$ g

$$= 14.98 = 15 \text{ g}$$

But 5 L of O_2 at NTP is produced from 1 L of 5 volumes H_2O_2

$\therefore$ Strength of H_2O_2 solution = 15 g L^{-1}

or percentage strength of H_2O_2 solution $= \dfrac{15}{1000} \times 100 = 1.5\%$

32. H_2SO_4 acts as a catalyst for decomposition of H_2O_2. Therefore, some weaker acids such as H_3PO_4, H_2CO_3 is preferred over H_2SO_4 for preparing H_2O_2 from peroxides.

$$3BaO_2 + 2H_3PO_4 \longrightarrow \underset{\text{(Insoluble)}}{Ba_3(PO_4)_2} + 3H_2O_2$$

33. Non-stoichiometric hydrides are formed by many *d*-block (except metals of 7, 8 and 9 group) and *f*-block elements. These hydrides are always non-stoichiometric, *i.e.*, deficient in hydrogen. In these hydrides hydrogen atom occupies interstitial sites, *e.g.*, $LaH_{2.87}$, $YbH_{2.55}$, $TiH_{1.5-1.8}$, $PdH_{0.6-0.8}$, etc.

34. Water is an electron precise hydride.

37. $M^+H^- \longrightarrow M^+ + \underset{\text{hydride ion}}{H^-}$

$$H^- \longrightarrow \frac{1}{2}H_2 + e^- \text{ (at anode)}$$

38. Electron deficient hydrides are obtained by elements of group 13 like BF_3, $AlCl_3$ etc. Being electron deficient (or electron accepting) these act as Lewis acids. They have trigonal planar geometry and react with metals as well as non-metals.

39. Saline hydrides (such as NaH, CaH_2, etc.), react with water violently to form the corresponding metal hydroxides with the evolution of dihydrogen.

$$NaH(s) + H_2O(l) \longrightarrow NaOH(aq) + H_2(g)$$
$$CaH_2(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + 2H_2(g)$$

These reactions are so much exothermic that the evolved H_2 catches fire. This type of fire cannot be extinguished by CO_2 because it gets reduced by the hot metal hydride to form sodium formate.

$$NaH + CO_2 \longrightarrow HCOONa$$

40. In metallic hydrides, hydrogen is adsorbed as H-atoms. This property of adsorption of hydrogen on transition metals is widely used as its storage media. Some of the metals such as Pd, Pt can accommodate a very large volume of hydrogen. This property has high potential for hydrogen storage and as a source of energy. Metallic hydrides on heating decompose to form hydrogen and very finely divided metal.

Round II

1. $Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2\uparrow$

2. Fe and Al become passive by HNO_3 and Cu being less reactive is unable to react. Mg is an active metal and react with dilute HNO_3 to give H_2 gas.

3. D_2O actually has higher freezing point (3.8°C) than water H_2O (0°C).

4. Disodium salt of EDTA is commonly used to determine the hardness of water.

5. Polyphosphates being negatively charged from soluble complexes with cationic species.

6. $Ca + H_2 \longrightarrow CaH_2 \xrightarrow{2H_2O} Ca(OH)_2 + 2H_2$

Thus, the element is calcium.

7. During the softening process, the reaction takes place as

$$Na_2Z + Ca(HCO_3)_2 \longrightarrow CaZ + 2NaHCO_3$$
$$Na_2Z + Mg(HCO_3)_2 \longrightarrow MgZ + 2NaHCO_3$$

After sometime, the zeolite is completely converted into calcium and magnesium zeolites. Eventually, the bed ceases to soften water, *i.e.*, it gets exhausted. At this stage, the supply of hard water is stopped and the exhausted zeolite is reclaimed by treating the bed with a 10% NaCl solution (brine solution) when the following reaction takes place

$$CaZ \text{ or } MgZ + 2NaCl \longrightarrow \underset{\substack{\text{reclaimed}\\ \text{zeolite}}}{Na_2Z} + CaCl_2 \text{ or } MgCl_2$$

8. $\begin{array}{l} Ca : C_2 \\ OD : D \\ OD : D \end{array} \xrightarrow{D_2O} C_2D_2 + Ca(OD)_2$

9. $$\begin{tikzcd} C + H_2O \arrow[r] & CO + H_2 \arrow[d, "KOH"] \\ & K_2CO_3 + H_2\uparrow \end{tikzcd}$$

10. In H_2O_2, the two —OH groups are not in the same plane.

11. Perhydrol is 30% H_2O_2.

∵ 10 vol $H_2O_2 = 3\%$

∴ 30% H_2O_2 has volume $= \frac{10}{3} \times 30 = 100$ volume

12. The reaction in which H_2O_2 is reduced, *i.e.*, oxidation state of oxygen decreases from –1 to –2 depicts the oxidising nature of H_2O_2. *e.g.*,

Reduction

$$2I^- + 2H^+ + \underset{\text{oxidising agent}}{\overset{-1}{H_2O_2}} \longrightarrow \overset{0}{I_2} + 2H_2\overset{-2}{O}$$

Increase in O.S. (oxidation)

13. $Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2$

$$2Al + 2NaOH + 2H_2O \longrightarrow NaAlO_2 + 3H_2$$
$$Si + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 2H_2$$

14. Force of attraction is minimum thus most volatile.

15. (a) $NaH \rightleftharpoons Na^+ + H^-$

At cathode

$$Na^+ + e^- \longrightarrow Na$$
$$Na + H_2O \longrightarrow NaOH + \frac{1}{2}H_2$$

At anode

$$H^+ + e^- \longrightarrow \frac{1}{2}H_2 + e^-$$

(b) $$HCOONa \rightleftharpoons HCOO^- + Na^+$$

At cathode same as above

At anode

$$HCOO^- \longrightarrow \frac{1}{2}H_2 + CO_2 + e^-$$

(c) $$NaCl \rightleftharpoons Na^+ + Cl^-$$

At cathode same as above

At anode

$$Cl^- \longrightarrow \frac{1}{2}Cl_2 + e^-$$

(d) $$LiH \rightleftharpoons Li^+ + H^-$$

At cathode

$$Li^+ + e^- \longrightarrow Li$$

$$Li + H_2O \longrightarrow LiOH + \frac{1}{2}H_2$$

At anode

$$H^- \longrightarrow \frac{1}{2}H_2 + e^-$$

16. Both the given statements are correct.

17. PbO_2 is a dioxide, not a true peroxide due to the absence of —O—O— (peroxide) linkage. Hence, it does not give H_2O_2 with dilute H_2SO_4.

18. Shorter the bond length, higher the bond dissociation energy. Thus, the correct order is

$$F—F < H—H < D—D$$

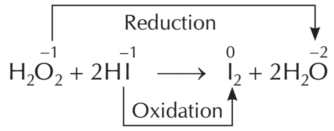
19. Metal hydrides are stronger reducing agents than non-metal hydrides. Thus, H_2O is a weaker reducing agent and NaH due to more electropositive nature of Na is strongest reducing agent among the given. Thus, the correct order is

$$H_2O < MgH_2 < NaH$$

20. More the ionic character, higher is the electrical conductance and larger the electronegativity difference, higher is the ionic character. Thus, the order of electrical conductance is

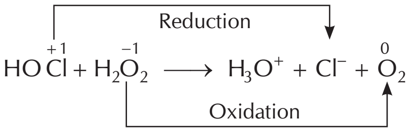
$$BeH_2 < CaH_2 < TiH_2$$

21. (A)



$$\overset{-1}{H_2O_2} + 2H\overset{-1}{I} \longrightarrow \overset{0}{I_2} + 2H_2\overset{-2}{O}$$

Thus, here H_2O_2 oxidises HI into I_2 hence, it behaves as oxidising agent.



$$HO\overset{+1}{Cl} + H_2\overset{-1}{O_2} \longrightarrow H_3O^+ + Cl^- + \overset{0}{O_2}$$

Here, H_2O_2 reduces HOCl to Cl^-, thus, it acts as reducing agent.

22. $$\text{Normality} = \frac{\text{Volume strength}}{5.6} = \frac{5.6}{5.6} = 1\,N$$

It is 1.7% weight by volume.

23. Boiling point of heavy water is higher than ordinary water and it is not as effective in the form of solvent as water due to its low dielectric constant.

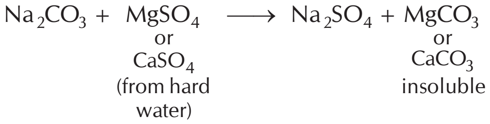
24. Among the three isotopes of hydrogen, protium is the most common. In ionic salts, hydrogen exists as hydride (H^-) ion.

25. Water is a universal solvent and exists to a larger extent in liquid state. It also contains H-bonding in frozen state. The density of ice is lower than that of water (liquid) due to the presence of vacant spaces.

26. Lime light is produced in an exothermic reaction.

27. Paramagnetic substance or ions, which contain unpaired electrons, catalyst *ortho-para* conversion.

28.



$$Na_2CO_3 + \underset{\substack{\text{or}\\ CaSO_4\\ \text{(from hard}\\ \text{water)}}}{MgSO_4} \longrightarrow Na_2SO_4 + \underset{\substack{\text{or}\\ CaCO_3\\ \text{insoluble}}}{MgCO_3}$$

29. Since metals like Pd and Pt adsorb a large volume of hydrogen, these are used as a storage media for it.

30. When blood is added to a solution of H_2O_2, the solution bubble furiously because of the evolution of O_2 which is obtained by the decomposition of H_2O_2 by catalysts present in the blood.

31. Both the statements are correct.

32. Drinking of D_2O mixed water could prove fatal because of the slower transfer rate of D^+ as compared to H^+ in acid-base reaction involved in enzyme catalysis.

33. Nuclear and solar both type of energy source help in the production of H_2 from H_2O.

34. $FeCl_2$ will be regenerated at the end of reaction after formed into $FeCl_3$ and Fe_3O_4.

35. $8FeCl_2 + 8H_2O \xrightarrow{h\nu} 2Fe_3O_4 + 2FeCl_3 + 3H_2 + 10HCl$

36. In the experiment of scholar *A*, the colour get changed because nascent H is obtained on adding zinc which is more reactive. The molecular hydrogen reduces Fe^{3+} into Fe^{2+}.

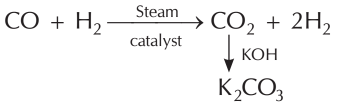
37. Zn generates nascent H.

$$FeCl_3 + [H] \longrightarrow FeCl_2 + HCl$$

38. Hydrides are instant source of hydrogen of higher purity. They react with H_2O forming H_2 gas

$$CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2$$

39. CO is oxidised to CO_2 with steam in the presence of a catalyst followed by absorption of CO_2 in alkali



$$CO + H_2 \xrightarrow[\text{catalyst}]{\text{Steam}} \underset{\substack{\downarrow \text{KOH}\\ K_2CO_3}}{CO_2} + 2H_2$$

40. Alkaline earth metal salts are causing hardness. Temporary hardness caused by soluble Ca and Mg hydrogen carbonates. Calcium and magnesium soluble sulphates and chlorides cause permanent hardness.

10 *s*-Block Elements

JEE Main MILESTONE

- Alkali Metals
- Anomalous Behaviour of Li
- Diagonal Relationship of Li with Magnesium
- Alkaline Earth Metals
- Anomalous Behaviour of Beryllium
- Diagonal Relationship of Be with Aluminium
- Biological Significance of Na, K, Mg and Ca

Alkali Metals and Their Compounds

10.1 Alkali Metals

Lithium ($Z = 3$), sodium ($Z = 11$), potassium ($Z = 19$), rubidium ($Z = 37$), caesium ($Z = 55$) and francium ($Z = 87$) are the elements of IA (or 1) group of the Periodic Table. These elements because of the highly alkaline nature of their water soluble hydroxides are known as **alkali metals.**

Occurrence

The alkali metals occur in nature only in the form of their compounds, *i.e.,* these never found in free state as these are highly reactive. Sodium and potassium are the sixth and seventh most abundant elements in the earth's crust. Among alkali metals, the less electropositive one, *i.e.,* lithium is found in the form of silicate while the more electropositive elements are found in the form of their chlorides.

Compounds of sodium and potassium are the most abundant, while those of remaining alkali metals occur in nature rarely. Francium is a radioactive element and short lived.

The elements in which the last (valence) electron enters in the ns energy shell are called s-block elements. The maximum capacity of this shell is of two electrons, thus, this block includes two groups : IA or I group having ns^1 configuration and IIA or 2 group with ns^2 configuration. This block lie on the extreme left of the Periodic Table. Because of the presence of 1 or 2 electrons, these elements generally form ionic compounds (with the execption of Li *and* Be).

Electronic Configuration

Atoms of alkali metals have single valence electron and form unipositive cation when they take part in compound formation. All the alkali metals are **paramagnetic** because of the presence of single unpaired valence electron in their valence shell. General outer electronic configuration of alkali metals is ns^1 (where, $n = 2, 3, 4, 5, 6$ and 7). Their penultimate quantum layers have the stable electronic configuration of noble gas s^2p^6, (for lithium s^2).

Element	Configuration
Li(3)	[He] $2s^1$
Na(11)	[Ne] $3s^1$
K(19)	[Ar] $4s^1$
Rb(37)	[Kr] $5s^1$
Cs(55)	[Xe] $6s^1$
Fr(87)	[Rn] $7s^1$

The alkali metal cations, Li^+, Na^+, K^+, Rb^+ and Cs^+ are diamagnetic because of the absence of unpaired electrons. All these cations have stable s^2p^6 noble gas configuration.

Due to the presence of only one electron in the valence shell, they exhibit only +1 oxidation state. *The relatively simple chemistry of alkali metals is probably due to the ease with which their valence electron can be lost in order to achieve stable noble gas electronic configuration.*

General Trends in Physical Properties of Elements

Alkali metals show following trends in their physical properties.

(i) Physical Appearance

They are all silvery white, soft and malleable metals. They are so soft that they can easily be cut with a knife. The reason of softness of alkali metals is the presence of weak metallic bonding because of the presence of only one valence electron in them. This softness increases down the group as increase in number of non-bonding electrons down the group increases repulsion resulting in decrease in cohesive force and energy.

(ii) Atomic and Ionic Radius

Their atomic and ionic radii are largest in the respective period and increases as we move down the group.

(iii) Density

All are light metals with low densities, Li, Na and K are even lighter than water. Density generally increases on moving down the group but K has slightly lower density as compared to Na due to increase in its atomic volume. Li *is the lightest metal known.*

(iv) Melting and Boiling Points

These metals have very low melting and boiling points which decrease on moving down the group. The reason for their low melting and boiling points is the presence of weak intermetallic bonds, which also become more weaker as the size increases.

(v) Ionisation Energy

The first ionisation enthalpy of these elements is the lowest among corresponding period, however their second ionisation enthalpy is very high. On moving down the group, ionisation enthalpies decrease progressively. The ionisation energies of K, Rb and Cs are so less that these show photoelectric effect, *i.e.*, these can emit electrons even with fall of light on them.

(vi) Electropositive or Metallic Character

Alkali metals are the most electropositive in the Periodic Table and their metallic character increases on moving down the group. These all are metals and thus, are good conductors of heat and electricity. They exhibit metallic lusture which is due to the oscillation of free electrons.

(vii) Electronegativity

Because of their electropositive nature, alkali metals have very low tendency to attract the electrons, *i.e.,* their electronegativity is low. The electronegativity decreases from Li to Cs as the electropositive character increases.

(viii) Flame Colouration

The vapours of alkali metals (in the form of their chlorides) impart characteristic colours to the flame. The reason for this is that the loosely bound electron gets excited on heating and jumps to higher energy level. When this excited electron returns to its ground state, energy is emitted in the form of radiations. This extra energy, in visible region give characteristic colour to the flame.

Different alkali metals give different colour to the flame as they have different ionisation energies, *e.g.*, colour obtained by lithium is caramine red, sodium is yellow, K is violet, Rb is violet rose and Cs is blue. In this test, concentrated HCl is added to convert the given salt into volatile chloride.

The various physical properties of alkali metals can be summarised in the form of table as

Table 10.1 **Physical Properties of Alkali Metals**

Property	Lithium	Sodium	Potassium	Rubidium	Caesium
Atomic number	3	11	19	37	55
Molar mass (g mol^{-1})	6.94	22.99	39.10	85.48	132.91
Density at 20°C (g cm^{-3})	0.534	0.972	0.859	1.530	1.903
Molar volume (cm^3 mol^{-1})	12.97	23.68	45.36	55.80	69.95
Melting point (°C)	180.0	97.8	64.0	38.9	28.7
Boiling point (°C)	1326	883	756	688	690
Atomic radius (Å)	1.34	1.54	1.96	2.11	2.25
Ionic radius (Å)	0.60	0.95	1.33	1.48	1.69
Heat of atomisation (kJ mol^{-1})	159.0	108.1	90.2	82.1	78.2
Ionisation energy (kJ mol^{-1})	520.1	495.2	418.7	403.0	375.7
Electronegativity	1.0	0.9	0.8	0.8	0.7
Flame colouration	Crimson red	Golden yellow	Violet	Violet	Violet

(ix) Hydration Enthalpy and Conductivity

The amount of energy released when one mole of gaseous ions combine with water to form hydrated ions is called the **hydration enthalpy**. The extent of hydration varies inversely with size. Thus, the degree of hydration decreases down the group from Li^+ to Cs^+. Consequently the ionic size of these ions in aqueous solution follows the order

$$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$$

Hence, among alkali metal ions, Cs^+ has the highest and Li^+ has the lowest mobility in aqueous solution.

(x) Reducing Character

Because of their strong tendency to lose the *s*-electron, **the alkali metals are powerful reducing agents.** Lithium in aqueous solution is strong reducing agent as compared to Cs. This is probably due to high hydration energy of small lithium ion, which compensates for high ionisation energy. As a result of high hydration energy, standard reduction potential of Li is lowest among alkali metals.

Thus, most powerful reducing agent in solution is lithium. Reducing power of alkali metals in aqueous solution is

$$Li > Na > K > Rb > Cs$$

Sample **Problem 1** *The alkali metals are low melting. Which of the following alkali metal is expected to melt if the room temperature rises to 30°C?* [**NCERT** Exemplar]

(*a*) Na (*b*) K (*c*) Rb (*d*) Cs

Interpret (*d*) The melting point of caesium, Cs is 28.7°C which is below 30°C. Thus, as the temperature rises above 30°C, it gets melted.

Hot Spot 1

TRENDS in Chemical Properties of Group 1 Elements

The questions based on this topic have seen frequently in JEE Main (AIEEE) examination. The question may be direct or indirect reason based. So deep study of the topic is required.

The chemical properties of alkali metals are as follows

(a) Reactivity

Due to the presence of only one electron in their outermost shell, alkali metals are highly reactive and their reactivity towards all reagents (except nitrogen) increases down the group from lithium to caesium. To prevent their reactivity, these elements are usually stored in kerosene. Lithium is the lightest or least dense of all metals, with a density roughly half that of water, thus it being lighter floats on kerosene. Hence, it is kept wrapped in paraffin wax.

(b) Nature of Compounds

The metals form ionic compounds because they readily give up the *s*-electron of their valence shell. Small highly polarizing ion such as Li^+ tend to form covalent compounds. Most other cations of IA group elements are large and have low charge densities. Hence, they form stable compounds even with polarizing ions such as carbonate, peroxides, tri-iodide etc. **LiCl is soluble in pyridine because of its covalent nature.** Bond present in the molecules like Li_2, Na_2, K_2, etc., is covalent. It should be noted that alkali metals form diatomic molecules such as Li_2, Na_2, K_2, etc. to the extent of 1% in vapour state.

(c) Reaction with Air
(Nature of Oxides and Hydroxides)

Alkali metals when exposed to air, react readily with O_2, H_2O and CO_2 and get tarnished. That's why these metals must be protected from exposure to air. However, when burnt in air, lithium forms monoxide (Li_2O) only, sodium forms monoxide in limited O_2 and peroxide in excess O_2. Other alkali metals form largely the superoxides. In the presence of atmospheric oxygen, we get a mixture of oxides in the case of rest of the metals.

$$2Li + \frac{1}{2} O_2 \longrightarrow Li_2O \qquad 2Na + O_2 \longrightarrow Na_2O_2$$

$$2Na + \frac{1}{2} O_2 \longrightarrow Na_2O \qquad Rb + O_2 \longrightarrow \underset{\substack{\text{(Superoxide,}\\ \text{containing } O_2^- \text{ ion)}}}{RbO_2}$$

The formation and stability of these oxides can be explained on the basis of lattice energy effects. Li^+ ion being a small ion has a strong positive field around it and can stabilise only a small anion, O^{2-} whereas Na^+ being a large cation can stabilise a large ion and so on.

O^{2-}
oxide ion

$[—O—O—]^{2-}$
peroxide ion


superoxide ion

In order to prepare any particular oxide, peroxide or superoxide for K, Rb and Cs with the help of atmospheric oxygen, the metal is dissolved in NH_3 and then, treated with required quantity of oxygen to get requisite product.

The higher oxides, *viz.*, peroxides and superoxides are strong oxidising agents. They react with dilute acids forming hydrogen peroxide and oxygen respectively.

$$Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$$

$$4KO_2 + 2H_2SO_4 \longrightarrow 2K_2SO_4 + 2H_2O + 3O_2$$
$$2KO_2 + 2H_2O \longrightarrow 2KOH + H_2O_2 + O_2$$

The peroxides are diamagnetic in nature (all the electrons are paired) and are regarded as the salts of the dibasic acid, H_2O_2. The superoxides are paramagnetic and coloured as odd electron bond is present between two oxygen atoms. Yellow colour of Na_2O_2 is probably due to the presence of small amount of superoxide. Superoxides are even stronger oxidising agents than peroxides.

The normal oxide 'M_2O' react with water to form hydroxides.

$$M_2O + H_2O \longrightarrow 2MOH$$

The basic nature of the oxides (M_2O) increases gradually on moving down in the group. The hydroxides (MOH) are hygroscopic, readily absorb CO_2 from air and destroy glass. These are colourless, strong alkaline and corrosive compounds. These are soluble in water and dissolve with the evolution of heat. The hydroxides are thermally stable except LiOH. The relative strength of the hydroxides increases from LiOH to CsOH.

$$CsOH > RbOH > KOH > NaOH > LiOH$$

They dissociate in solution almost completely.

$$Na + O_2 \longrightarrow Na_2O \xrightarrow{H_2O,\ air} NaOH \xrightarrow{CO_2,\ air} Na_2CO_3$$

(d) Reaction with Water

All alkali metals are more reactive than hydrogen. Thus, these are easily and readily oxidised by water. The reaction with water is so exothermic that the heat generated often ignites the $H_2(g)$ produced, if air is present. These metals displace hydrogen from water.

The vigorous nature of the reaction of water with alkali metals increases from Li to Cs. Lithium is only slowly attacked by water at 298 K, though it liberates more energy in this reaction. Sodium reacts more vigorously, whereas potassium catches fire and rubidium and caesium react violently or explosively.

The fact that lithium reacts with water less vigorously, may probably be due to its higher melting point. Other alkali metals have low melting points (below 373 K) and melt due to the heat liberated in their initial reaction with water, thus exposing more metal surface to attack. The reaction, therefore, proceeds much more rapidly than with lithium which remains in solid state.

(e) Reaction with Oxidising and Non-oxidising Acids

The alkali metals replace hydrogen from non-oxidising acids (*e.g.,* HCl, dil H_2SO_4). While reacting with oxidising acids such as conc. H_2SO_4, conc HNO_3 and dil HNO_3, these metals do not replace hydrogen but H_2S, N_2O and NH_3 are formed respectively as,

$$5H_2SO_4 + 8M \longrightarrow 4M_2SO_4 + H_2S + 4H_2O$$
$$10HNO_3(\text{conc}) + 8M \longrightarrow 8MNO_3 + N_2O + 5H_2O$$
$$9HNO_3(\text{dil}) + 8M \longrightarrow 8MNO_3 + NH_3 + 3H_2O$$

(Here, M = alkali metals)

(f) Reaction with Ammonia

When heated with NH_3 gas at 300–400°C in the presence of Fe, alkali metals form amides of the type MNH_2. The expected order of reactivity of the metals and the corresponding stability of the salt formed is Cs > Rb > K > Na > Li.

The alkali metals are soluble in liquid ammonia giving a solution which is paramagnetic, highly conducting, highly reducing and deep blue in colour. The solution is blue when dilute and acquires a intense blue colour as more metal is added. Blue solutions have a broad absorption band at 1450 nm. Properties of these solutions strongly suggest that alkali metal atoms ionise in liquid ammonia forming **solvated cations** and **solvated electrons.**

Step I Ionisation of alkali metal

$$M(s) \longrightarrow M^+(g) + e^-$$

Step II Cation M^+ and e^- both are solvated by NH_3 forming $[M(NH_3)_x]^+$ and $[e(NH_3)_y]^-$.

$$M^+ + (x + y)NH_3 \longrightarrow [M(NH_3)_x]^+ + [e(NH_3)_y]^-$$

It is the ammoniated electron which is responsible for the blue colour of the solution, and the electrical conductivity is due to the ammoniated cation, $[M(NH_3)_x]^+$, as well as the ammoniated electron, $[e(NH_3)_y]^-$, values of x and y depend on the extent of solvation (by NH_3). Dilute solutions are paramagnetic due to free electrons. In concentrated solutions ammoniated electrons associate to form electron-pairs and their paramagnetic character decreases.

The solutions are strong reducing agents due to the presence of free electrons. It reduces (i) metal halides to metals (ii) N_2O to N_2 (iii) O_2 to O_2^- and then to O_2^{2-}.

(g) Nature of Nitrates

These form nitrates of the type, MNO_3 which are colourless, soluble in water and electrovalent in nature. The nitrates do not hydrolysed. Except $LiNO_3$, the other nitrates decompose to nitrites and oxygen.

$$2MNO_3 \xrightarrow{\Delta} 2MNO_2 + O_2$$

Lithium nitrate decomposes to oxide on heating, it is due to more polarising nature of small Li^+ towards small oxide ion.

$$2LiNO_3 \xrightarrow{\Delta} Li_2O + 2NO_2 + \frac{1}{2}O_2$$

(h) Nature of Sulphates

These form sulphates of the type M_2SO_4 except Li_2SO_4, other sulphates are soluble in water. The sulphates when fused with carbon form sulphides.

$$M_2SO_4 + 4C \longrightarrow M_2S + 4CO$$

The sulphates of alkali metals form double salts with the sulphates of the trivalent metals like Fe, Al, Cr, etc. The double sulphates crystallise with large number of water molecules as potash alum, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ consists of 24 water molecules. Sulphate of lithium are not known to form alum.

(i) Reaction with Nitrogen and Carbon

Despite its high ionisation energy, lithium is the only alkali metal, which reacts directly with nitrogen and carbon to form the nitride and carbide respectively. Other alkali metals do not react directly with either nitrogen or carbon. This is probably due to the fact that small size of the nitride and carbide ions coupled with the small size of Li^+ ions results in high lattice energies for these compounds. Thus, heats of formation of these compounds are also high resulting in more stability.

(j) **Alkali Metal Hydrides**

Hydrides of the type *M*H have been prepared for all alkali metals, except francium. They are colourless, crystalline, ionic solids. The hydrides are largely ionic with the negative hydride ion H^- present in the lattice. *The alkali metal hydrides posses* NaCl *type structure. The ionic character of the bonds in these hydrides increases as the atomic number of metal increases. Their stability decreases in the same order i.e., from* LiH *to* CsH.

Lithium hydride is by far the most stable hydride which dissociates above 1273 K. Sodium and potassium hydrides dissociate below 773 K.

The alkali metal hydrides are strong reducing agents and their reducing property increases with decrease in stability. Lithium also forms some complex, *i.e.,* $LiAlH_4$ and $LiBH_4$, which like simple hydrides, are also good reducing agents.

(k) **Alkali Metal Halides**

Alkali metals readily react with halogens to form *MX* type of halides. These are mainly ionic compounds having NaCl type of structure with a coordination number of 6 : 6 except for CsCl, CsBr and CsI, which have a CsCl type structure with a coordination number of 8 : 8. Due to more favourable lattice energy, lithium also exhibits a coordination number of 6, although the theoretically expected value is 4. Because of small size of Li^+ ion, its all halides form hydrated salts more readily than other alkali metals. In fact, LiCl, LiBr and LiI, all exist as trihydrates, $LiX \cdot 3H_2O$. Other alkali metal halides are anhydrous. All alkali metal halides (except LiF) are soluble in water.

For a substance to dissolve, the hydration energy must be greater than lattice energy. Due to small size of Li^+ ion, the hydration energy of LiF is considerably high, but it has low solubility in water because of its higher lattice energy. The hydration and lattice energies of LiF are −1034 and −1039 kJ/mol respectively.

Caution Points

(*i*) *ΔH_f° for fluorides becomes less negative as we go down the group, while reverse is true for chlorides, bromides and iodides.*

(*ii*) *For a given metal, ΔH_f° always becomes less negative as we go from the fluoride to iodide.*

(l) **Alkali Metal Carbonates** (Oxysalts)

The alkali metals are highly electropositive and hence, their **oxysalts** are quite stable. Carbonates are remarkable stable. Li_2CO_3 is less stable and decomposes readily. *The strong polarising action of the small cation on the large carbonate ion presumably assists the decomposition.*

$$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$$

The gain in lattice energy resulting from the substitution of a smaller oxide ion from larger CO_3^{2-} ion enables the decomposition. Bicarbonates of all alkali metals, except that of Li, can be obtained in the solid form. All carbonates and bicarbonates are soluble in water. Lithium carbonate is sparingly soluble.

The above written decomposition reaction is not shown by any other alkali metal, i.e., the carbonates of other alkali metals are thermally stable and do not evolve CO_2 *on heating in air.*

(m) **Complex Formation**

Alkali metals have a very little tendency to form complexes. Lithium being small in size forms certain complexes but this tendency decreases as the size increases.

Caution Point *The alkali metals cannot be prepared by the reduction of their oxides, as these metals themselves are strong reducing agents. Electrolysis of the aqueous solutions of their salts produces the metal hydroxide, as the metals are very reactive towards water. For these reasons, the isolation of alkali metals is usually carried out by the electrolysis of their molten salts.*

Sample Problem 2 Li_2CO_3 *decomposed at a lower temperature whereas* Na_2CO_3 *at higher temperature. This is due to* **[NCERT]**

(*a*) *small* Li *ion*

(*b*) *large* CO_3^{2-} *ion*

(*c*) *high hydration enthalpy of* Li

(*d*) *All of the above*

Interpret (*a*) Lithium being very small in size polarises a large CO_3^{2-} ion leading to the formation of more stable Li_2O and CO_2. All the carbonates of alkali metals (except lithium carbonate) are thermally quite stable. That's why Li_2CO_3 is decomposed at a lower temperature whereas Na_2CO_3 at higher temperature.

10.2 **Anomalous Behaviour of Li**

Li, due to its small size and high charge density, differs from rest of the first group elements.

It shows the following anomalous properties :

1. Li is the hardest metal. Its boiling point and melting point are highest among the group.
2. It is the only alkali metal which reacts directly with N_2 to give **nitride** (Li_3N).
3. LiH is much more stable.

$$Li + H_2 \xrightarrow{700-800^\circ C} \text{hydrides}$$

(Remaining hydrides are formed at 350−430°C.)

4. With air or O_2, it only gives Li_2O, *i.e.,* monoxide while remaining gives M_2O_2 (peroxide) and MO_2 (superoxide) also.
5. Lithium hydroxide decomposes at red heat to form Li_2O. Hydroxides of other alkali metals do not decompose.

$$2LiOH \xrightarrow{\text{Red hot}} Li_2O + H_2O$$

$$\text{Other hydroxides} \xrightarrow[\text{hot}]{\text{Red}} \text{No reaction}$$

LiOH shows lowest solubility.

6. $LiHCO_3$ is known in solution but not in solid state while the bicarbonates of other alkali metals are known in solid state.
7. Li_2O is least basic.
8. Fluoride, phosphates, oxalate and carbonates of Li are sparingly soluble while that of other metals are freely soluble.
9. Carbonates and hydroxide of Li are least stable (thermally) while that of other alkalies are highly stable (thermally).
10. $LiNO_3$, on heating gives a mixture of NO_2 and O_2 while nitrates of rest of alkali metals yield only oxygen.

$$LiNO_3 \xrightarrow{\Delta} Li_2O + NO_2\uparrow + O_2\uparrow$$

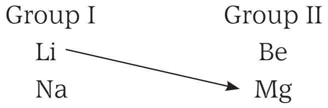
$$NaNO_3 \longrightarrow NaNO_2 + O_2\uparrow \text{ (thermally stable)}$$

(Nitrates of other alkali metals also give same reactions).

11. Li_2SO_4 is the only alkali metal sulphate which does not form double salts, *e.g.,* alum.
12. Lithium reacts with bromine very slowly. Other alkali metals react violently.
13. LiCl is highly deliquescent and soluble in alcohol and pyridine. LiCl separates out from aqueous solution as hydrated crystals $LiCl \cdot 2H_2O$ whereas chlorides of other alkali metals are insoluble in organic solvents and do not form hydrated crystals under ordinary temperature.

10.3 Diagonal Relationship of Li with Magnesium

Lithium shows resemblance with magnesium, (Mg) an element of group IIA placed diagonally opposite. This resemblance is termed as **diagonal relationship.**



Reason for the diagonal relationship are

(i) Comparable electronegativity of Li and Mg (Li = 1.00 and Mg = 1.20)

(ii) Small difference in radii of Li and Mg

Atomic radii (pm)	Li	152	Mg	160
Ionic radii (pm)	Li^+	76	Mg^{2+}	72

(iii) Both have high polarising power (ionic potential)

$$\text{Polarising power } (\Phi) = \frac{\text{Ionic charge}}{(\text{Ionic radius})^2}$$

Lithium resembles magnesium in the following respects

1. Both Li and Mg are harder and have higher melting points than the other metals in their respective groups.
2. Li like Mg decomposes water slowly to liberate hydrogen.

$$2Li + 2H_2O \longrightarrow 2LiOH + H_2$$
$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$$

3. Lithium forms only monoxide when heated in oxygen. Mg also forms the monoxide.

$$4Li + O_2 \longrightarrow 2Li_2O$$
$$2Mg + O_2 \longrightarrow 2MgO$$

Both the oxides are less soluble in water.

4. Both the elements combine with nitrogen on heating to give nitrides.

$$6Li + N_2 \longrightarrow 2Li_3N$$
$$3Mg + N_2 \longrightarrow Mg_3N_2$$

Both the nitrides get decomposed by water to give ammonia (NH_3).

$$Li_3N + 3H_2O \longrightarrow 3LiOH + NH_3$$
$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$

5. Carbonates of Li and Mg decompose on heating.

$$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$$
$$MgCO_3 \xrightarrow{\Delta} MgO + CO_2$$

6. Hydroxides of Li and Mg are weak bases and are slightly soluble in water. Both decompose on heating.

$$2LiOH \xrightarrow{\Delta} Li_2O + H_2O$$
$$Mg(OH)_2 \xrightarrow{\Delta} MgO + H_2O$$

7. Nitrates of Li and Mg decompose on heating giving mixture of nitrogen dioxide and oxygen.

$$4LiNO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2 + O_2$$
$$2Mg(NO_3)_2 \xrightarrow{\Delta} 2MgO + 4NO_2 + O_2$$

8. Lithium fluoride, phosphate, oxalate and carbonate, like the corresponding salts of Mg, are sparingly soluble in water.
9. Chlorides of both Li and Mg are deliquescent and soluble in alcohol and pyridine. Lithium chloride like magnesium chloride, $(MgCl_2 \cdot 6H_2O)$ separates out from solutions as hydrated crystals, $LiCl \cdot 2H_2O$.
10. Li_2SO_4 like $MgSO_4$ does not form double sulphates, *i.e.,* alums.
11. Lithium salts like magnesium salts undergo hydrolysis.

Compounds of Elements of Group 1

Being highly reactive, all the elements of group 1 form compounds. Although here we will discuss only some important of them.

Sodium Chloride (NaCl)

Sodium chloride (NaCl), also known as **common salt** or **table salt,** is responsible for the salinity of the ocean and of the extracellular fluid of many multicellular organisms. It is commonly used as a flavour enhancer and preservative for food.

Preparation

Now a days, salt is produced by evaporation of seawater or brine from other sources, such as brine wells and salt lakes, and by mining **rock salt,** called halite.

Properties and Uses

A large number of chemicals like NaOH, Na_2CO_3, Cl_2, HCl, bleaching powder etc., are synthesised from sodium chloride. 0.9% NaCl *in water is called a physiological solution as it is iso-osmotic with blood plasma*.

It is used in a plethora of applications from manufacturing pulp and paper to setting dyes in textiles and fabric, to producing soaps and detergents. In the Northern USA, large quantities of NaCl are used to help clear highways of ice during winter.

Sodium Hydroxide or Caustic Soda (NaOH)

Preparation

It is prepared by the electrolysis of NaCl [brine] in **Nelson cell** or **Caster Kellner cell** or in **Kellner Solvay cell.**

(i) Reactions occurring in **Nelson cell** (shown in the figure) are as

$$NaCl \rightleftharpoons Na^+ + Cl^- \quad \text{(in solution)}$$

At cathode $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$

$$Na^+ + OH^- \rightleftharpoons NaOH$$

At anode $2Cl^- \longrightarrow Cl_2 + 2e^-$

The solution containing NaOH and NaCl as impurity is taken out and evaporated to dryness.

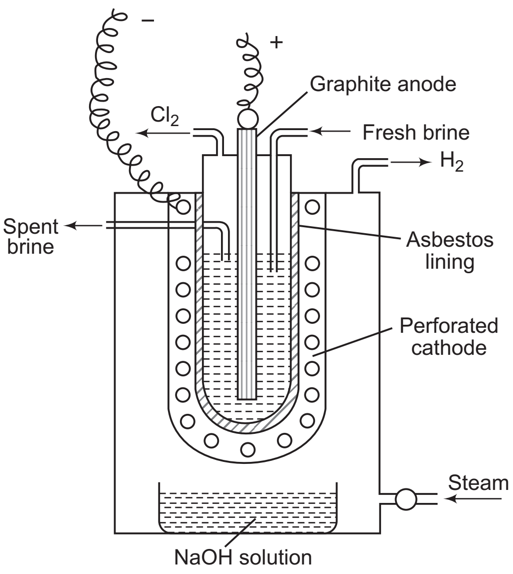


Fig. 10.1 Nelson cell

This process is also called porous diagram process.

(ii) **Castner-Kellner cell** is the common cell in which mercury is used as cathode. The advantage of using Hg as a cathode is that the discharge potential of Na^+ ions is less than that of H^+ ions. Na^+ ions get discharged on mercury and sodium so deposited combines with mercury to form sodium amalgam. The cell is shown in the Fig. 10.2.

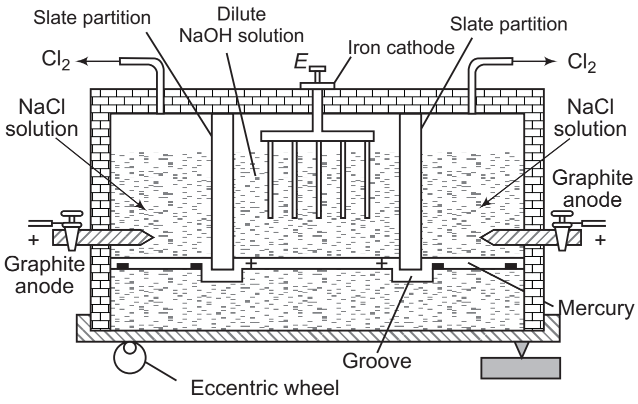


Fig 10.2 Castner-Kellner cell

Reactions occurring in this cell are

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

At anode $2Cl^- \longrightarrow 2Cl + 2e^- \longrightarrow Cl_2$

At anode $Na^+ + e^- \longrightarrow Na$

$Na + Hg \longrightarrow \text{Amalgam}$

The sodium amalgam, thus formed, comes in the inner compartment due to rocking. Here, the sodium amalgam acts as the anode and iron rods act as cathode.

At anode $\text{Na-amalgam} \longrightarrow Na^+ + Hg + e^-$

At cathode $2H_2O + 2e^- \longrightarrow H_2\uparrow + 2OH^-$

The concentrated solution of sodium hydroxide (about 20%) is taken out from inner compartment and evaporated to dryness to get solid NaOH.

(iii) A modified cell is **Kellner-Solvay cell.** It has no compartments. The flowing mercury as shown in figure 10.3 acts as cathode. A number of graphite rods dipping in sodium chloride solution act as anode. A constant level of sodium chloride solution is maintained in the cell. On electrolysis chlorine gas is liberated and Na^+ ions are discharged at cathode (mercury). Discharged sodium dissolves in Hg and forms amalgam. This amalgam flows out in a vessel containing water. Sodium hydroxide is formed with the evolution of hydrogen.

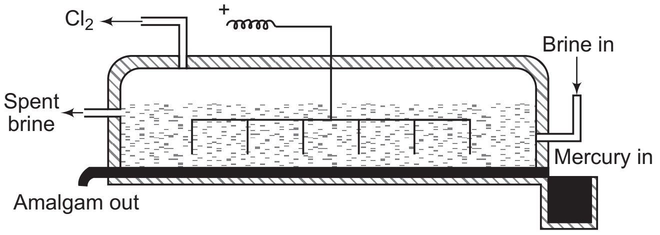


Fig 10.3 Kellner-Solvay cell

Purification of Sodium Hydroxide

Commercial sodium hydroxide is purified with the help of alcohol. Sodium hydroxide dissolves in alcohol while impurities like NaCl, Na_2CO_3, Na_2SO_4, etc., remain insoluble. The alcoholic filtrate is distilled. The alcohol distills off while pure solid sodium hydroxide is left behind.

Properties

1. It is white solid with melting point 318°C. It is hygroscopic, highly soluble in water and gives strongly alkaline solution. However, it is sparingly soluble in alcohol but less soluble than KOH.
2. It decomposes at 1300° as

$$2NaOH \longrightarrow 2Na + H_2 + O_2$$

3. It combines with acidic oxides to form salts, *e.g.,*

$$2NaOH + CO_2 \longrightarrow \underset{\text{sodium carbonate}}{Na_2CO_3} + H_2O$$

$$2NaOH + SO_2 \longrightarrow \underset{\text{sodium sulphite}}{Na_2SO_3} + H_2O$$

$$2NaOH + 2NO_2 \longrightarrow \underset{\text{sodium nitrate}}{NaNO_3} + \underset{\text{sodium nitrite}}{NaNO_2} + H_2O$$

4. It dissolves amphoteric oxides of aluminium, zinc, tin and lead to give corresponding salts.

$$Al_2O_3 + 2NaOH \longrightarrow \underset{\text{sodium meta-aluminate}}{2NaAlO_2} + H_2O$$

$$ZnO + 2NaOH \longrightarrow \underset{\text{sodium zincate}}{Na_2ZnO_2} + H_2O$$

$$PbO + 2NaOH \longrightarrow \underset{\text{sodium plumbite}}{Na_2PbO_2} + H_2O$$

$$PbO_2 + 2NaOH \longrightarrow \underset{\text{sodium plumbate}}{Na_2PbO_3} + H_2O$$

$$SnO + 2NaOH \longrightarrow \underset{\text{sodium stannite}}{Na_2SnO_2} + H_2O$$

$$SnO_2 + 2NaOH \longrightarrow \underset{\text{sodium stannate}}{Na_2SnO_3} + H_2O$$

5. With non-metals (*e.g.,* B, Si, white P, S and halogens) sodium salt of oxyacid of non-metal are obtained, *e.g.,*

   (i) **Halogens** give hypohalites and halides with cold and dilute solution of NaOH.

$$Cl_2 + \underset{\text{cold and dilute}}{2NaOH} \longrightarrow NaCl + \underset{\text{sodium hypochlorite}}{NaClO} + H_2O$$

$$Br_2 + \underset{\text{cold and dilute}}{2NaOH} \longrightarrow NaBr + \underset{\text{sodium hypobromite}}{NaBrO} + H_2O$$

$$I_2 + \underset{\text{cold and dilute}}{2NaOH} \longrightarrow NaI + \underset{\text{sodium hypoiodite}}{NaIO} + H_2O$$

   Halogens form halates and halides with hot and concentrated solution of NaOH.

$$3Cl_2 + \underset{\text{hot and conc.}}{6NaOH} \longrightarrow 5NaCl + \underset{\text{sodium chlorate}}{NaClO_3} + 3H_2O$$

$$3Br_2 + \underset{\text{hot and conc}}{6NaOH} \longrightarrow 5NaBr + \underset{\text{sodium bromate}}{NaBrO_3} + 3H_2O$$

$$3I_2 + \underset{\text{hot and conc}}{6NaOH} \longrightarrow 5NaI + \underset{\text{sodium iodate}}{NaIO_3} + 3H_2O$$

   (ii) Yellow phosphorus (white) when heated with NaOH solution evolves phosphine gas (PH_3) along with the formation of sodium hypophosphite.

$$P_4 + 3NaOH + 3H_2O \longrightarrow \underset{\text{sodium hypophosphite}}{3NaH_2PO_2} + \underset{\text{phosphine}}{PH_3}$$

   (iii) Sulphur on heating with sodium hydroxide solution forms sodium thiosulphate.

$$4S + 6NaOH \longrightarrow \underset{\text{sodium thiosulphate}}{Na_2S_2O_3} + \underset{\text{sodium sulphide}}{2Na_2S} + 3H_2O$$

(iv) Silicon evolves hydrogen when heated with NaOH solution.

$$2NaOH + Si + H_2O \longrightarrow \underset{\text{sodium silicate}}{Na_2SiO_3} + 2H_2$$

(v) Boron also evolves hydrogen when fused with NaOH.

$$2B + 6NaOH \longrightarrow \underset{\text{sodium borate}}{2Na_3BO_3} + 3H_2$$

6. Weakly electropositive metals dissolve in NaOH and evolve H_2, after forming complexes like

$$Zn \longrightarrow \underset{\text{sodium zincate}}{Na_2ZnO_2};$$

$$Al \longrightarrow \underset{\text{sodium meta aluminate}}{NaAlO_2}$$

$$Sn \longrightarrow \underset{\text{sodium stannate}}{Na_2SnO_3}$$

7. It precipitates hydroxide from many salt solutions, *e.g.*, it precipitates $Fe(OH)_2$ from $FeSO_4$ solution. However, hydroxides of amphoteric elements like Al, Zn, etc., are initially precipitated by NaOH followed by re-dissolution due to complex formation like sodium zincate, sodium meta aluminate as,

$$ZnSO_4 + 2NaOH \longrightarrow \underbrace{Na_2SO_4 + Zn(OH)_2\,(ppt.)}$$

$$\Big\downarrow \text{NaOH}$$

$$Na_2ZnO_2 \text{ (soluble)}$$

8. **With CO** under pressure, it gives sodium formate.

$$NaOH + CO \xrightarrow[5\text{–}10\text{ atm.}]{150\text{–}200°C} \underset{\text{sodium formate}}{HCOONa}$$

9. Ammonium salts are decomposed on heating with sodium hydroxide solution with the evolution of ammonia gas.

$$NH_4Cl + NaOH \longrightarrow NH_3\uparrow + NaCl + H_2O$$

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2NH_3\uparrow + 2H_2O$$

10. Sodium hydroxide breaks down the proteins of skin to a pasty mass. On account of this property, it is commonly called as **caustic soda.**

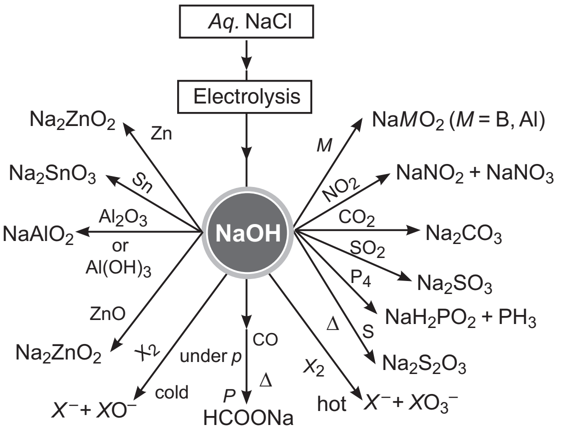


Fig. 10.4 Flow chart showing chemistry of NaOH

Uses

NaOH *is used*

(i) as a reagent in the laboratory.
(ii) in the manufacture of soap.
(iii) in the manufacture of paper and rayon.
(iv) in the manufacture of dyes and drugs.
(v) as an absorber of gases.
(vi) in the manufacture of sodium hypochlorite, sodium chlorate and sodium nitrite.
(vii) for mercerizing cotton.

Sodium Carbonate or Soda Ash (Na_2CO_3)

Since pre-historic times a natural deposit called Trona, $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ (sesqui-carbonate) has been obtained from dried-up lake beds in Egypt. Trona is sometimes called sodium sesqui-carbonate (sesqui means one and a half) and on heating it, Na_2CO_3 is obtained.

$$2(Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O) \xrightarrow{\Delta} 3Na_2CO_3 + CO_2 + 5H_2O$$

Preparation

It is manufactured by **Solvay ammonia process.**

The process involves following three steps :

Step I CO_2 is passed through a solution of NH_3, NH_4HCO_3 is produced. The CO_2 used is obtained by heating $CaCO_3$.

$$NH_3 + H_2O + CO_2 \longrightarrow NH_4HCO_3$$

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

Step II NH_4HCO_3 is then reacted with NaCl. $NaHCO_3$ and NH_4Cl are formed. In this step, ammonia is recovered back from NH_4Cl as

$$NaCl + NH_4HCO_3 \longrightarrow NaHCO_3 + NH_4Cl$$

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

$$2NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + 2NH_3 + 2H_2O$$

Step III The bicarbonate formed, on heating gives Na_2CO_3, H_2O and CO_2.

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$$

Raw materials NaCl, NH_3 and limestone (for CO_2).

Most of NH_3 can be recovered in the process. $CaCl_2$ is the only by-product.

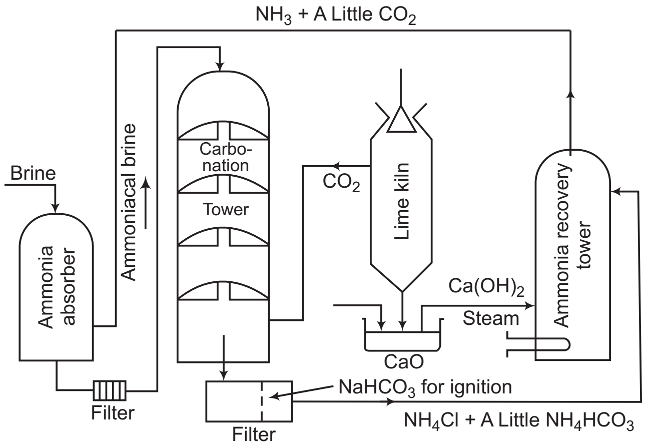


Fig. 10.5 Flow sheet diagram of Solvay's ammonia soda process for the manufacture of sodium carbonate

Caution Point *Le-Blanc process and electrolytic process can also be used to prepare* Na_2CO_3.

Properties

1. It crystallises as decahydrate. (Sodium carbonate decahydrate, $Na_2CO_3 \cdot 10H_2O$, is also known as washing soda). The decahydrate form on standing in air effloresces and crumbles to powder. It is the monohydrate form, $Na_2CO_3 \cdot H_2O$. It also forms a heptahydrate, $Na_2CO_3 \cdot 7H_2O$.

   On heating, the monohydrate changes into the anhydrous form which does not decompose on further heating even to redness. It is the amorphous powder and called **soda ash**. It melts at 852°C.

$$Na_2CO_3 \cdot 10H_2O \xrightarrow[\text{to air}]{\text{On exposure}} \underset{\substack{\text{soluble in water;}\\ \text{solution alkaline}}}{Na_2CO_3 \cdot H_2O} + 9H_2O$$

$$\downarrow \Delta$$

$$\underset{\text{decomposition}}{\text{No}} \longleftarrow \underset{\substack{\text{thermally}\\ \text{stable;}}}{Na_2CO_3}$$

2. It is soluble in water with the evolution of considerable amount of heat. The solution is alkaline in nature due to hydrolysis.

$$Na_2CO_3 + 2H_2O \rightleftharpoons 2NaOH + H_2CO_3$$

   When the hot solution of sodium carbonate is concentrated and cooled, crystals of decahydrate form are obtained.

3. On passing CO_2 through the concentrated solution of sodium carbonate, sodium bicarbonate gets precipitated.

$$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3$$

4. It is readily decomposed by acids. The reaction occurs in two steps.

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$$
$$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$$

5. When the mixture of sodium carbonate and silica is fused, sodium silicate (soft glass) is formed.

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2\uparrow$$

   Sodium silicate is called **soluble glass** or **water glass** as it is soluble in water.

6. When the solution of sodium carbonate and slaked lime is heated, sodium hydroxide is formed.

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow 2NaOH + CaCO_3$$

7. When aqueous solution of sodium carbonate containing sulphur is treated with sulphur dioxide, sodium thiosulphate ($Na_2S_2O_3$) is formed.

$$Na_2CO_3 + SO_2 \xrightarrow{H_2O} Na_2SO_3 + CO_2\uparrow$$
$$Na_2SO_3 + S \longrightarrow Na_2S_2O_3$$

8. Sodium carbonate reacts with metal salts (except alkali metal salts) to form insoluble normal or basic carbonates.

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$$
$$BaCl_2 + Na_2CO_3 \longrightarrow BaCO_3 + 2NaCl$$

9. Carbonates of metals like Fe, Al, Sn, etc., when formed are immediately hydrolysed to hydroxides.

$$Fe_2(SO_4)_3 + 3Na_2CO_3 \longrightarrow Fe_2(CO_3)_3 + 3Na_2SO_4$$
$$Fe_2(CO_3)_3 + 3H_2O \longrightarrow 2Fe(OH)_3 + 3CO_2$$

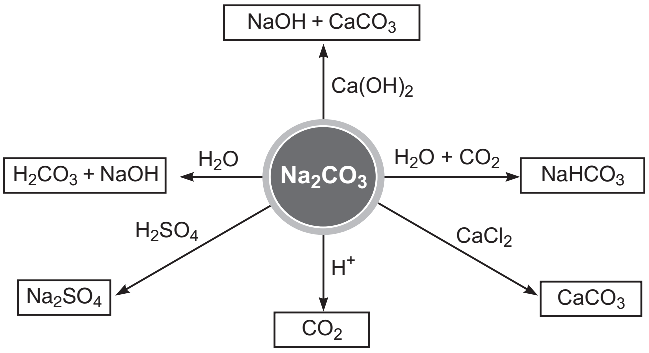


Fig. 10.6 Summary of reactions of Na_2CO_3

Uses

Sodium carbonate is used

(i) in laundries and in softening of water as washing soda.
(ii) in the manufacture of glass, sodium silicate, paper, borax, soap powders, caustic soda, etc.
(iii) in textile and petroleum refining.
(iv) for the preparation of various carbonates of metals.
(v) The mixture of Na_2CO_3 and K_2CO_3, called the **fusion mixture,** is used in quantitative analysis to standarise acid solutions. In qualitative analysis, it is used in the detection of acidic radicals especially of insoluble salts.

Sodium Hydrogen Carbonate ($NaHCO_3$)

It is also called sodium bicarbonate.

Manufacture by Solvay Process in Laboratory

$NaHCO_3$ is prepared by saturating a solution of Na_2CO_3 (cold) with CO_2. In this process, $NaHCO_3$ separates as white crystals (due to its poor solubility in water).

$$Na_2CO_3 + CO_2 + H_2O \longrightarrow \underset{\text{sparingly soluble}}{2NaHCO_3}$$

Properties

1. It is a white crystalline solid, sparingly soluble in water. The solution is alkaline in nature due to hydrolysis. The solution is weakly basic.

   $$NaHCO_3 + H_2O \rightleftharpoons NaOH + H_2CO_3$$

   The solution gives yellow colour with methyl orange but no colour with phenolphthalein.
2. The metal salt which forms basic carbonate with sodium carbonate, gives normal carbonate with sodium bicarbonate.

   $$ZnSO_4 + 2NaHCO_3 \longrightarrow ZnCO_3 + Na_2SO_4 + H_2O + CO_2$$
3. If heated (solid or solution), it decomposes to Na_2CO_3 and CO_2.

   $$2NaHCO_3 \xrightarrow[\text{to}]{\text{Decomposes}} Na_2CO_3 + CO_2$$

   That's why it is used as a constituent of **"baking powder"** and effervescent drinks.

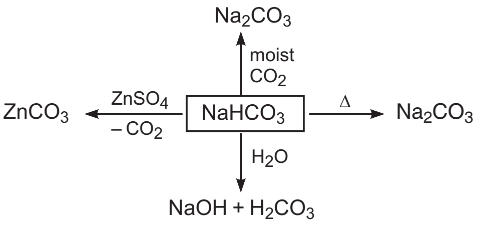


Fig. 10.7 Summary of reactions of $NaHCO_3$

Uses

(i) It is used as a medicine antacid to neutralise the acidity in the stomach.

(ii) It is largely used for making baking powder, a mixture of potassium hydrogen tartrate and sodium bicarbonate.

(iii) It is used in making effervescent drinks.

(iv) It is used in free extinguishers.

(v) It is used for the production of carbon dioxide.

Sodium Thiosulphate or Hypo ($Na_2S_2O_3 \cdot 5H_2O$)

An important salt of thiosulphuric acid is sodium thiosulphate, $Na_2S_2O_3 \cdot 5H_2O$. Unlike thiosulphuric acid, it is quite stable.

Methods of Preparation

1. Sodium thiosulphate is prepared by boiling sodium sulphate solution with flowers of sulphur and stirring till the alkaline reaction has disappeared.

   $$Na_2SO_3 + S \longrightarrow Na_2S_2O_3$$

   - The excess of sulphur is filtered off and the filtrate evaporated to crystallisation when crystals of sodium thiosulphate, $Na_2S_2O_3 \cdot 5H_2O$ separate on slow cooling.
   - Sodium sulphite used above is prepared from sodium carbonate. A concentrated solution of sodium carbonate is prepared. One half of this is saturated with sulphur dioxide and the other half of the solution is then added when we get sodium sulphite.

   $$Na_2CO_3 + 2SO_2 + H_2O \longrightarrow 2NaHSO_3 + CO_2$$
   $$2NaHSO_3 + Na_2CO_3 \longrightarrow 2Na_2SO_3 + H_2O + CO_2$$
2. Sodium thiosulphate is also formed together with sodium sulphide when sulphur is boiled with sodium hydroxide solution.

   $$6NaOH + 4S \xrightarrow{\text{Boil}} Na_2S_2O_3 + 2Na_2S + 3H_2O$$

Properties

Properties of sodium thiosulphate are as follows

1. It is a colourless, crystalline and efflorescent substance of the formula $Na_2S_2O_3 \cdot 5H_2O$. It is soluble in water.
2. On heating, it decomposes to give sulphur dioxide, hydrogen sulphide and sulphur.
3. Dilute acids decompose it with the evolution of sulphur dioxide and precipitation of sulphur.

   $$Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + SO_2 + S + H_2O$$
4. Silver halides are dissolved by sodium thiosulphate solution (hence, used in photography for fixing).

   $$\underset{\substack{\text{silver}\\\text{bromide}}}{AgBr} + \underset{\substack{\text{sodium}\\\text{thiosulphate}}}{2Na_2S_2O_3} \longrightarrow \underset{\substack{\text{sodium argento}\\\text{thiosulphate}}}{Na_3[Ag(S_2O_3)_2]} + NaBr$$
5. Silver nitrate gives, with a very dilute solution of it, a white precipitate which quickly changes colour to yellow, brown and finally black due to the formation of silver sulphide.

   $$Na_2S_2O_3 + 2AgNO_3 \longrightarrow Ag_2S_2O_3 + 2NaNO_3$$
   $$Ag_2S_2O_3 + H_2O \longrightarrow Ag_2S + H_2SO_4$$

With a concentrated solution of sodium thiosulphate, silver nitrate gives no precipitate. This is because silver thiosulphate formed, is readily soluble in excess of sodium thiosulphate.

$$Ag_2S_2O_3 + 3Na_2S_2O_3 \longrightarrow 2Na_3[Ag(S_2O_3)_2]$$

6. Chlorine oxidises hypo to sodium sulphate while iodine is decolourised due to the formation of tetrathionate.

$$\begin{array}{c} Cl_2 + H_2O \longrightarrow 2HCl + O \\ Na_2S_2O_3 + O \longrightarrow Na_2SO_4 + S \\ \hline Na_2S_2O_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + 2HCl + S \\ \hline \end{array}$$

$$2Na_2S_2O_3 + I_2 \longrightarrow \underset{\substack{\text{sodium}\\\text{tetrathionate}}}{Na_2S_4O_6} + 2NaI$$

7. A moderately concentrated solution of sodium thiosulphate gives a white precipitate of barium thiosulphate with barium chloride. *No precipitate is obtained with calcium chloride. Since, calcium thiosulphate is fairly soluble in water.*

$$Na_2S_2O_3 + BaCl_2 \longrightarrow BaS_2O_3 + 2NaCl$$

8. On addition of a few drops of ferric chloride to thiosulphate solution, a violet colouration is obtained due to the formation of ferric thiosulphate.

$$3Na_2S_2O_3 + 2FeCl_3 \rightleftharpoons Fe_2(S_2O_3)_3 + 6NaCl$$

The violet colour disappears quickly due to the reduction of ferric chloride by thiosulphate. This shifts the above equilibrium to the left.

$$\begin{array}{c} [FeCl_3 \longrightarrow FeCl_2 + Cl] \times 2 \\ 2Na_2S_2O_3 + 2Cl \longrightarrow Na_2S_4O_6 + 2NaCl \\ \hline 2FeCl_3 + 2Na_2S_2O_3 \longrightarrow 2FeCl_2 + Na_2S_4O_6 + 2NaCl \\ \hline \end{array}$$

Uses

Sodium thiosulphate is used

(i) in photography for fixing, under the name hypo.
(ii) in textile industry as antichlor.
(iii) in the extraction.
(iv) in the laboratory for the volume estimation of iodine and as a reagent.
(v) in medicine.

Potassium Superoxide (KO_2)

Preparation

It is formed as a chrome-yellow (orange) powder by burning potassium in excess of moisture free oxygen or air.

$$K + O_2 \longrightarrow KO_2$$

Properties and Uses

KO_2 is a better oxidising agent than K_2O_2, since it produces O_2 and H_2O_2 both in aqueous or acidic solution.

$$\begin{array}{rcl} 2KO_2 + 2H_2O & \longrightarrow & 2KOH + H_2O_2 + O_2 \\ 2KO_2 + H_2SO_4 & \longrightarrow & K_2SO_4 + H_2O_2 + O_2 \\ 2KO_2 + CO & \longrightarrow & K_2CO_3 + O_2 \\ 4KO_2 + 2CO_2 & \longrightarrow & 2K_2CO_3 + 3O_2 \\ 4KO_2 + 4CO_2 + 2H_2O & \longrightarrow & 4KHCO_3 + 3O_2 \end{array}$$

KO_2 thus, finds applications in **space capsules, submarines** and **breathing masks,** because it both produces O_2 and removes CO_2 and CO. Both functions are important in life support systems.

Check Point 1

1. Li^+ ions is far smaller than the other alkali metal ions but it moves through a solution less rapidly than others. Explain.
2. Explain, why sodium is less reactive than potassium?
3. Why sodium forms Na^+ ions and not Na^{2+}?
4. Explain, why alkali metals are good reducing agents?
5. Explain, why LiI is more soluble than KI in ethanol?

Alkaline Earth Metals and Their Compounds

10.4 Alkaline Earth Metals

Be, Mg, Ca, Sr, Ba and **Ra** also belong to s-block and are called **alkaline earth metals.** These are called **"alkaline earth metals"** due to the following facts

1. Their hydroxides form alkaline aqueous solutions.
2. Their oxides are **earthen**, *i.e.,* soil like means having very high melting points.

Radium is the radioactive element of this group.

Electronic Configuration

General electronic configuration of alkaline earth metals is ns^2 (where $n \neq 1$), *i.e.,* atoms of IIA group elements have two electrons in their outermost shell. The penultimate layer has, as in case of alkali metals, 8 electrons (s^2p^6), except beryllium, which contains 2 electrons in the penultimate shell, *i.e.,* in the s-subshell. Thus, they possess an inert gas core and two electrons in the s-orbital of the valence shell (ns^2).

Element	Configuration
$_4$Be	[He] $2s^2$
$_{12}$Mg	[Ne] $3s^2$
$_{20}$Ca	[Ar] $4s^2$
$_{38}$Sr	[Kr] $5s^2$
$_{56}$Ba	[Xe] $6s^2$
$_{88}$Ra	[Rn] $7s^2$

Trends in Physical Properties of Elements

Following trends are observed in physical properties of alkaline earth metals.

(a) Physical State

They are all silvery white metals. They have greyish white lustre when freshly cut, but tarnish soon after their exposure in air due to surface oxidation. They are soft in nature but harder than alkali metals because metallic bonding is stronger than IA elements due to possession of 2 valence electrons. However, hardness decreases with increase in atomic number. These elements are malleable and ductile but less than alkali metals.

(b) Atomic Size

These atoms are large in size but smaller than the corresponding alkali metals, since the increased nuclear charge draws the orbitals electrons in. The ionic radii of these metallic ions is also large but smaller as compared to that of alkali metal ions. The metal atom changes into a bipositive ion by the loss of two electrons present in the outermost shell. Then the outer shell is eliminated and the effective nuclear charge further increases. Hence, size of the ion is smaller than the parent atom. *Due to smaller size of their ions, these are more extensively hydrated than alkali metals and form hydrated salts like* $MgCl_2 \cdot 6H_2O$; $CaCl_2 \cdot 6H_2O$ *etc.*

(c) Density

Their density does not show any regular trend but in general these are more dense than alkali metals.

(d) Electropositive Character or Metallic Character

It increases down the group. But these elements are less basic than alkali metals which can be confirmed by the fact that last three alkali metals (K, Rb and Cs) show photoelectric effect which is not shown by any of the alkaline earth metals.

(e) Metallic Bonding and Hardness

These elements are more rigid (harder) than alkali metals due to the stronger metallic bonding in them as compared to alkali metals. More strength of metallic bonding is due to increase in number of electrons available for it (electrons for metallic bonding available in alkali metals is one which is doubled in number as we see alkaline earth metals). But inspite of their hardness these can also be cut by a sharp knife similar to alkali metals.

(f) Melting Point and Boiling Point

The melting and boiling points are not regular in the group, mainly due to different crystal structures of the metals. However, these are higher than those of alkali metals.

(g) Ionisation Energy

Due to larger nuclear charge and smaller atomic radius of IIA group elements (as compared to alkali metals), the valence electrons are more tightly held. Thus, the first ionisation energies of these elements are higher than those of alkali metals. The +1 oxidation state might be easily attained by the alkaline earth metal, but the second ionisation energy is more than four times greater than that required for ionising the alkali metals. This high energy requirement is more than compensated by the energy released during lattice formation and hydration of ions. These elements form colourless, largely ionic compound in +2 oxidation state, *e.g.,* $MgCl_2$.

(h) Electronegativity

Their electronegativities decrease down the group but these are more than the electronegativity values of alkali metals.

(i) Flame Colouration

Like alkali metals, these also impart characteristic colour to the flame. However, Mg and Be, being smaller in size, do not impart colour as electrons are very tightly bound and a large amount of energy is required to excite them.

(j) Reducing Character

The high negative values of standard reduction potentials indicate that metals of IIA group are *good reducing agents but less stronger as compared to alkali metals.* Although the energies required to vaporise and ionise the atoms of IIA group elements to M^{2+} ions are high. The high lattice energies in the solid salts and high hydration energies of $M^{2+}(aq)$ ions compensate for this and hence, E° values are almost near to those of alkali metals.

The above properties of alkaline earth metals can be summarized in the following table :

Table 10.2 **Physical Properties of Alkaline Earth Metals**

Property	Be	Mg	Ca	Sr	Ba	Ra
Atomic number	4	12	20	38	56	88
Molar mass (g mol^{-1})	9.01	24.31	40.08	87.67	137.34	226.05
Molar volume (cm^3 mol^{-1})	4.90	13.97	25.91	34.54	36.72	38.00
Density (g cm^{-3})	1.84	1.74	1.55	2.54	3.75	6.00
Melting point (°C)	1277	650	838	768	714	700
Boiling point (°C)	2770	1107	1440	1380	1640	1140
Atomic radius (Å)	0.90	1.36	1.74	1.92	1.98	—
Ionic radius (Å)	0.30	0.65	0.94	1.10	1.29	1.32
Heat of hydration of ions (kJ mol^{-1})	2494	1921	1577	1443	1305	—
Heat of atomisation (kJ mol^{-1})	78.2	35.2	42.5	39.1	42.2	—
Ionisation energy (kJ mol^{-1}) First	899	737	590	549	503	509
Second	1757	1450	1146	1064	965	979
Electronegativity	1.5	1.0	1.2	1.0	0.9	0.9
Flame colouration	None	None	Brick red	Crimson	Grassy green	Crimson
Oxidation state	+2	+2	+2	+2	+2	+2

Comparison Between the Properties of Alkaline Earth Metals and Alkali Metals

Unlike the members of group IA, the chemistry of IIA group elements is not completely dominated by the chemistry of cations. When compared with alkali metals, it is found that

1. They are less reactive than alkali metals.
2. They are less electropositive, *i.e.,* less metallic than alkali metals.
3. Their reducing power is much less than those of alkali metals.
4. They are less basic than alkali metals.
5. The gradation in properties of these elements is not as regular as in the case of alkali metals, because of different structures of their crystal lattices.

The difference in properties with alkali metals is due to

1. Small size of atoms and ions.
2. Stronger metallic bonds (resulting to more density and hardness).
3. Higher melting and boiling points.

Hot Spot 2

TRENDS in Chemical Properties of Group 2 Elements

It is also an important topic for JEE Main examination. The nature of question is moderate to easy. Learn the trends and reason of the trend to solve out the problems based on this topic.

Alkaline earth metals give all the usual reactions of alkali metals. However, in these reactions, these are less reactive.

(a) Reaction with Air

These are slowly oxidised on exposure to air forming oxides. These oxides are white crystalline solid and basic in nature. However, **the oxide of Be is amphoteric in nature** due to the smaller size of Be^{2+} ion. As a result of smaller size, this ion has more polarising power resulting to appearance of covalent character in the compounds of this ion. **The basic strength of oxides increases down the group.**

BeO is very hard solid (4 : 4 coordination) while rest oxides are with 6 : 6 coordination. These oxides are highly stable due to their large ionic crystal lattice energies. BeO and MgO are almost insoluble in water. **Due to their high melting points, MgO and CaO are used as basic lining of furnaces.**

(b) Reaction with Water

Be shows no reaction with water (cold as well as hot in the forms of steam); Mg does not react with cold water, *i.e.,* it reacts with hot water (steam) only while rest of the members react with cold water as

$$Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2 \uparrow$$

The basic character and solubility of hydroxides increases down the group. This is because solubility is decided by hydration and the lattice energies which decrease with increase in size of metal ions. Decreasing lattice energy favours increased solubility, whilst decreasing hydration energy favours decreased solubility. Since on moving down the group the lattice energy decreases more rapidly than the hydration energy, the compound becomes more soluble.

The aqueous suspension of $Mg(OH)_2$ is called milk of magnesia and used as anti acid drug (antacid). $Ba(OH)_2$ is almost as strong as the alkali metal hydroxides and most soluble among all hydroxides, while $Be(OH)_2$ is amphoteric.

(c) Reaction with Hydrogen

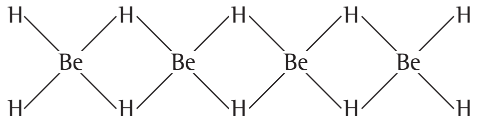
Be does not react directly with hydrogen. Rest of the elements react with hydrogen to form ionic hydrides of MH_2 type. The hydride of Be is prepared by reducing its chloride as

$$2BeCl_2 + LiAlH_4 \longrightarrow 2BeH_2 + LiCl + AlCl_3$$

BeH_2 and MgH_2 are covalent in nature while other hydrides are ionic in nature. Calcium, strontium and barium hydrides liberate hydrogen at anode on electrolysis in the fused state. Ionic hydrides are violently decomposed by water evolving hydrogen. CaH_2 is technically called **hydrolith** and used on large scale for the production of hydrogen.

$$CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2$$

BeH_2 and MgH_2 are known to have polymeric bridge structure with hydrogen present as bridge between two metal atoms.



Three centre bonds are present in which a banana shaped molecular orbital covers three atoms Be---H---Be and contains two electrons. Hydrogen atoms lie in the plane perpendicular to the plane of molecule containing beryllium atoms.

The stability of the hydrides decreases with increasing atomic number because the metallic nature of the elements increases.

(d) Reaction with Halogens

All alkaline earth metals react with halogens at elevated temperatures to form halides of MX_2 type. Among the halides, BeX_2 and MgX_2 have covalent character in them due to the higher polarising powers or more covalent character of their ions. These halides are readily soluble in water and their solubility decreases down the group due to decrease in the hydration energy.

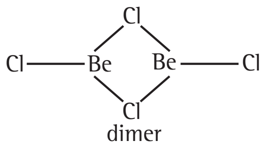
On moving down the group, ionic character increases, thus their melting point and conductivity increases from MgX_2 to BaX_2. These are good conductors in molten state.

The halides are hygroscopic in nature and readily form hydrates, *e.g.,* $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 6H_2O$, $BaCl_2 \cdot 2H_2O$, etc. Calcium chloride has a strong affinity for water and is used as a dehydrating agent.

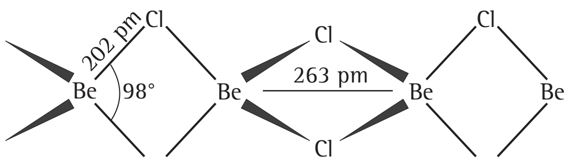
The above statement is not applicable on alkaline earth metals fluorides as these are practically almost insoluble in water.

$BeCl_2$ shows polymeric bridge structure in its solid state which is monomeric in vapour phase with zero dipole moment.

monomer



dimer



polymer

(e) Reaction with Nitrogen

All of them react with nitrogen to form nitrides of M_3N_2 type. These nitrides liberate NH_3 on reaction with water as

$$3Ca + N_2 \longrightarrow Ca_3N_2 \xrightarrow{6H_2O} 3Ca(OH)_2 + 2NH_3\uparrow$$

The ease of formation of nitrides decreases from Be to Ba. This is contrast to alkali metals where only Li_3N is formed. Because the N_2 molecule is very stable, it requires very high energy to form N^{3-} ions. The large amount of energy comes from the very large amont of lattice energy evolved when the crystalline solid is formed. The lattice energy is particularly high because of the high charges on the ions M^{2+} and N^{3-}.

Be_3N_2 is volatile (covalent character) while other nitrides are not volatile as they are ionic crystalline solids.

(f) Carbonates and Bicarbonates of Alkaline Earth Metals

The carbonates of alkaline earth metals are insoluble in water. However, if CO_2 is passed in the saturated solutions of carbonates, their bicarbonates are formed as

$$CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2$$

Thus, carbonates dissolve in water containing CO_2. Bicarbonates of Ca and Mg impart hardness to water. These bicarbonates can be converted back to carbonates on heating. Thus, hardness imparted by these bicarbonates is removed by boiling the water as these are converted to insoluble carbonates which is normally removed as precipitate. Solubility of carbonates decreases on moving down the group white stability increases.

Increasing stability can be explained on the basis of polarisation and covalent character. Be^{2+} is smallest in size hence show high polarising power. $BeCO_3$ is least ionic and has least stability.

$$\xrightarrow[\text{Increasing ionic character and stability}]{BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3}$$

The carbonates are all ionic, but $BeCO_3$ is unusual because it contains hydrated ion $[Be(H_2O)_4]^{2+}$ rather than Be^{2+}.

(g) Sulphates of Alkaline Earth Metals

They form sulphates of the type MSO_4. These are slightly soluble in water and the solubility decreases down the group, *i.e.,* $BaSO_4$ and $RaSO_4$ are almost insoluble. The solubilities of $BeSO_4$ and $MgSO_4$ are due to high energy of solvation of smaller Be^{2+} and Mg^{2+} ions. The values of solubility products which decrease gradually also explain the decrease in solubility on moving down the group.

Metal sulphate	$BeSO_4$	$MgSO_4$	$CaSO_4$	$SrSO_4$	$BaSO_4$
Solubility product	very high	10	2.4×10^{-5}	7.6×10^{-7}	1.5×10^{-9}

The sulphates decompose on heating to give the corresponding oxide (MO).

$$2MSO_4 \xrightarrow{\text{Heat}} 2MO + 2SO_2 + O_2$$

The stability increases as the basic nature of the metal increases.

Sulphates are reduced into sulphides on heating with carbon. There are normally seen as hydrates, *e.g.,* $MgSO_4 \cdot 7H_2O$ (epsom salt), $CaSO_4 \cdot 2H_2O$ (gypsum).

Caution Point $BaSO_4$ *being extremely insoluble, does not pass from digestive system into the circulatory system that's why. it is given to patients prior to taking stomach X-ray, although it is poisonous.*

(h) Nitrates

Alkaline earth metals form nitrates of the type $M(NO_3)_2$. Nitrates of these metals are soluble in water. On heating they decompose into their corresponding oxides with the evolution of a mixture of nitrogen dioxide and oxygen.

$$2M(NO_3)_2 \xrightarrow{\Delta} 2MO + 4NO_2 + O_2$$

Beryllium also forms a basic nitrate in addition to the normal salt. Basic nitrate is a covalent compound.

$$Be(NO_3)_2 \xrightarrow{125°C} \underset{\text{Basic beryllium nitrate}}{[Be_4O(NO_3)_6]}$$

(i) Reaction with Acids

All these metals liberate H_2 with dilute acid solution as

$$Mg + 2HCl \longrightarrow MgCl_2 + H_2\uparrow$$
$$Ca + H_2SO_4 \longrightarrow CaSO_4 + H_2\uparrow$$

(j) Reaction with Mercury and Other Metals

All alkaline earth metals form amalgams with Hg in the same manner as formed by alkali metals but here, in addition, they form **alloy** also with other metals like **magnalium** – Mg + Al;

(k) Solutions of Metals in Liquid Ammonia

Like alkali metals, alkaline earth metals dissolve also in liquid ammonia to form coloured solutions. Dilute solutions are bright blue in colour due to solvated electrons. These solutions decompose very slowly forming amides and evolving hydrogen.

$$M \longrightarrow M^{2+} + 2e^-$$
$$2NH_3 + 2e^- \longrightarrow 2NH_2^- + H_2$$
$$M^{2+} + 2NH_2^- \longrightarrow M(NH_2)_2$$

When the solution is evaporated, hexammoniate, $M(NH_3)_6$, is formed. These slowly decompose to give amides.

$$M(NH_3)_6 \longrightarrow M(NH_2)_2 + 4NH_3\uparrow + H_2\uparrow$$

Concentrated solutions of the metals in ammonia are bronze coloured.

(l) Carbides of Alkaline Earth Metals

Alkaline earth metals form different types of carbides with C, which are useful in preparing different saturated and unsaturated hydrocarbons on reaction with water, *e.g.,* Be forms Be_2C which forms CH_4 on reaction with water, Mg also forms Mg_2C_3 which forms $CH_3-C\equiv CH$ on reaction with water, Mg forms MgC_2 which forms $CH\equiv CH$ with water, Ca to Ba all metals form carbides of MC_2 type which on reaction with water form $CH\equiv CH$.

(m) **Complex Formation**

Generally, the alkaline earth metals do not form complexes. However, the smaller ions have some tendency to form complexes. Beryllium forms stable complexes such as $[BeF_3]^-$, $[BeF_4]^{2-}$ and $[Be(H_2O)_4]^{2+}$. Beryllium is unique in forming a series of stable complexes of formula $[Be_4O(R)_6]$, where R may be NO_3^-, $HCOO^-$, CH_3COO^-, $C_6H_5COO^-$, etc.

The most important complex formed by magnesium is chlorophyll in which magnesium is bonded to the four heterocyclic nitrogen atoms. Calcium, strontium and barium form complexes only with strong complexing agent, like acetylacetone, EDTA, etc.

Sample **Problem 3** *Some of the group 2 metal halides are covalent and soluble in organic solvents. Among the following metal halides, the one which is soluble in ethanol is* **[NCERT Exemplar]**

(*a*) $BeCl_2$ (*b*) $MgCl_2$ (*c*) $CaCl_2$ (*d*) $SrCl_2$

Interpret (*a*) Because of its small size and high charge, Be^{2+} ion has high polarising power, thus, $BeCl_2$ is covalent in nature and hence, dissolves in organic solvents like ethanol (like dissolves like).

Sample **Problem 4** *Metals form basic hydroxides. Which of the following metal hydroxide is the least basic?* **[NCERT Exemplar]**

(*a*) $Mg(OH)_2$ (*b*) $Ca(OH)_2$

(*c*) $Sr(OH)_2$ (*d*) $Ba(OH)_2$

Interpret (*a*) Basicity is the tendency to give hydroxyl ion. As the size of alkaline earth metal ion increases, the *M*—OH bond length increases, *i.e.*, *M*—OH bond weakens and hence, tendency to give OH^- increases. Thus, $Mg(OH)_2$ because of the smaller size of Mg is least basic among alkaline earth metal hydroxides.

Sample **Problem 5** *Which of the carbonates given below is unstable in air and is kept in CO_2 atmosphere to avoid decomposition?* **[NCERT Exemplar]**

(*a*) $BeCO_3$ (*b*) $MgCO_3$

(*c*) $CaCO_3$ (*d*) $BaCO_3$

Interpret (*a*) $BeCO_3$ is least stable among alkaline earth metal carbonates due to the small size of Be^{2+} ion because of which its polarising power and covalent character are high.

10.5 **Anomalous Behaviour of Beryllium**

Beryllium, the first member of alkaline earth metals, shows an anomalous behaviour, *i.e.*, differs in properties due to its small size, high ionisation enthalpy. It differs from rest of the metals in the following properties

1. Beryllium is harder than other members of its group.
2. It has higher melting and boiling points.
3. Beryllium does not react with water even at high temperature while other alkaline earth metals do.
4. Beryllium forms covalent compounds because of high charge density and greater polarising power.
5. Beryllium oxide and hydroxide are amphoteric in nature, whereas, oxides of other alkaline earth metals are basic.

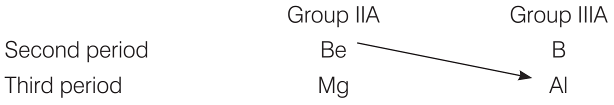
$$BeO + 2HCl \longrightarrow BeCl_2 + H_2O$$
$$BeO + 2NaOH \longrightarrow Na_2BeO_2 + H_2O$$

6. Carbides of beryllium are covalent, whereas carbides of other alkaline earth metals are ionic.
7. Beryllium carbide reacts with water to produce methane while other earth metals give acetylene gas.
8. $BeCO_3$ is unstable to heat and Be_3N_2 is volatile.
9. $BeSO_4$ is soluble in water.
10. $BeCl_2$ is a covalent compound and does not impart any colour to the flame.
11. It has strong tendency to form complex compounds.

10.6 **Diagonal Relationship of Be with Aluminium**

Be exhibits similarities in properties with Al placed diagonally opposite, which is termed as diagonal relationship. The reasons for such a relationship are

1. High polarising power of Be^{2+} and Al^{3+} ion
2. Comparable electronegativity of Be and Al
3. Almost similar E°_{oxi}.



Be shows similarity with Al in the following properties

1. Both are not affected by atmosphere.
2. Both do not decompose water.
3. Both become passive when treated with concentrated HNO_3.
4. Both dissolve in caustic alkalies liberating hydrogen.

$$Be + 2NaOH \longrightarrow Na_2BeO_2 + H_2$$
$$2Al + 2NaOH + 2H_2O \longrightarrow \underset{\text{sod. meta aluminate}}{2NaAlO_2} + 3H_2$$

5. BeO and Al_2O_3 both are amphoteric in nature.

$$BeO + H_2SO_4 \longrightarrow BeSO_4 + H_2O$$
$$BeO + 2NaOH \longrightarrow Na_2BeO_2 + H_2O$$
$$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$$
$$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$$

These oxides are extremely hard, non-volatile and have high melting points.

6. Their hydroxides are also amphoteric in nature.

$$Be(OH)_2 + 2HCl \longrightarrow BeCl_2 + 2H_2O$$
$$Be(OH)_2 + 2NaOH \longrightarrow Na_2BeO_2 + 2H_2O$$
$$Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$$
$$Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$$

The hydroxides are insoluble in water and decompose on heating into corresponding oxides.

$$Be(OH)_2 \longrightarrow BeO + H_2O$$
$$2Al(OH)_3 \longrightarrow Al_2O_3 + 3H_2O$$

7. Beryllium and aluminium both form polymeric covalent hydrides.
8. Both combine with nitrogen when strongly heated in its atmosphere.

$$3Be + N_2 \longrightarrow Be_3N_2$$
$$2Al + N_2 \longrightarrow 2AlN$$

Nitrides on action with water evolve ammonia.

$$Be_3N_2 + 6H_2O \longrightarrow 3Be(OH)_2 + 2NH_3$$
$$AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$$

9. Both the metals are obtained by the electrolysis of their fused salts in the presence of fluorides.
10. Beryllium carbide (Be_2C) and aluminium carbide (Al_4C_3) both evolve methane on treatment with water.

$$Be_2C + 2H_2O \longrightarrow 2BeO + CH_4$$
$$Al_4C_3 + 6H_2O \longrightarrow 2Al_2O_3 + 3CH_4$$

11. Be^{2+} and Al^{3+} ions have strong tendency to form chelate type complexes. Both form fluoride complexes, like $[BeF_4]^{2-}$, $[AlF_6]^{3-}$ respectively.
12. Both the ions give hydrated ions in solution (aqueous) like $[Be(H_2O)_4]^{2+}$ and $[Al(H_2O)_6]^{3+}$ respectively.
13. The salts of both Be and Al do not impart a colour to the flame when heated in it.

Compounds of Elements of Group 2

All the alkaline earth metals form several compounds. *Some important of which are given below.*

Quick Lime (CaO)

Preparation

It is prepared by heating limestone to 1000°C in lime klines as

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

The reaction is reversible and proceeds efficiently in forward direction when CO_2 is allowed to escape from the system. It is only above 1100 K, the gas escapes freely.

Properties

1. It is an amorphous white solid, with high melting point (2273K), usually obtained in the form of hard lumps.
2. When heated in oxyhydrogen flame, it emits a bright light, called **lime light.**
3. CaO absorbs CO_2 and H_2O easily.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$
$$\text{Exothermic } \Delta H = -64.5 \text{ kJ/mol}$$
$$CaO + CO_2 \longrightarrow CaCO_3$$

The addition of limited quantity of water converts lump of lime to slaked lime (as the process is called slaking). Similarly, if we use soda in the place of water, the product is called **soda lime** (NaOH/CaO).

4. It combines with solid acidic oxides at high temperature to give their salts as

$$CaO + SiO_2 \longrightarrow CaSiO_3$$
$$6CaO + P_4O_{10} \longrightarrow 2Ca_3(PO_4)_2$$

Uses

It is very useful as drying agent, in bleaching powder production (as used for the preparation of slaked lime) and as a constituent of **mortar.** As it has high melting point (2600°C), it is used for furnace linings. It is used as a basic flux in metallurgy as it combines with acidic impurities.

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

It is used as a disinfectant and *germicide,* as a drying agent for ammonia and alcohol. It is employed for the purification of coal gas and softening of water.

Calcium Hydroxide or Slaked Lime

$[Ca(OH)_2]$

Preparation

It is prepared by adding water to quick lime as

$$CaO + 2H_2O \longrightarrow Ca(OH)_2 + H_2\uparrow$$

Properties

1. It is white powder, sparingly soluble in water and the *aqueous solution is called lime water while the aqueous suspension is called milk of lime.* CO_2 has the ability to turn lime water milky as

$$Ca(OH)_2 + CO_2 \longrightarrow \underset{\text{(milky ppt.)}}{CaCO_3} + H_2O$$

This milkiness disappears with excess of CO_2 as soluble calcium hydrogen carbonate is formed.

$$CaCO_3 + H_2O + CO_2 \longrightarrow \underset{\text{soluble}}{Ca(HCO_3)_2}$$

2. Being basic in nature, it reacts with acids and acidic gases forming their salts.
3. On reaction with chlorine, it forms hypochlorite, a constituent of bleaching powder as

$$2Ca(OH)_2 + 2Cl_2 \longrightarrow CaCl_2 + CaOCl_2 + 2H_2O$$

Uses

Slaked lime is used in mortar production, lime water production, disinfectant, bleaching powder production etc.

Calcium Carbonate or Lime Stone

$(CaCO_3)$

It is found as chalk, marble, coral, calcite, aragonite etc. It is a precursor of quick lime and slaked lime.

Preparation

It is prepared as

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 + H_2O + CO_2\uparrow$$

Properties

It gets decomposed easily on heating as

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2\uparrow$$

Uses

As precipitated chalk it is used in tooth pastes and face powders, in medicine for indigestion, in adhesives, in cosmetics, in paints and distempers. Marble is used, (i) for building purposes, (ii) in the production of CO_2 in laboratory.

Limestone is used, (i) in the manufacture of quick lime, slaked lime, cement, washing soda and glass, (ii) as a flux in the smelting of iron and lead ores.

Plaster of Paris $\left(CaSO_4 \cdot \frac{1}{2}H_2O\right)$

It is chemically calcium sulphate hemihydrate.

Preparation

It is prepared by heating gypsum at 390 K. Gypsum is dihydrate of calcium sulphate.

$$\underset{\text{gypsum}}{2CaSO_4 \cdot 2H_2O} \xrightarrow{390\text{ K}} (CaSO_4)_2H_2O + 3H_2O$$

$$\text{or}\quad \underset{\text{plaster of Paris}}{CaSO_4 \cdot \frac{1}{2}H_2O}$$

In this reaction, temperature plays an important role because if temperature is above 390 K, whole the water of crystallisation is lost and dead burnt plaster or anhydrous $CaSO_4$ is obtained which does not have a property of setting with water.

Properties

1. It is white solid.
2. When mixed with water, it takes up the water of crystallisation and sets into a hard mass.

$$\underset{\text{plaster of Paris}}{CaSO_4 \cdot \frac{1}{2}H_2O} \xrightarrow{H_2O\text{ (setting)}} \underset{\text{orthorhombic}}{CaSO_4 \cdot 2H_2O}$$

$$\xrightarrow{\text{Hardening}} \underset{\text{monoclinic (gypsum)}}{CaSO_4 \cdot 2H_2O}$$

Uses

It is used for producing moulds for industries such as pottery, ceramics etc., for setting fractured bones and for making statues, models and other decorative materials.

Caution Point *The setting of plaster of Paris may be catalysed by sodium chloride, while it is retarded by borax or alum. Addition of alum to plaster of Paris makes the setting very hard. The mixture is known as keen's cement.*

Cement

It is one of the most important building materials at the present time. It is used in the construction of buildings, roads, bridges, dams, etc. It was discovered, in 1824, by an English Mason, **Joseph Aspdin** who observed that when strongly heated mixture of limestone and clay was mixed with water and allowed to stand, it hardened to a stone-like mass which resembled Portland rock–a famous building stone of England. Since then the name Portland cement has been given to a mixture containing high percentage of lime with silica, iron oxide, alumina, etc.

It is a mixture of silicates and aluminates of calcium with small amount of gypsum.

Chemical Composition

Its chemical composition CaO = 50–60%, SiO_2 = 20–25%, Al_2O_3 = 5–10%; MgO = 2–3%, Fe_2O_3 = 1–2%; SO_3 = 1–2%

The essential constituents are lime, silica and alumina. These are generally kept in the following ratio :

$$\frac{\%\text{ Silica}}{\%\text{ }Al_2O_3} = 2.5 - 4.0$$

$$\frac{\%\text{ CaO}}{\%\text{ }SiO_2 + \%\text{ }Al_2O_3 + \%\text{ }Fe_2O_3} = 1.9 - 2.1$$

The cement containing no iron is white.

Essential Raw Materials

Limestone for CaO etc., clay for SiO_2, Al_2O_3, Fe_2O_3 etc.

If lime is in excess ⟶ Cement cracks during settings;

If lime is less ⟶ Cement with weak strength.

Reactions which forms constituents of cement include

$$2CaO + SiO_2 \longrightarrow \underset{\text{dicalcium silicate}}{2CaO \cdot SiO_2}; \underset{\text{tricalcium silicate}}{3CaO \cdot SiO_2}$$

$$3CaO + Al_2O_3 \longrightarrow \underset{\text{tricalcium aluminate}}{3CaO \cdot Al_2O_3}$$

$$4CaO + Al_2O_3 + Fe_2O_3 \longrightarrow \underset{\text{tetracalcium aluminoferrite}}{4CaO \cdot Al_2O_3 \cdot Fe_2O_3}$$

Mechanism of Setting of Cement

The exact mechanism of this setting process is not known. It is believed that various aluminiate and silicates present in the cement form hydrates with water which separate in the form of gel.

$$3CaO \cdot Al_2O_3 + 6H_2O \xrightarrow{\text{Hydration}} \underset{\text{colloidal gel}}{3CaO \cdot Al_2O_3 \cdot 6H_2O}$$

$$2CaO \cdot SiO_2 + xH_2O \xrightarrow{\text{Hydration}} \underset{\text{colloidal gel}}{2CaO \cdot SiO_2 \cdot xH_2O}$$

$$4CaO \cdot Al_2O_3 \cdot Fe_2O_3 + 6H_2O \xrightarrow{\text{Hydration}} \underset{\text{colloidal gel}}{3CaO \cdot Al_2O_3 \cdot 6H_2O} + Fe_2O_3 \cdot CaO$$

At the same time some $Ca(OH)_2$ and $Al(OH)_3$ are formed as precipitates due to hydrolysis.

$$3CaO \cdot SiO_2 + H_2O \xrightarrow{\text{Hydrolysis}} Ca(OH)_2 + 2CaO \cdot SiO_2$$

$$3CaO \cdot Al_2O_3 + 6H_2O \xrightarrow{\text{Hydrolysis}} 3Ca(OH)_2 + 2Al(OH)_3$$

Gypsum combines with tricalcium aluminate to form calcium sulpho-aluminate.

$$3CaO \cdot Al_2O_3 + 3CaSO_4 + 2H_2O \longrightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 2H_2O$$

This reaction slow down the setting.

The gels formed start losing water partly by evaporation and partly by forming hydrates with unhydrated constituents. This results in the formation of a hard mass. $Ca(OH)_2$ binds the particles of calcium silicate together, while $Al(OH)_3$ fills the interstices resulting in hardening the mass.

Caution Point *Setting of cement is an exothermic process. Hence, cement structures have to be cooled during setting by sprinkling water.*

Mortar

Slaked lime is mixed with three to four times its weight of sand and the mixture is made into a thick paste with gradual addition of water which is called mortar and is used in building construction. It sets to a hard mass by loss of water and gradual absorption of CO_2 from the air. Sometimes coal ash is mixed with lime instead of sand. A mortar obtained from hydraulic lime is called hydraulic mortar. It has greater strength and is used for the construction of bridges.

Concrete

A mixture of cement, sand, gravel or small pieces of stone and water is known as concrete. It sets to an exceedingly hard structure. It is mainly used for the construction of floors. If the cement concrete is filled in around a wire netting or skeleton of iron rods and allowed to set, the resulting structure is known as **reinforced concrete**. These structures have great strength and are used for the construction of roofs, bridges, etc.

10.7 Biological Significance of Na, K, Mg and Ca

Biological Significance of Na and K

Sodium and potassium are the vital elements. Na^+ ions are found mainly in extracellular region (outside the cell) and play an important role in the transmission of nerve signals. They also regulate the flow of water across cell membranes and in transport of sugars and amino acids into the cells. Thus, it is essential that human diet must contain a sensible amount of Na. Prolonged sweating results in sodium ion loss in sweat, thus, it is important that Na^+ ions are replaced through proper diet.

Potassium ions are the most abundant cations within cell fluids, where they activate many enzymes, participate in oxidation of glucose to produce ATP (adenosine triphosphate). Potassium ions along with sodium ions are responsible for transmission of nerve signals. The functional features of nerve cells depend upon the sodium-potassium ion gradient that is established in the cell. Their ionic gradients are maintained by sodium-potassium pumps that operate across the cell membranes.

In the body of a 70 kg adult about 90 g Na^+ ions and 170 g K^+ ions are present. The daily requirement of sodium and potassium is about 2 g each.

Biological Significance of Mg and Ca

Mg^{2+} ions are present inside the animal cells while Ca^{2+} ions are in the body fluids, *i.e.,* in the extracellular region, in much the same way as K^+ are inside the cell and Na^+ outside the cell. All enzymes that utilize ATP in phosphate transfer require Mg^{2+} as cofactor. In green plants, magnesium is present in chlorophyll. Ca^{2+} and Mg^{2+} are also essential for the transmission of impulses along nerve fibres.

In bones and teeth, Ca is present as apatite, $Ca_3(PO_4)_2$, and in enamel on teeth as fluorapatite, $3Ca_3(PO_4)_2 \cdot CaF_2$. Ca^{2+} ions play an important role in blood clotting and are required to trigger the contraction of muscles. Ca^{2+} ions also regulate the heart beats. Calcium ions in bones exchange readily with those in the blood plasma. In a normal adult this exchange is in balance, but in elderly people, especially woman, there is sometimes net loss of bone calcium, leading to the disease known as **osteoporosis.**

An adult body contains about 25 g of Mg and 1200 g of Ca. The daily requirement of Mg is about 350 mg while that of Ca is 800 mg. The important source for Ca are milk, cheese and other dairy products while that of Mg are nuts, green vegetables etc.

Check Point 2

1. Explain, why $Be(OH)_2$ is almost insoluble in water, while $Ba(OH)_2$ is soluble?
2. Why $BeCO_3$ is less stable than $MgCO_3$?
3. Be and Mg do not give colour to flame whereas, other alkaline metals do so, explain why?
4. Beryllium chloride fumes in air why? (Hint due to evolution of HCl)
5. Barium ion, Ba^{2+}, is poisonous, yet $BaSO_4$ is given to patients prior to taking stomach X-ray. Why is it safe to use $BaSO_4$ internally?
6. How gypsum slow the rate of setting of cement?

WORKED **OUT**
Examples

Example 1 *A white solid X is a compound of s-block element. A piece of red litmus paper turns white when it is dipped into a freshly made aqueous solution of the white solid. The white solid ' X' is*

(*a*) Na_2O_2 (*b*) Na_2O
(*c*) CaO (*d*) Both Na_2O_2 and Na_2O

Solution (*a*) The substance is Na_2O_2. When N_2O_2 is dissolved in water, it forms NaOH along with H_2O_2. NaOH is a strong base while H_2O_2 is a weak acid.

$$Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$$

H_2O_2 turns colour of red litmus paper white due to its bleaching action (which is due to its oxidising character.)

$$H_2O_2 \longrightarrow H_2O + [O]$$
$$Na_2O + H_2O \longrightarrow 2NaOH$$

NaOH solution turns colour of red litmus paper into blue due to its stronger alkaline character.

Thus, the white solid *X* must be Na_2O_2 and not Na_2O.

Example 2 *Anhydrous potassium nitrate is heated with excess of metallic potassium.*

$$KNO_3(s) + K(s) \longrightarrow X + Y$$

In this reaction, the products X and Y are

(*a*) KNO_2, O_2 (*b*) K_2O, N_2
(*c*) K_2O, N_2O (*d*) K_2O, NO_2

Solution (*b*) $2KNO_3(s) + \underset{\text{(excess)}}{10K(s)} \xrightarrow{\Delta} 6K_2O(s) + N_2$

Example 3 *Identify the product D in the following reaction sequence.*

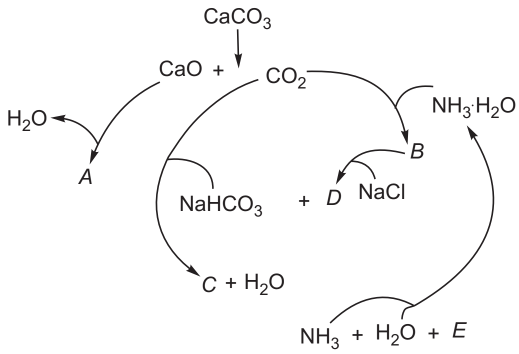
$$Na_2CO_3 \xrightarrow{SO_2} A \xrightarrow{Na_2CO_3} B \xrightarrow[\Delta]{\text{Elemental S}} C \xrightarrow{I_2} D$$

(*a*) Na_2SO_3 (*b*) $Na_2S_2O_3$
(*c*) $Na_2S_4O_6$ (*d*) $NaHSO_3$

Solution (*c*) $Na_2CO_3 + 2SO_2 + H_2O \longrightarrow \underset{A}{2NaHSO_3} + CO_2$

$$2NaHSO_3 + Na_2CO_3 \longrightarrow \underset{B}{2Na_2SO_3} + H_2O + CO_2$$
$$\underset{B}{Na_2SO_3} + S \longrightarrow \underset{C}{Na_2S_2O_3}$$
$$2Na_2S_2O_3 + I_2 \longrightarrow \underset{D}{Na_2S_4O_6} + 2NaI$$

Example 4 *The Haber process can be represented by the following scheme*



Identify D and E in this sequence

(*a*) NH_4HCO_3, Na_2CO_3
(*b*) $NH_4Cl, Ca(OH)_2$
(*c*) $NH_4Cl, CaCl_2$
(*d*) $Ca(OH)_2, CaCl_2$

Solution (*c*) In such scheme

$A = Ca(OH)_2, B = NH_4HCO_3, C = Na_2CO_3, D = NH_4Cl$ and $E = CaCl_2$

Example 5 *Identify X in the following reaction.*

$$Ba\overset{*}{C}O_3 + H_2SO_4 \longrightarrow X(\text{gas}) \quad (C^* \text{ denotes } C^{14})$$

(*a*) $C_2O_4^-$ (*b*) CO_2
(*c*) $\overset{*}{C}O_2$ (*d*) H_2O

Solution (*c*) $Ba\overset{*}{C}O_3 + H_2SO_4 \longrightarrow \underset{(X)}{\overset{*}{C}O_2} + H_2O + \underset{\text{white ppt.}}{BaSO_4\downarrow}$

$$C^* = C^{14}$$

Example 6 *Calcium burns in nitrogen to produce a white powder which dissolves in sufficient water to produce a gas A and an alkaline solution. The solution on exposure to air produces a thin solid layer of B on the surface. The compounds A and B will be*

(*a*) Ca_3N_2, NH_3
(*b*) NH_3, CO_2
(*c*) $Ca(OH)_2, CaCO_3$
(*d*) $NH_3, CaCO_3$

Solution (*d*) $A = NH_3$ and $B = CaCO_3$

The reactions are as follows

$$3Ca + N_2 \longrightarrow \underset{\text{calcium nitride}}{Ca_3N_2}$$

$$Ca_3N_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + \underset{A}{2NH_3}$$

$$Ca(OH)_2 + \underset{\text{from air}}{CO_2} \longrightarrow \underset{B}{CaCO_3} + H_2O$$

(solid layer is due to $CaCO_3$)

Example 7 *Element A burns in nitrogen to give an ionic compound B. Compound B reacts with water to give C and D. A solution of C becomes 'milky' on bubbling carbon dioxide. The element A is*

(*a*) Na
(*b*) Mg
(*c*) Ca
(*d*) Be

Solution (c) $\underset{A}{3M} + N_2 \longrightarrow \underset{B}{M_3N_2}$

$$\underset{B}{M_3N_2} + 6H_2O \longrightarrow \underset{C}{3M(OH)_2} + \underset{D}{2NH_3}$$

$$\underset{C}{M(OH)_2} + CO_2 \longrightarrow \underset{D}{MCO_3} + H_2O$$

M may be either Ca or Ba. It is not magnesium because $Mg(OH)_2$ has very low solubility in water.

Example 8 *An element (A) reacts quitely with water librating a colourless, odourless gas and a solution of (B). Passing* CO_2 *gas through B yield a white precipitate (C) which dissolves in excess of* CO_2*. C gives red colour to Bunsen burner flame. C on heating gives a caustic white compound which on further heating with carbon at 1000°C gives D, a compound of immense commercial importance. Compound D is*

(*a*) $Ca(OH)_2$
(*b*) $CaCO_3$
(*c*) CaO
(*d*) CaC_2

Solution (*d*) CO_2 gives white precipitate (*C*) with *B*, thus, *C* is $CaCO_3$ and *B* is $Ca(OH)_2$. Thus, the compound *A* is CaO. Since, *C* gives red colour to the flame it contains Ca elements.

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

$$2CaO + 4C \xrightarrow{1000^\circ C} 2CaC_2 + O_2$$

Example 9 *A white salt (A) evolves a colourless gas (B) with dilute* HCl. *Bubbling (B) through lime water gives a precipitate 'C' which dissolves in excess of the gas. 'A' imparts apple green colour to the flame. Compound A is*

(*a*) $CaCO_3$
(*b*) $BaCO_3$
(*c*) $Ca(OH)_2$
(d) $MgCO_3$

Solution (*b*) Since '*A*' imparts apple green colour to the flame, it must contain Ba. Moreover, '*B*' gas turns lime water milky, so *B* is CO_2 and *A* is $BaCO_3$. The reactions are as

$$\underset{'A'}{BaCO_3} \xrightarrow{\Delta} BaO + \underset{'B'}{CO_2}$$

$$CO_2 + Ca(OH)_2 \longrightarrow \underset{\text{white ppt}}{CaCO_3} + H_2O$$

Start Practice for JEE Main

Round I (Topically Divided Problems)

Elements of Group 1

1. Alkali metals react with water vigorously to form hydroxides and dihydrogen. Which of the following alkali metals reacts with water least vigorously? **[NCERT Exemplar]**

(a) Li (b) Na (c) K (d) Cs

2. The reducing power of a metal depends on various factors. Suggest the factor which makes Li, the strongest reducing agent in aqueous solution. **[NCERT Exemplar]**

(a) Sublimation enthalpy
(b) Ionisation enthalpy
(c) Hydration enthalpy
(d) Electron gain enthalpy

3. Shine at freshly cut sodium is because of

(a) oscillation of free electrons
(b) weak metallic bonding
(c) absorption of light in crystal lattice
(d) presence of free valency at the surface

4. Sodium is less reactive than potassium because **[NCERT Exemplar]**

(a) of its higher ionisation enthalpy
(b) of its less negative E°
(c) of its more negative E°
(d) Both (a) and (b)

5. Why are potassium and caesium, rather than lithium used in photoelectric cells? **[NCERT Exemplar]**

(a) Because of their lower IE
(b) Because of their lower EA
(c) Because of their higher IE
(d) Both (a) and (b)

6. The order of decreasing ionisation enthalpy in alkali metals is **[NCERT Exemplar]**

(a) $Na > Li > K > Rb$ (b) $Rb < Na < K < Li$
(c) $Li > Na > K > Rb$ (d) $K < Li < Na < Rb$

7. The characteristic not related to alkali metal is

(a) high ionisation energy
(b) their ions are isoelectronic with noble gases
(c) low melting point
(d) low electronegativity

8. When sodium is dissolved in liquid ammonia, a solution of deep blue colour is obtained. The colour of the solution is due to **[NCERT Exemplar]**

(a) ammoniated electron
(b) sodium ion
(c) sodium amide
(d) ammoniated sodium ion

9. Ions of an element of group 1 participate in the transmission of nerve signals and transport of sugars and amino acids into cells. This element imparts yellow colour to the flame in flame test and forms an oxide and a peroxide with oxygen. Identify the element. **[NCERT Exemplar]**

(a) Sodium (b) Potassium
(c) Francium (d) Caesium

10. Which of the following oxides is formed when potassium metal is burnt in excess of air?

(a) KO_2 (b) K_2O_2 (c) KO (d) K_2O

11. Which sequence of reactions shows correct chemical relation between sodium and its compounds?

(a) $Na + O_2 \longrightarrow Na_2O \xrightarrow{HCl(aq)} NaCl \xrightarrow{CO_2} Na_2CO_3 \xrightarrow{\Delta} Na$

(b) $Na \xrightarrow{O_2} Na_2O \xrightarrow{H_2O} NaOH \xrightarrow{CO_2} Na_2CO_3 \xrightarrow{\Delta} Na$

(c) $Na + H_2O \longrightarrow NaOH \xrightarrow{HCl} NaCl \xrightarrow{CO_2} Na_2CO_3 \xrightarrow{\Delta} Na$

(d) $\text{Na} + \text{H}_2\text{O} \longrightarrow \text{NaOH} \xrightarrow{\text{CO}_2} \text{Na}_2\text{CO}_3 \xrightarrow{\text{HCl}} \underset{\text{(molten)}}{\text{NaCl}} \xrightarrow{\text{Electrolysis}} \text{Na}$

12. Which is the most basic in character?
(a) NaOH (b) KOH
(c) RbOH (d) LiOH

13. Which one of the following is the highest melting halide?
(a) NaCl (b) NaI
(c) NaBr (d) NaF

14. A solid is a compound of group 1 element and it gives a bright red colour in the flame test. The solid is
(a) LiBr (b) CsCl
(c) KCl (d) NaCl

15. Which of the following does not illustrate the anomalous properties of lithium?
(a) Li is much softer than the other group first metals
(b) The m.p. and b.p. of Li are comparatively high
(c) Li forms a nitride Li_3N unlike group first metals
(d) The ion of Li and its compounds are more heavily hydrated than those of the rest of the group elements

Compounds of Elements of Group I

16. Baking powder contains
(a) $NaHCO_3, Ca(H_2PO_2)_2$ and starch
(b) $NaHCO_3, Ca(H_2PO_2)_2$
(c) $NaHCO_3$, starch
(d) $NaHCO_3$

17. In which of the following processes,fused sodium hydroxide is electrolysed at 330°C temperature for the extraction of sodium?
(a) Castner's process (b) Cyanide process
(c) Down's process (d) Both (b) and (c)

18. When sodium chloride solution is electrolysed, the gas that is liberated at the cathode is
(a) oxygen (b) chlorine
(c) hydrogen (d) air

19. In the synthesis of sodium carbonate, the recovery of ammonia is done by treating NH_4Cl with $Ca(OH)_2$. The by product obtained in this process is **[NCERT Exemplar]**
(a) $CaCl_2$ (b) NaCl
(c) NaOH (d) $NaHCO_3$

20. When washing soda is heated
(a) CO_2 is released (b) CO + CO_2 is released
(c) CO is released (d) water vapour is released

21. Sodium thiosulphate is used in photography
(a) as AgBr grain is reduced to non-metallic silver
(b) to convert metallic silver into silver salt
(c) to remove reduced silver
(d) to remove undecomposed AgBr in the form of $Na_3[Ag(S_2O_3)_2]$ (a complex salt)

22. Potassium carbonate cannot be prepared by Solvay process because **[NCERT]**
(a) it is highly unstable
(b) it reacts with the other by products
(c) potassium bicarbonate is highly soluble
(d) it is highly soluble

Elements of Group 2

23. Which of the following elements does not form hydride by direct heating with dihydrogen? **[NCERT Exemplar]**
(a) Be (b) Mg
(c) Sr (d) Ba

24. Which of the following metal carbonates gets decomposed on heating?
(a) Na_2CO_3 (b) $MgCO_3$
(c) K_2CO_3 (d) Rb_2CO_3

25. In the alkaline earth metals, the element forming predominantly covalent compound is
(a) Ca (b) Sr
(c) Mg (d) Be

26. Select the incorrect statement.
(a) Be can form complexes due to its very small size
(b) Mg cannot form complexes
(c) Mg burns in air releasing dazzling light rich in UV rays
(d) $CaCl_2 \cdot 6H_2O$ when mixed with ice gives freezing mixture

27. The right order of the solubility of sulphates of alkaline earth metals in water is
(a) Be > Ca > Mg > Ba > Sr
(b) Mg > Be > Ba > Ca > Sr
(c) Be > Mg > Ca > Sr > Ba
(d) Mg > Ca > Ba > Be > Sr

28. The metal ion, that plays an important role in muscle contraction, is
(a) Be^{2+} (b) Mg^{2+}
(c) Ca^{2+} (d) Ba^{2+}

29. $Be(OH)_2$ is insoluble in water, while $Ba(OH)_2$ is highly soluble due to
(a) lattice energy difference
(b) common ion effect
(c) bond order
(d) hard acid

30. Dehydration of hydrates of halides of calcium, barium and strontium, *i.e.,* $CaCl_2 \cdot 6H_2O$, $BaCl_2 \cdot 2H_2O$, $SrCl_2 \cdot 2H_2O$, can be achieved by heating. These become wet on keeping in air. Which of the following statements is correct about these halides? **[NCERT** Exemplar**]**

(a) Act as dehydrating agent
(b) Can absorb moisture from air
(c) Tendency to form hydrate decreases from calcium to barium
(d) All of the above

31. Beryllium and magnesium do not give colour to the flame whereas other alkaline earth metals do so. This is because of their **[NCERT]**

(a) Small size
(b) High effective nuclear charge
(c) High ionisation energy
(d) All of the above

32. Metal carbonates decompose on heating to give metal oxide and carbon dioxide. Which of the metal carbonates is most stable thermally? **[NCERT]**

(a) $MgCO_3$ (b) $CaCO_3$
(c) $SrCO_3$ (d) $BaCO_3$

33. An element of group 2 forms covalent oxide which is amphoteric in nature and dissolves in water to given an amphoteric hydroxide. Identify the element.

(a) Beryllium (b) Magnesium
(c) Calcium (d) Barium

34. The property of the alkaline earth metals that increases with their atomic number is

(a) solubility of their sulphates
(b) ionisation energy
(c) solubility of their hydroxides
(d) electronegativity

35. A metal M readily forms its sulphate MSO_4 which is water soluble. It forms its oxide MO which becomes inert on heating. It forms its insoluble hydroxide $M(OH)_2$ which is soluble in NaOH solution. Then, M is

(a) Be (b) Ba
(c) Ca (d) Mg

Compounds of Elements of Group 2

36. Plaster of Paris on making paste with little water sets to hard mass due to the formation of

(a) $CaSO_4$ (b) $CaSO_4 \cdot \frac{1}{2} H_2O$
(c) $CaSO_4 \cdot H_2O$ (d) $CaSO_4 \cdot 2H_2O$

37. Setting of plaster of Paris is

(a) dehydration
(b) oxidation with atmospheric oxygen
(c) combination with atmospheric CO_2
(d) hydration to yield another hydrate

38. Gypsum, $CaSO_4 \cdot 2H_2O$ on heating to about 120°C forms a compound which has the chemical composition represented by

(a) $CaSO_4 \cdot H_2O$
(b) $2CaSO_4 \cdot 3H_2O$
(c) $2CaSO_4 \cdot H_2O$
(d) $CaSO_4$

39. The difference of water molecules in gypsum and plaster of Paris is

(a) $\frac{5}{2}$ (b) 2
(c) $\frac{1}{2}$ (d) $1\frac{1}{2}$

40. Which of the following substances is used in the laboratory for fast drying of neutral gases?

(a) Sodium sulphate
(b) Phosphorus pentoxide
(c) Sodium phosphate
(d) Anhydrous calcium chloride

41. By adding gypsum to cement **[NCERT** Exemplar**]**

(a) setting time of cement become less
(b) setting time of cement increases
(c) colour of cement becomes light
(d) shining surface is obtained

42. Suspension of slaked lime in water is known as **[NCERT** Exemplar**]**

(a) lime water
(b) quick lime
(c) milk of lime
(d) aqueous solution of slaked lime

43. Which of the following statements is true about $Ca(OH)_2$? **[NCERT** Exemplar**]**

(a) It is used in the preparation of bleaching powder
(b) It is a light blue solid
(c) It does not possess disinfectant property
(d) It is used in the manufacture of cement

44. A chemical A is used for the preparation of washing soda to recover ammonia. When CO_2 is bubbled through an aqueous solution of A, the solution turns milky. It is used in white washing due to disinfectant nature. What is the chemical formula of A? **[NCERT** Exemplar**]**

(a) $Ca(HCO_3)_2$ (b) CaO
(c) $Ca(OH)_2$ (d) $CaCO_3$

Miscellaneous

45. Which of the following metals has stable carbonate?
(a) Al (b) Si (c) Mg (d) Na

46. Which of the following is weakest base?
(a) $Zn(OH)_2$ (b) NaOH (c) $Ca(OH)_2$ (d) KOH

47. Alkaline earth metals are denser than alkali metals, because metallic bonding in alkaline earth metal is
(a) weaker (b) stronger
(c) volatile (d) not present

48. In India, on the occasion of marriages, the fireworks used give green flame. Which one of the following radicals may be present?
(a) Na (b) K (c) Ba (d) Ca

49. Compared with the alkaline earth metals, the alkali metals exhibit
(a) greater hardness
(b) smaller ionic radii
(c) lower ionisation energies
(d) highest boiling points

50. Which of the following pairs of substances would give same gaseous product on reaction with water?
(a) Na and Na_2O_2
(b) Ca and CaH_2
(c) Ca and CaO
(d) Ba and BaO_2

Round II (Mixed Bag)

Only One Correct Option

1. Which of the following has the highest solubility product?
(a) KOH (b) CsOH
(c) LiOH (d) RbOH

2. Crude common salt is hygroscopic because of the presence of impurities of
(a) $CaSO_4$ and $MgSO_4$
(b) $CaCl_2$ and $MgCl_2$
(c) $CaBr_2$ and $MgBr_2$
(d) $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$

3. Sodium nitrate decomposes above 800°C to give
(a) N_2 (b) O_2
(c) NO_2 (d) Na_2O

4. When sodium is heated with moist air, then the product obtained is
(a) Na_2O_2 (b) Na_2CO_3
(c) NaOH (d) Na_2O

5. On dissolving moderate amount of sodium metal in liquid NH_3 at low temperature, which one of the following does not occur?
(a) Na^+ ions are formed in the solution
(b) Blue coloured solution is obtained
(c) Liquid NH_3 becomes good conductor of electricity
(d) Liquid ammonia remains diamagnetic

6. The solubility of metal halides depends on their nature, lattice enthalpy and hydration enthalpy of the individual ions. Amongst fluorides of alkali metals, the lowest solubility of LiF in water is due to
[NCERT Exemplar]
(a) Ionic nature of lithium fluoride
(b) High lattice enthalpy
(c) High hydration enthalpy for lithium ion
(d) Low ionisation enthalpy of lithium atom

7. Amphoteric hydroxides react with both alkalies and acids. Which of the following group 2 metal hydroxides is soluble in sodium hydroxide?
[NCERT Exemplar]
(a) $Be(OH)_2$ (b) $Mg(OH)_2$
(c) $Ca(OH)_2$ (d) $Ba(OH)_2$

8. A substance which gives brick red flame and breaks down on heating to give oxygen and a brown gas is
[NCERT Exemplar]
(a) magnesium nitrate (b) calcium nitrate
(c) barium nitrate (d) strontium nitrate

9. In curing cement plasters, water is sprinkled from time to time. This helps in
(a) developing interlocking needle like crystals of hydrated silicates
(b) hydrated sand gravel mixed with cement
(c) converting sand into silicic acid
(d) keeping it cool

10. Iron pipes lying under acidic soil are often attached to blocks of magnesium for protection from rusting. Magnesium offers protection to iron against corrosion because it
(a) is more readily converted into positive ions
(b) is more stable than iron
(c) forms a corrosion resistance alloy with iron
(d) prevents air from reaching the surface of iron

11. Chemical '*A*' is used for water softening to remove temporary hardness. *A* reacts with sodium carbonate to generate caustic soda. When CO_2 is bubbled through a solution of '*A*', it turns cloudy. What is the chemical formula of *A*?

(a) CaO (b) $Ca(OH)_2$ (c) $CaCO_3$ (d) $Ca(HCO_3)_2$

12. A metal '*M*' reacts with N_2 to give a compound '*A*' (M_3N). '*A*' on heating at high temperature gives back '*M*' and '*A*' on reacting with H_2O give a gas *B*. '*B*' turns $CuSO_4$ solution blue on passing through it. *M* and *B* can be

(a) Al and NH_3 (b) Li and NH_3
(c) Na and NH_3 (d) Mg and NH_3

13. Which one of the following statements is true for all the alkali metals?

(a) Their nitrates decompose on heating to give NO_2 and O_2
(b) Their carbonates decompose on heating to give CO_2 and the metal oxide
(c) They react with oxygen to give mainly the oxide M_2O
(d) They react with halogens to give the halides *MX*

14. When water is added to compound (*A*) of calcium, solution of compound (*B*) is formed. When carbon dioxide is passed into the solution, it turns milky due to the formation of compound (*C*). If excess of carbon dioxide is passed into the solution milkiness disappears due to the formation of compound (*D*). The milkiness disappears in the last step due to the formation of **[NCERT Exemplar]**

(a) $CaCO_3$ (b) $Ca(HCO_3)_2$
(c) $NaHCO_3$ (d) Na_2CO_3

15. Lithium hydride can be used to prepare other useful hydrides. Beryllium hydride is one of them. The reagents that are required to prepare BeH_2 from lithium hydride are **[NCERT Exemplar]**

(a) $BeCl_2$ only (b) $Al_2Cl_6, BeCl_2$
(c) AlH_3, CH_4 (d) $AlH_3, BeCl_2$

16. LiF is almost insoluble in water whereas LiCl is soluble not only in water but also in acetone. This is because **[NCERT Exemplar]**

(a) of high hydration enthalpy of Li^+
(b) of low hydration enthalpy of Li^+
(c) of more ionic character in LiCl
(d) None of the above

17. Consider the following statements.

I. BeO is insoluble but $BeSO_4$ is soluble in water.
II. BaO is insoluble but $BaSO_4$ is soluble in water.
III. LiI is more soluble than KI in ethanol.

The true statements is/are **[NCERT]**

(a) I and II only (b) I and III only
(c) II and III only (d) I, II and III

18. The product which is not common in the given reaction is **[NCERT Exemplar]**

$$O_2^{2-} + H_2O \longrightarrow$$
$$O_2^{-} + H_2O \longrightarrow$$

(a) OH^- (b) H_2O_2
(c) O_2 (d) None of these

19. In which of the following processes gaseous products are obtained? **[NCERT]**

I. Mg is burnt in air.
II. Quicklime is heated with silica.
III. Chlorine reacts with slaked lime.
IV. Calcium nitrate is heated.

(a) II and IV only (b) I, II and IV only
(c) IV only (d) III and IV only

20. Prepartion of which of the following substance does not involve electrolysis of NaCl as its one step? **[NCERT]**

(a) Na metal (b) NaOH
(c) Na_2O_2 (d) Na_2CO_3

More than One Correct Option

21. Which of the following groups of elements have chemical properties that are most similar?

(a) Be, Al, Ca (b) Mg, Ba, Sr
(c) Be, Ra, Cs (d) Na, K, Ca

22. Several sodium compounds find use in industries. Which of the following compounds are used for textile industry? **[NCERT Exemplar]**

(a) Na_2CO_3 (b) $NaHCO_3$ (c) NaOH (d) NaCl

23. Which of the following compounds are readily soluble in water? **[NCERT Exemplar]**

(a) $BeSO_4$ (b) $MgSO_4$ (c) $BaSO_4$ (d) $SrSO_4$

24. Identify the correct formula of halides of alkaline earth metals from the following. **[NCERT Exemplar]**

(a) $BaCl_2 \cdot 2H_2O$ (b) $BaCl_2 \cdot 4H_2O$
(c) $CaCl_2 \cdot 6H_2O$ (d) $SrCl_2 \cdot 4H_2O$

25. Choose the correct statements from the following. **[NCERT Exemplar]**

(a) Beryllium is not readily attacked by acids because of the presence of an oxide film on the surface of the metal.
(b) Beryllium sulphate is readily soluble in water as the greater hydration enthalpy of Be^{2+} overcomes the lattice enthalpy factor.
(c) Beryllium exhibits coordination number more than four
(d) Beryllium oxide is purely acidic in nature

26. Which of the following are correct reasons for anomalous behaviour of lithium? **[NCERT Exemplar]**

(a) Exceptionally small size of its atom
(b) Its high polarising power
(c) It has high degree of hydration
(d) Exceptionally low ionisation enethalpy

Assertion and Reason

Directions (Q. Nos. 27 to 31) *Each of these questions contains two statements : Statement* I (*Assertion*) *and Statement* II (*Reason*). *Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes* (*a*), (*b*), (*c*), (*d*) *given below :*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

27. Statement I The carbonate of lithium decomposes easily on heating to form lithium oxide and CO_2.

Statement II Lithium being very small in size polarises large carbonate ion leading to the formation of more stable Li_2O and CO_2. **[NCERT Exemplar]**

28. Statement I Potassium and caesium emit electrons on exposure to light.

Statement II Potassium and caesium are used in photo electric cells.

29. Statement I Mg continue to burn in nitric oxide.

Statement II During burning, heat evolved do not decompose NO.

30. Statement I Superoxides of alkali metals are paramagnetic.

Statement II Superoxides contain the ion O^{2-} which has one unpaired electron.

31. Statement I Beryllium carbonate is kept in the atmosphere of carbon dioxide.

Statement II Beryllium carbonate is unstable and decomposes to give beryllium oxide and carbon dioxide. **[NCERT Exemplar]**

Comprehension Based Questions

Directions (Q. Nos. 32 to 34) Lithium only forms monoxide when heated in oxygen. Sodium forms monoxide and peroxide in excess of oxygen. Other alkali metals form superoxide with its oxygen. The abnormal behaviour of lithium is due to its small size. The larger size of higher alkali metals also decides the role of formation of superoxides. All the three anions abstract proton from water. The three anions are related to each other as follows

$$\underset{\text{oxide ion}}{O^{2-}} \xrightarrow{\frac{1}{2}O_2} \underset{\text{peroxide ion}}{O_2^{2-}} \xrightarrow{O_2} \underset{\text{superoxide ion}}{2\,O_2^-}$$

32. In hydrolysis, the alkali metal oxides, peroxides and superoxides act as

(a) Lewis acid (b) Lewis base
(c) Bronsted acid (d) Bronsted base

33. Which anion is unstable towards water?

(a) O_2^- (b) O^{2-}
(c) O_2^{2-} (d) All of these

34. Which compound will liberate oxygen when reacts with water?

(a) KO_2 (b) Na_2O (c) Cs_2O_2 (d) Na_2O_2

Directions (Q. Nos. 35 to 37) A halide of Be(X) sublimes on heating and is a bad conductor of electricity. From its aqueous solution, it is difficult to obtain anhydrous salt. This halide of beryllium (X) is obtained by heating beryllium oxide with carbon tetrachloride at 800°C. This halide of beryllium forms complex of the type $M_2[BeX_4]$.

35. Beryllium chloride forms $Na_2[BeCl_4]$ with NaCl because Be has

(a) smaller size (b) vacant '*d*' orbitals
(c) Both (a) and (b) (d) None of these

36. What compound is formed when $BeCl_2$ is dissolved in water in cold conditions?

(a) BeO_2 (b) BeO
(c) $Be(OH)_2$ (d) $[Be(H_2O)_4]Cl_2$

37. What is compound X?

(a) $BeCl_2$ (b) BeF_2
(c) $BeBr_2$ (d) None of these

Directions (Q. Nos. 38 to 40) Cement is one of the most important building material of the present time. It is a dirty greyish heavy powder containing calcium aluminates and silicates. The important raw materials needed for the manufacture of cement are, limestone, clay and gypsum. The main step in the manufacture of cement is the heating of raw material or slurry in the rotary kiln at a very high temperature 1400-1600°C. Finally 2 or 3% gypsum is added.

When cement is mixed with water and left as such for sometime, it becomes a hard mass. This is known as setting of cement. It is believed that various aluminates and silicates present in the cement form hydrates with water which separate in the form of gel. The gels formed start losing water partly by evaporation and partly by forming hydrates with unhydrated constituents. This results in the formation of a hard mass.

38. Portland cement does not contain
(a) $CaSiO_4$ (b) $CaSiO_3$
(c) $Ca_3 \cdot Al_2O_6$ (d) $Ca_3(PO_4)_2$

39. The percentage of lime in Portland cement is approximately
(a) 20-25% (b) 30-40% (c) 60-65% (d) 40-50%

40. Concrete is a mixture of
(a) cement, sand, gravel and water
(b) cement, limestone and water
(c) cement, slaked lime and water
(d) cement, sand and water

Previous Years' Questions

41. Which of the following on thermal decomposition yields a basic as well as acidic oxide? **[AIEEE 2012]**
(a) $NaNO_3$ (b) $KClO_3$ (c) $CaCO_3$ (d) NH_4NO_3

42. KO_2 is used in space and submarines because it **[AIEEE 2012]**
(a) absorbs CO_2 and increases O_2 concentration
(b) absorbs moisture
(c) absorbs CO_2
(d) produces ozone

43. The products obtained on heating $LiNO_3$ will be **[AIEEE 2011]**
(a) $LiNO_2 + O_2$ (b) $Li_2O + NO_2 + O_2$
(c) $Li_3N + O_2$ (d) $Li_2O + OH + O_2$

44. What is the best description of the change that occurs when $Na_2O(s)$ is dissolved in water? **[AIEEE 2011]**
(a) Oxidation number of sodium decreases
(b) Oxide ion accepts sharing in a pair of electrons
(c) Oxide ion donates a pair of electrons
(d) Oxidation number of oxygen increases

45. Beryllium and aluminium exhibit many properties which are similar. But the two elements differ in **[AIEEE 2004]**
(a) exhibiting maximum covalency in compounds
(b) forming polymeric hydrides
(c) forming covalent halides
(d) exhibiting amphoteric nature in their oxides

46. One mole of magnesium nitride on reaction with an excess of water gives **[AIEEE 2004]**
(a) one mole of ammonia
(b) one mole of nitric acid
(c) two moles of ammonia
(d) two moles of nitric acid

47. The solubilities of carbonates decrease down the magnesium group due to a decrease in **[AIEEE 2003]**
(a) lattice energies of solids
(b) hydration energies of cations
(c) inter ionic attraction
(d) entropy of solution formation

48. The substance not likely to contain $CaCO_3$, is **[AIEEE 2003]**
(a) a marble statue
(b) calcined gypsum
(c) sea shells
(d) dolomite

49. The metallic sodium dissolves in liquid ammonia to form a deep blue coloured solution. The deep blue colour is due to the formation of **[AIEEE 2002]**
(a) solvated electron $e^-(NH_3)_y$
(b) solvated atomic sodium, $Na(NH_3)_y$
(c) $(Na^+ + Na^-)$
(d) $NaNH_2 + H_2$

Answers

Round I

1. (a)	**2.** (c)	**3.** (a)	**4.** (d)	**5.** (a)	**6.** (c)	**7.** (a)	**8.** (a)	**9.** (a)	**10.** (a)
11. (d)	**12.** (c)	**13.** (d)	**14.** (a)	**15.** (a)	**16.** (a)	**17.** (a)	**18.** (c)	**19.** (a)	**20.** (d)
21. (d)	**22.** (c)	**23.** (a)	**24.** (b)	**25.** (d)	**26.** (b)	**27.** (c)	**28.** (c)	**29.** (a)	**30.** (d)
31. (d)	**32.** (d)	**33.** (a)	**34.** (c)	**35.** (a)	**36.** (d)	**37.** (d)	**38.** (c)	**39.** (d)	**40.** (d)
41. (b)	**42.** (c)	**43.** (a)	**44.** (c)	**45.** (d)	**46.** (a)	**47.** (b)	**48.** (c)	**49.** (c)	**50.** (b)

Round II

1. (b)	**2.** (b)	**3.** (b)	**4.** (c)	**5.** (d)	**6.** (b)	**7.** (a)	**8.** (b)	**9.** (a)	**10.** (a)
11. (b)	**12.** (b)	**13.** (d)	**14.** (b)	**15.** (b)	**16.** (a)	**17.** (b)	**18.** (c)	**19.** (c)	**20.** (d)
21. (a,b)	**22.** (a,c)	**23.** (a,b)	**24.** (a,c)	**25.** (a,b)	**26.** (a,b)	**27.** (a)	**28.** (b)	**29.** (c)	**30.** (a)
31. (a)	**32.** (d)	**33.** (d)	**34.** (a)	**35.** (a)	**36.** (d)	**37.** (a)	**38.** (d)	**39.** (c)	**40.** (a)
41. (c)	**42.** (a)	**43.** (b)	**44.** (c)	**45.** (a)	**46.** (c)	**47.** (b)	**48.** (b)	**49.** (a)	

the Guidance

Round I

1. Among alkali metals , reactivity increases on moving down the group because ionisation energy decreases. Thus, ionisation energy is highest for Li among alkali metals, so it is less reactive and hence, reacts less vigorously with water.

2. Because of its small size hydration energy of Li is high which compensates for its high ionisation energy. Consequently, its reduction potential is lowest amongst alkali metal and hence , it is the strongest reducing agent.

3. Shining at freshly cut sodium is due to oscillation of free electrons.

4. The ionization enthalpy ($\Delta_1 H_1$) of potassium (419 kJ mol^{-1}) is less than that of sodium (496 kJ mol^{-1}) and the standard electrode potential ($E°$) of potassium (-2.925 V) is more negative than that of sodium (-2.714 V) that's why potassium is more reactive than sodium.

5. Metals having very high tendency to lose electrons are used in photoelectric cells. Lower the ionisation energy, higher is the tendency to lose electrons.

Potassium and caesium have much lower ionisation enthalpy than that of lithium. Therefore, these metals on exposure to light emit electrons easily but lithium does not. That's why K and Cs rather than Li are used in photoelectric cells.

6. The distance between the valence electron and nucleus increases as the size of alkali metal increases, *i.e.,* nucleus binds the valence electron less tightly. Thus, the amount of energy required to remove valence electron (*i.e.,* ionisation energy) decreases.

$\therefore$ The order of IE is $\text{Li} > \text{Na} > \text{K} > \text{Rb}$.

8. On dissolving sodium in liquid ammonia, its colour turns deep blue due to the generation of ammoniated electrons.

$$\text{Na} + (x+y)\,\text{NH}_3 \longrightarrow [\text{Na}\,(\text{NH}_3)_x]^+ + \underset{\substack{\text{solvated or}\\ \text{ammoniated}\\ \text{electron}}}{e(\text{NH}_3)_y}$$

9. The element is sodium.

11. $2\text{Na} + 2\text{H}_2\text{O} \longrightarrow 2\text{NaOH} + \text{H}_2\uparrow$

$$2\text{NaOH} + \text{CO}_2 \longrightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$$

$$\text{Na}_2\text{CO}_3 + 2\text{HCl} \longrightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$$

$$\underset{\text{(molten)}}{\text{NaCl}} \xrightarrow{\text{Electrolysis}} \begin{array}{ccc} \text{Na}^+ & + & \text{Cl}^- \\ \big\downarrow {\scriptstyle +e^-} & & \big\downarrow {\scriptstyle -e^-} \\ \text{Na} & & \text{Cl} \end{array}$$

12. $$\xrightarrow[\text{Down the group basic character increases}]{\text{LiOH} < \text{NaOH} < \text{KOH} < \text{RbOH}}$$

13. Because of the smaller size of F-ions, NaF has the highest lattice energy and hence, the highest melting point.

14. Lithium salts impart bright red colour to the flame.

15. Li is much softer than the other group first metals. Actually, Li is harder than other alkali metals.

16. Baking powder contains NaHCO_3, $\text{Ca(H}_2\text{PO}_2)_2$ and starch.

18. $2\text{NaCl} + 2\text{H}_2\text{O} \xrightarrow{\text{Electrolysis}} 2\text{NaOH} + \underset{\text{anode}}{\text{Cl}_2} + \underset{\text{cathode}}{\text{H}_2}$

19. $2\text{NH}_4\text{Cl} + \text{Ca(OH)}_2 \longrightarrow \text{CaCl}_2 + 2\text{NH}_3 + 2\text{H}_2\text{O}$

20. $\text{Na}_2\text{CO}_3\cdot 10\text{H}_2\text{O} \xrightarrow{\Delta} \text{Na}_2\text{CO}_3\cdot\text{H}_2\text{O} \xrightarrow{\Delta}$

$$\text{Na}_2\text{CO}_3 + \text{H}_2\text{O}\uparrow$$

22. Potassium carbonate cannot be prepared by Solvay process because potassium bicarbonate being highly soluble in water, would not be precipitated out.

23. Be because of its small size does not form hydride directly by heating with dihydrogen.

24. $\text{MgCO}_3 \xrightarrow{\text{Heat}} \text{MgO} + \text{CO}_2$

The metal oxide of which is stable, has unstable carbonate.

25. From Be to Ba ionic character increases. Thus, Be forms predominantly covalent compound.

27. On moving down the group, lattice energy remains almost constant as the sulphate is so big that small increase in size of the cations does not make difference. Hydration energy causes decrease in the solubility of the sulphates as the ionic size increases. Thus, the correct order is

$$\text{Be} > \text{Mg} > \text{Ca} > \text{Sr} > \text{Ba}$$

30. CaCl_2, BaCl_2 and SrCl_2 act as dehydrating agent, thus, absorb moisture from air. Their hydrate forming tendency reduces from Ca to Ba because of the large size of Ba.

31. The colour of the flame is due to the excitation of loosely bound electrons of the metal atom.

Be and Mg atoms due to their small size and high effective nuclear charge bind their electrons more strongly. Therefore, they require high excitation energy and are not excited by Bunsen flame. While other alkaline earth metals impart a characteristic colour to the flame, due to easy excitation of electrons to higher energy levels.

32. On moving down the group size of alkaline earth metal ion increases, and hence, its polarising power or covalent character decreases, *i.e.*, $BaCO_3$ is most ionic (have strong interactions) among the given and hence, is most stable thermally.

Note Stability of alkaline earth metal carbonates increases as the size of alkaline earth metal increases due to its low polarising power.

33. The element is beryllium.

36. Plaster of Paris becomes very hard by the process of hydration. It changes into a hard mass, called gypsum, on mixing with water. There is a slight increase in volume during this process.

$$\underset{\text{Plaster of Paris}}{CaSO_4 \cdot \frac{1}{2}H_2O} + 1\frac{1}{2}H_2O \longrightarrow \underset{\text{gypsum}}{CaSO_4 \cdot 2H_2O} + \text{Heat}$$

37. Setting of plaster of Paris is exothermic process.

$$CaSO_4 \cdot \frac{1}{2}H_2O \xrightarrow{H_2O} \underset{\text{orthorhombic}}{CaSO_4 \cdot 2H_2O} \xrightarrow{\text{Heating}} \underset{\substack{\text{mono orthorhombic}\\ \text{gypsum}}}{CaSO_4 \cdot 2H_2O}$$

38. $$\underset{\text{gypsum}}{2(CaSO_4 \cdot 2H_2O)} \xrightarrow[\text{Dehydration}]{120°C} \underset{\text{plaster of Paris}}{2CaSO_4 \cdot H_2O} + 3H_2O$$

39. Formula of gypsum $= CaSO_4 \cdot 2H_2O$

Formula of plaster of Paris $= CaSO_4 \cdot \frac{1}{2}H_2O$

Difference of water molecule $= 2H_2O - \frac{1}{2}H_2O = 1\frac{1}{2}H_2O$

40. Anhydrous calcium chloride is used in the laboratory for fast drying of neutral gases.

41. Gypsum, when added to cement, reduces its setting rate by combining with tricalcium aluminate as

$$3\,CaO \cdot Al_2O_3 + 3\,CaSO_4 + 2\,H_2O \longrightarrow 3CaO \cdot Al_2O_3 \cdot 3\,CaSO_4 \cdot 2H_2O$$

Thus, setting time increases.

42. Milk of lime is a suspension of slaked lime in water.

43. $$\underset{\text{slaked lime}}{Ca(OH)_2} + Cl_2 \longrightarrow \underset{\substack{\text{bleaching}\\ \text{powder}}}{CaOCl_2} + H_2O$$

$Ca(OH)_2$ is colourless and not used in cement manufacturing. It is used in white washing due to its disinfectant nature.

44. Since solution of *A* produces milkiness with CO_2, it must be lime water *i.e.*, solution of $Ca(OH)_2$.

45. When carbonates are heated, they decompose to form the oxide. Sodium carbonate and potassium carbonate do not decompose. The carbonate become more difficult to decompose as we go down the 1st group.

46. The hydroxides of alkali and alkaline earth metals are strong bases. Thus, $Zn(OH)_2$ is the weakest base.

47. Alkaline earth metals (ns^2) are denser than alkali metal (ns^1) because metallic bonding in alkaline earth metal is stronger.

48.

Na	K	Ba	Ca	Sr
yellow	pale violet	apple green	brick red	crimson

49. Because of the larger size and smaller nuclear charge, alkali metals have low ionisation potential relative to alkaline earth metals.

50. The given substances react with water in the following manner

$$\begin{aligned}
Na + H_2O &\longrightarrow NaOH + H_2(g)\\
2Na_2O_2 + 2H_2O &\longrightarrow 4NaOH + O_2(g) + H_2(g)\\
Ca + H_2O &\longrightarrow CaO + H_2\\
CaO + H_2O &\longrightarrow Ca(OH)_2\\
CaH_2 + 2H_2O &\longrightarrow Ca(OH)_2 + 2H_2\\
Ba + 2H_2O &\longrightarrow Ba(OH)_2 + H_2\\
BaO_2 + H_2O &\longrightarrow Ba^{2+} + O_2 + H_2O_2
\end{aligned}$$

Hence, Ca and CaH_2 is the pair that gives same gaseous product on reaction with water.

Round II

1. Higher the solubility, higher is the solubility product. Thus, CsOH being more soluble, has the highest solubility product.

2. $CaCl_2$ and $MgCl_2$ are deliquescent salts so absorb moisture from air to impart hygroscopic nature to crude common salt.

3. $$2\,NaNO_3 \xrightarrow[\text{above } 800°C]{\Delta} 2\,NaNO_2 + O_2$$

4. $$2\,Na + \frac{1}{2}O_2 \xrightarrow{\text{Moist air}} Na_2O$$

$$Na_2O + H_2O \longrightarrow 2\,NaOH$$

5. Due to the presence of free electrons, liquid ammonia becomes paramagnetic.

6. The lattice energy of LiF is much higher due to their comparable size, hence it is less soluble in water.

7. $Be(OH)_2$ being amphoteric reacts with sodium hydroxide to give salt and water.

$$Be(OH)_2 + 2\,NaOH \longrightarrow Na_2BeO_2 + 2\,H_2O$$

All other hydroxides being alkaline in nature do not react with alkali (NaOH).

8. Calcium gives brick red colour to the flame in flame test and calcium nitrate when heated decomposed into oxygen and a brown gas NO_2.

$$2\,Ca(NO_3)_2 \xrightarrow{\Delta} 2\,CaO + O_2 + 4\,NO_2$$

9. Sprinkling water on cement plasters helps in interlocking needle like crystals of hydrated silicates.

10. Due to its electropositive and reactive nature, magnesium is readily converted into positive ions in contact with iron pipes and hence, iron pipes remains as such.

11. $Ca(OH)_2$ is used for the softening of temporary hard water.

12. The formula of 'A' is M_3N suggests that M is a monovalent metal.

$$\underset{(M)}{6\,Li} + N_2 \longrightarrow \underset{\substack{(A)\\ \text{lithium nitride}}}{2\,Li_3N} \xrightarrow{\Delta} 6\,Li + N_2$$

$$Li_3N + 3\,H_2O \longrightarrow 3\,LiOH + \underset{(B)}{NH_3}$$

$$CuSO_4 + 4\,NH_3 \longrightarrow \underset{\text{blue solution}}{[Cu(NH_3)_4]\,SO_4}$$

Hence, M and B are Li and NH_3 respectively.

13. Alkali metals react with halogen to give halides. They are normally represented by M^+X^-.

14. Compound : A : CaO; B : $Ca(OH)_2$; C : $CaCO_3$; D : $Ca(HCO_3)_2$

$Ca(HCO_3)_2$ is soluble in water. Hence, milkiness of solution disappears on passing excess carbon dioxide into the solution of compound B.

15. $8\,LiH + Al_2Cl_6 \longrightarrow 2\,LiAlH_4 + 6\,LiCl$

$LiAlH_4 + 2\,BeCl_2 \longrightarrow 2\,BeH_2 + LiCl + AlCl_3$

16. LiF is almost insoluble in water due to its high lattice energy. But LiCl is soluble in water due to high hydration energy of Li^+ ion. LiCl is also soluble in acetone due to its predominantly covalent nature. (Because covalent character increases with increase in the size of anion).

$$LiF < LiCl < LiBr < LiI$$

17. (i) Lattice energy of BeO is greater than its hydration energy so, it is insoluble in water while in case of $BeSO_4$, hydration energy is greater than lattice energy, so it is readily soluble in water.

(ii) Lattice energy of BaO is much smaller than that of its hydration energy, so it is soluble in water. In $BaSO_4$, lattice energy predominates over hydration energy, so it is insoluble in water.

(iii) LiI is more covalent because Li^+ is smallest and polarised anion (I^-) to maximum extent, so it is more soluble than KI in ethanol.

18. (i) Peroxide ions react with water to form H_2O_2.

$$O_2^{2-} + 2\,H_2O \longrightarrow 2OH^- + H_2O_2$$

(ii) Superoxides react with water to form H_2O_2 and O_2.

$$2O_2^- + 2\,H_2O \longrightarrow 2OH^- + H_2O_2 + O_2$$

19. (i) $2\,Mg(s) + O_2(g) \xrightarrow{\Delta} 2\,MgO\,(s)$

and $3\,Mg(s) + N_2(g) \longrightarrow Mg_3N_2(s)$

(ii) $\underset{\text{quicklime}}{CaO\,(s)} + \underset{\text{silica}}{SiO_2(s)} \longrightarrow \underset{\text{calcium silicate}}{CaSiO_3\,(s)}$

(iii) It reacts with Cl_2 to form calcium hypochlorite, $Ca(OCl)_2$

$$\underset{\text{slaked lime}}{2\,Ca(OH)_2} + 2Cl_2 \longrightarrow \underbrace{CaCl_2 + Ca(OCl)_2}_{\text{bleaching powder}} + 2\,H_2O$$

(iv) $2\,Ca(NO_3)_2(s) \xrightarrow{\Delta} 2\,CaO\,(s) + 4\,NO_2(g) + O_2(g)$

20. (a) **Sodium metal** It is manufactured by electrolysis of fused mixture of NaCl (40%) and $CaCl_2$ (60%) in Down's cell at 873 K. Na, liberated at the cathode is collected, in kerosene oil while Cl_2 is evolved at the anode.

$$NaCl\,(l) \xrightarrow{\text{Electrolysis}} Na^+ + Cl^-$$

At cathode $Na^+ + e^- \longrightarrow Na(l)$

At anode $2Cl^- \longrightarrow Cl_2(g) + 2e^-$

Na metal obtained on oxidation gives Na_2O_2.

(b) **Sodium hydroxide** It is manufactured by electrolysis of an aqueous solution of NaCl (brine) in Castner-Kellner cell using mercury cathode and carbon anode. Sodium metal which is discharged at the cathode combines with mercury to form sodium amalgam. Cl_2 gas is evolved at the anode.

At cathode $Na^+ + e^- \xrightarrow{Hg}$ Na-amalgam

At anode $2\,Cl^- \longrightarrow Cl_2 + 2\,e^-$

21. Mg, Sr and Ba belong to alkaline earth metal while Be and Al are diagonally similar and Ca belongs to alkaline earth metal of Be.

22. Sodium carbonate (Na_2CO_3) and caustic soda (NaOH) are used in textile industry.

23. Since SO_4^{2-} ion is much larger than the alkaline earth metal ions, the lattice enthalpy of sulphates of alkaline earth metals remain almost constant. Thus, the solubility is decided by hydration energy, which decreases from Be to Ba (*i.e.*, with increase in atomic number). Hence, $BeSO_4$ and $MgSO_4$ are soluble in water.

24. The formula of the hydrates of halides of Ca, Ba and Sr are $CaCl_2 \cdot 6\,H_2O, BaCl_2 \cdot 2\,H_2O$ and $SrCl_2 \cdot 2\,H_2O$.

25. Due to the absence of *d*-orbitals, Be cannot extend its coordination number more than four. BeO is an amphoteric oxide *i.e.*, reacts with acids as well as alkalies. Other given statements are true.

26. Lithium because of its exceptionally small size and high polarising power exhibits anomalous behaviour.

27. Lithium carbonate decomposes readily when heated to give Li_2O and CO_2. This is due to the fact that small Li ion polarises large CO_3^{2-} to give more stable Li_2O and CO_2.

28. K and Cs emit electrons on exposure to light due to their low ionisation potential.

29. When Mg is burnt in nitric oxide, it continue to burn because during burning the heat evolved decompose NO to N_2 and O_2. Oxygen thus, produced helps Mg to burn.

30. Presence of one unpaired electron in superoxides of alkali metals make them paramagnetic.

31. $BeCO_3$ is unstable and decomposes readily into BeO and CO_2 so in order to take the reaction in backward direction, *i.e.*, for stabilising $BeCO_3$, concentration of CO_2 must be high (or $BeCO_3$ must be stored in an atmosphere of CO_2).

32. All abstract proton from water so, they are Bronsted bases.

33. All the three ions O^{2-}, O_2^{2-}, O_2^- are unstable in the presence of water and abstract proton from water.

34. All superoxides liberated oxygen with water.

$$2O_2^- + 2H_2O(l) \longrightarrow 2OH^-(aq) + H_2O_2(l) + O_2(g)$$

35. The factors which help in forming complexes are high charge and small size.

$$BeCl_2 + 2NaCl \longrightarrow \underset{\text{complex}}{Na_2[BeCl_4]}$$

36. $BeCl_2 + 4H_2O \xrightarrow{\text{cold}} [Be((H_2O)_4]Cl_2 \xrightarrow{\Delta} Be(OH)_2$
$+ 2HCl + 2H_2O$

37. Since, the halide is obtained by heating BeO with CCl_4. Hence, the halide must be $BeCl_2$.

$$2BeO + CCl_4 \xrightarrow[\Delta]{800^\circ C} 2BeCl_2 + CO_2$$

38. Portland cement does not contain $Ca_3(PO_4)_2$.

39. The percentage of lime in Portland cement is approximately 60-65%.

40. Concrete is a mixture of cement, sand, gravel and water.

41. (a) $2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2$

(b) $2KClO_3 \xrightarrow{\Delta} 2KCl + 3O_2$

(c) $CaCO_3 \xrightarrow{\Delta} \underset{\text{basic}}{CaO} + \underset{\text{acidic}}{CO_2}$

(d) $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$

42. $4KO_2 + 2CO_2 \longrightarrow 2K_2CO_3 + 3O_2$

43. $LiNO_3$ behaves differently from other alkali metal nitrates.

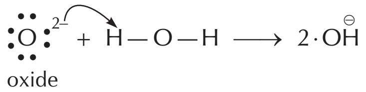
$$2LiNO_3 \xrightarrow{\Delta} Li_2O + 2NO_2 + \frac{1}{2}O_2$$

$$NaNO_3 \xrightarrow{\Delta} NaNO_2 + \frac{1}{2}O_2$$

44.

$$\begin{array}{llll} & Na_2O + & H_2O \longrightarrow & 2NaOH \\ \text{Oxidation number} & \uparrow & & \uparrow \\ \text{of Na} & +1 & & +1 \\ \text{oxygen} & -2 & -2 & -2 \end{array}$$

No change in oxidation number, so (a) and (d) are not true.
(b) is also not true.



Oxide ion donates a pair of electrons, thus changes to OH^-.

45. Be ($Z = 4$) has maximum covalency of 4 while Al ($Z = 13$) has maximum covalency of 6.

46. $\underset{1\text{ mol}}{Mg_3N_2(s)} + 6H_2O(l) \longrightarrow 3Mg(OH)_2 + \underset{2\text{ mol}}{2NH_3(g)}$

47. Solubilites of carbonates decrease down the group because lattice energy decrease is almost constant while decrease in hydration energy happens sharply. Finally difference of hydration energy and lattice energy decreases, thus solubility decreases.

48. Calcined gypsum does not contain $CaCO_3$ (that's sulphate one).

49. All alkali metals dissolve in liquid ammonia.

$$M + (x+y)NH_3 \longrightarrow M^+(NH_3)_x + e^-(NH_3)_x$$

These electrons are excited to higher energy levels and the absorption of photons occurs in the red region of the spectrum. Thus, solution appears blue.

11 *p*-Block Elements-I

JEE Main MILESTONE

- Elements of Group 13 (or IIIA)
- Unique Behaviour of Boron
- Chemistry of Boron
- Chemistry of Aluminium
- Compounds of Elements of Group 13
- Elements of Group 14 (or IV A)
- Unique Behaviour of Carbon
- Crystalline Forms of Carbon
- Oxides of Carbon
- Compounds of Silicon

Elements of Group 13(or IIIA) and Their Compounds

11.1 Elements of Group 13 (or IIIA)

The group 13th of long form of the Periodic Table contains 5 elements namely **boron** (B), **aluminium** (Al), **gallium** (Ga), **indium** (In) and **thallium** (Tl). Thallium is also known as Duckbill platypus because of its similarities with many other elements.

Elements belonging to group IIIA, IVA, VA, VIA, VIIA and zero, in which p-orbitals are being progressively filled, are collectively known as ***p-block elements.*** *These elements show regular gradation in properties along a period and along a group.*

Here, we will study only group IIIA and IVA. Remaining groups will be discussed in Ch-7, "p-block elements-II."

Occurrence

Boron occurs in two isotopic forms, *viz*, ${}_5B^{10}$ (18%) and ${}_5B^{11}$ (82%). Its abundance in earth's crust is very low and is found mainly in the form of borax. Aluminium is the third most abundant element and the most abundant metal in the earth's crust. The other members of this family are, however, less common.

Electronic Configuration

General electronic configuration of the elements of boron family is ns^2p^1 (where, $n = 2, 3, 4, \ldots$). These elements have three electrons in their valence shell and exist as M^{3+} (where, $M = 13$ group elements).

Table 11.1 **Electronic Configuration of Elements of Group 13**

Element	Electronic configuration
${}_5$B	[He] $2s^2 2p^1$
${}_{13}$Al	[Ne] $3s^2, 2p^1$
${}_{31}$Ga	[Ar] $3d^{10}\ 4s^2, 4p^1$
${}_{49}$In	[Kr] $4d^{10}, 5s^2, 5p^1$
${}_{81}$Tl	[Xe] $4f^{14}, 5d^{10}, 6s^2 6p^1$

Trends in Physical Properties of Group 13 Elements

The trends of various physical properties of elements of group 13 are discussed below one by one.

(a) Atomic and Ionic Radii

Their atomic and ionic radii are smaller as compared to that of the elements of II group due to increase in effective nuclear charge. On moving down the group, the ionic radii increases while there is an anomaly at gallium in case of atomic radii. **Atomic radii of Ga is lesser as compared to Al.** This is because ten *d*-electrons present in Ga atom do not screen the nucleus effectively. Consequently, electrons of Ga are more attracted by nucleus.

(b) Density

Density increases on moving down the group with Al lying in between having exceptionally low density. The exceptional low density of Al is attributed to its unexpected large molar volume.

(c) Melting and Boiling Points

Melting point decreases considerably on moving down the group up to Ga and then increases again in the case of In and Tl. Ga because of its unusual structure exists as Ga_2 molecules and thus, has low melting point. Due to its property to remain in liquid state even at 2000°C, Ga is used in high temperature thermometry. Boiling points follow a more regular trend. It decreases regularly on moving down the group. This is an indication of the fact that atoms of the elements are held less and less closely as we move down the group.

(d) Ionisation Energy

The first ionisation energy of 13th group elements is rather low as compared to the corresponding ionisation energies of *s*-block elements. The second and third ionisation energies are considerably higher.

It is clear from the table 11.2 that the ionisation energies change in oscillating manner. It decreases from B to Al, increases from Al to Ga, again decreases from Ga to In and again increases from In to Tl.

The ionisation energy of boron is highest in the group since its atomic size is the smallest and the shielding effect is lowest. The sharp decrease from B to Al is due to appreciable increase in atomic size and the shielding effect of *s* and *p* electrons of the penultimate energy shell. In case of Ga, there are 10*d* electrons in the penultimate energy shell which shield the nuclear charge less effectively, so that the outer electron is held firmly by the nucleus. As a result, the ionisation energy remains nearly the same as that of aluminium inspite of the fact that atomic size increases. In case of In, the number of *d* electrons and their shielding effect remains the same as in gallium. The ionisation energy, however, decreases in indium due to increase in atomic size from Ga to In. The increase in ionisation energy from In to Tl is due to poor shielding effect of 14*f* electrons present in the inner energy shell.

Since, the total of three successive ionisation energies is very high, these elements have very little tendency to form trivalent ion, *i.e.,* ions of the type M^{3+}.

Due to its very small size, B does not form M^{3+} ion. The sum of three ionisation energies is so large in the case of B that small atom of B is not able to accommodate that energy even if given artificially from outside. In other words, we can say that if such a quantity of energy is given from outside to B atom, the repulsion between subatomic particles become so large that these cannot be remain together in the form of an atom.

(e) Oxidation States

Boron show consistently +3 oxidation state in its compounds, while rest of the elements show +1 as well as +3 oxidation states. The +1 oxidation state becomes more and more stable as we move down the group, *i.e.,* as compared to the compounds in which Tl is univalent, the compounds which contain trivalent Tl are less stable. Such a presence of two oxidation states in *p*-block elements can be explained on the basis of **inert pair effect.**

The compounds of Tl(I) show close resemblance with alkali metals, *e.g.*, TlOH is highly soluble and a strong base, like NaOH; similarly Tl_2CO_3 show resemblance with Na_2CO_3 and K_2CO_3.

Ga, the third element of the group, appears to be bivalent in some of its compounds, *e.g.,* $GaCl_2$ but infact it is believed to contain univalent and trivalent ions as Ga^+ and $[GaCl_4]^-$ respectively.

Caution Point *The term II inert pair effect" is defined as the tendency of* **s***-electrons to remain together or the reluctance of s-electrons to participate in a reaction. However, this term is some what misleading. In a nut shell, we can say that because of decrease in bond energy with increase in size, the energy required to unpair the* ns^2 *electrons is not compensated by energy released in forming two additional bonds. Thus, two s-electrons develop more and more tendency to remain together as we move down the group.*

(f) Electropositive or Metallic Character

The electropositive (or metallic) character increases from B to Al. B, in fact, is regarded as a **semi-metal** and is more closer to non-metals than to metals in its properties. Aluminium is metal and most electropositive. The increase in electropositive character from boron to aluminium is due to increased size of aluminium. The remaining three elements are weakly metallic in nature and their electropositive nature is less than aluminium and decreases from gallium to thallium. The extra d^{10} electrons in gallium and indium while d^{10} and f^{14} electrons in thallium do not shield the nuclear charge very effectively and therefore, these metals are less electropositive.

(g) Nature of Compounds

Boron have a tendency to form covalent compounds as B^{3+} ion is unstable, while other members form electrovalent compounds as well.

The physical properties of the III A group elements are summarised in the following table

Table 11.2 **Physical Properties of IIIA Group Elements**

Property	Boron	Aluminium	Gallium	Indium	Thallium
Atomic number	5	13	31	49	81
Molar mass (g mol^{-1})	10.81	26.96	69.72	114.82	204.37
Density (g cm^{-3})	2.35	2.70	5.91	7.31	11.90
Melting point (°C)	2030	659	29.8	156.4	303
Boiling point (°C)	2550	2450	2237	2000	1457
Atomic radius (Å)	0.82	1.26	1.24	1.50	1.55
Molar volume (cm^3 mol^{-1})	4.62	10.0	11.8	15.1	17.2
Radius of trivalent ion (Å)	0.20	0.50	0.62	0.80	0.95
Ionisation energy (kJ mol^{-1})					
I	800	577	579	558	589
II	2427	1816	1979	1820	1971
III	3659	2744	2962	2704	2877
Electronegativity	2.0	1.5	1.6	1.7	1.8
Oxidation states	+3	+3	+1, +3	+1, +3	+1, +3
Heat of sublimation (kJ mol^{-1})	564.8	324.3	273.2	241.4	179.1

Caution Point *There is no evidence for the existence of* B^{3+} *and the value of ionic radius is an estimate.*

Hot Spot 1

TRENDS in Chemical Properties of Group 13 Elements

Previous Years' examination papers reveals that the questions are generally asked from this topic. These may be based on gradation of stability, reactivity or any such character or reason based. The level of question is easy to moderate.

(a) Reaction with Air Water and Acid

Pure **boron is unreactive to air** at ordinary temperature. It reacts with air only when heated. It does not react with water. It is attacked only by hot concentrated acids like H_2SO_4, etc. **Al reacts readily with air,** even at ordinary temperature forming a protective layer of oxide. (The oxide film protects it from further reaction). Al decomposes cold water.

$$2B + 3H_2O \longrightarrow B_2O_3 + 3H_2$$

$$2Al + 3H_2O \longrightarrow Al_2O_3 + 3H_2$$

Ga and In are attacked neither by cold water nor by hot water unless oxygen is present. Tl is a little more reactive than Ga and forms an oxide larger on its surface.

$$4Tl + 2H_2O + O_2 \longrightarrow 4TlOH$$

Caution Point *Thallium is preserved under oil or by smearing with vaseline.*

(b) Hydrides

Elements of group 13 do not react directly with hydrogen, however a large number of hydrides (of 13 group elements) are known. Boron forms a number of covalent hydrides with general formulae B_nH_{n+4} and B_nH_{n+6}. These are called **boranes.** The representative compounds of two series include B_2H_6 and B_4H_{10} respectively.

Al forms a polymeric hydride of formula $(AlH_3)_n$, which is commonly known as **alane.** It decomposes on heating above 200°C into its elements. GaH_3 is even less stable, while InH_3 and TlH_3 are extremely unstable.

B, Al and Ga have the tendency to form complex anionic hydrides like $Li[AlH_4]$, $Li[BH_4]$, $Li[GaH_4]$ etc. The formation of these complexes is due to the presence of a vacant *p*-orbital in their outermost shells due to which these readily accepts electron pair from the hydride ion (H^-) as

$$AH_3 + H^- \longrightarrow [AH_4]^- \qquad \text{[Here, } A = \text{Al, Ga and B]}$$

LAH (lithium aluminium hydride) is the most important of these hydrides and is prepared by reacting LiH with $AlCl_3$ as

$$4LiH + \underset{\text{(anhydrous)}}{AlCl_3} \xrightarrow{\text{Ether}} Li^+[AlH_4]^- + 3LiCl$$

These complex hydrides are infact good reducing agents.

(c) Oxides and Hydroxides

All the elements of this group form oxides of M_2O_3 type in which elements are in +3 oxidation state, *e.g.,* $B_2O_3, Al_2O_3, Ga_2O_3, In_2O_3$ and Tl_2O_3 etc. The oxide of B is feebly acidic while that of Al and Ga are amphoteric, In and Tl oxides have strong basic character. Thus, we can say that **basic character of these oxides increases or acidic character decreases down the group.** *e.g.,*

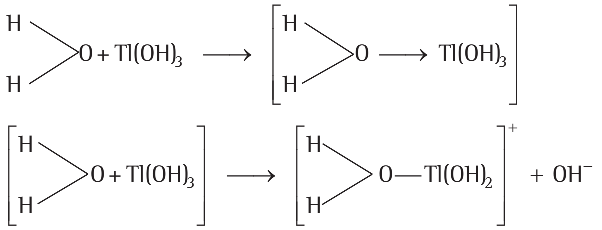
$$\underset{\text{basic oxide}}{CuO} + \underset{\text{acidic oxide}}{B_2O_3} \longrightarrow Cu(BO_2)_2$$

$$\underset{\text{basic oxide}}{Al_2O_3} + \underset{\text{acid}}{6HCl} \longrightarrow 2AlCl_3 + 3H_2O$$

$$\underset{\text{acidic oxide}}{Al_2O_3} + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$$

$$\underset{\text{basic oxide}}{Tl_2O_3} + \underset{\text{acid}}{3H_2SO_4} \longrightarrow Tl_2(SO_4)_3 + 3H_2O$$

The hydroxides of 13th group elements are $M(OH)_3$ type. Tl also give hydroxide of TlOH type which is a very strong base and comparable to hydroxides of alkali metals. $M(OH)_3$ type hydroxides follow the same trend of basicity as shown by oxides. This is because as the size of the ion increases, the tendency to rupture the O—H bond decreases and hence, acidic nature decreases, *i.e.,* basic nature increases. $Al(OH)_3$ and $Ga(OH)_3$ are amphoteric and $In(OH)_3$ and $Tl(OH)_3$ are basic in nature.



(d) Halides

Group 13 elements form trihalides of MX_3 type (where, *M* is the metal and *X* is halogen). All the halides of group 13 elements are known except Tl(III) iodide.

The halides of boron (BX_3) are covalent compounds with sp^2 hybridisation and trigonal planar structure. All the four halides of boron namely boron trifluoride (BF_3), boron trichloride (BCl_3), boron tribromide (BBr_3) and boron triiodide (BI_3) are known. All of them are volatile, monomeric and highly reactive. BF_3 and BCl_3 are gases at room temperature, BBr_3 is a volatile liquid while BI_3 is a solid. They do not conduct electricity in the liquid state. Their boiling points are also very low as compared to the halides of elements of Ist and IInd group.

The fluorides of Al, Ga, In and Tl are ionic and have high melting points while other halides of these elements are covalent when anhydrous, *e.g.,* **anhydrous** $AlCl_3$ **is covalent but in water it gets hydrolysed to give** Al^{3+} *(aq)* **ions.** Change from covalent compound to ionic in aqueous solution (as stated about $AlCl_3$) is mainly due to high hydration energy of Al^{3+} ions which easily compensate its ionisation energy while B does not show this characteristic just because of its small size and inability to accommodate energy given. All other halides of elements of this group also have sp^2 hybridisation and trigonal planar structure.

These halides have an ability of complex formation. The boron trihalides have the tendency to form BX_3L type of complexes, where, *L* is a neutral or anionic donor (*i.e.,* **ligand**) *e.g.,* BF_4^-. **These complexes are tetrahedral in shape.** Tendency to form this type of complexes decreases down the group. The trihalides of other elements of this group have more tendency to form complexes like $[AlF_6]^{3-}$, $[GaCl_6]^{3-}$ and $[InCl_6]^-$, etc., due to the availability of vacant *d*-orbital in central atoms.

The trihalides of Al exist as discrete molecules (monomeric) while the trihalides of other elements **exist as dimers both in vapour state and in non-polar solvent,** *e.g.,*

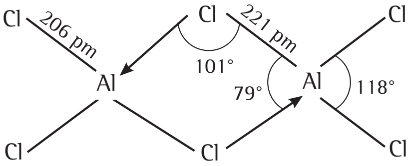


Fig. 11.1 Dimeric structure $AlCl_3$

Dimer structure disappears when the halides are dissolved in water. This is due to high hydration energy when $[M(H_2O)_6]^{3+}$ and $3X^-$ ions are formed making the solution as good conductor of electricity.

The solution becomes acidic owing to hydrolysis.

$$AlCl_3 + 9H_2O \longrightarrow [Al(H_2O)_6](OH)_3 + 3H^+ + 3Cl^-$$

However, B atom owing to its small size, cannot coordinate with four larger halide ions and hence, cannot form the dimeric molecules. That is why boron trihalides always exist in monomeric forms.

The trihalides of all the elements of this group act as Lewis acids, *i.e.,* they are electron deficient and have the tendency to accept the electron pair. The electron accepting tendency of trihalides follow the order

$$B > Al > Ga > In$$

The relative strengths of trihalides of B as Lewis acids have been determined by measuring their heats of formation as well as by studying their infrared spectra. The result of these studies is

$$BF_3 < BCl_3 < BBr_3$$

This order is just the reverse of what should be expected normally from the electronegativities of halogens. This anomalous behaviour can be explained **on the basis of tendency of halogen atom to back donate its electron to the boron atom,** which can be shown as

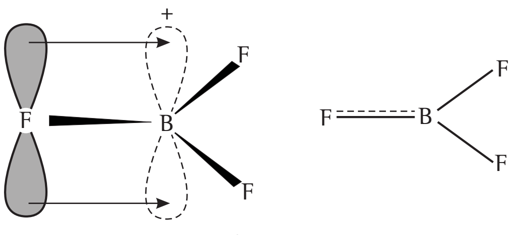


Fig. 11.2 Phenomenon of back bonding in BF_3 molecule

Infact in BF_3 molecule, where the 2*p*-orbitals of each F atom are fully-filled, one of the 2*p*-orbitals of B is vacant. Therefore, an additional *pπ-pπ* bond is established between these 2*p*-orbitals of same energy due to partial transference of electronic character from fully-filled orbital to vacant orbital as shown in the figure above. Thus, the B—F bond acquires some double bond character. This type of bond formation is called **back bonding.** Similar structure for other two B—F bonds are equally probable as

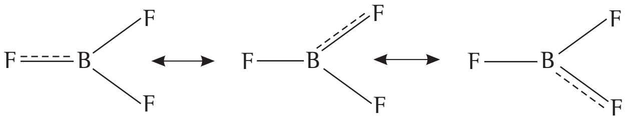
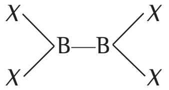


Fig. 11.3 Various resonating structures of BF_3 molecules involving $p\pi$-$p\pi$ back bonding

As the result of back donation of electrons from F to B, the electron deficiency of B atom get compensated resulting in decrease in Lewis acid character.

This tendency to form back bonds is maximum in case of BF_3 and falls rapidly as we move to BCl_3 and BBr_3 due to the fact that the energy difference between fully-filled orbital of halogen (Cl–3*p*; Br–4*p*) and vacant orbital of B (2*p*) increases.

In addition to trihalides, these elements form di as well as monohalides. Boron forms dihalides, B_2X_4.



In solid state, B_2X_4 has planar structure but in liquid and vapour state, it has non-eclipsed structure.

(planar molecule) (non-eclipsed structure)

Tetrahalides can be synthesised by heating trihalides with mercury at low pressure.

$$2BCl_3 + 2Hg \xrightarrow[\text{low pressure}]{\text{Electric discharge}} B_2Cl_4 + Hg_2Cl_2$$

Gallium and indium also form dihalides. Gallium dihalide is more properly represented as $Ga^+[GaCl_4]^-$ showing gallium in +1 and +3 oxidation states.

The elements of IIIA group in gaseous state form monohalides, *MX*. These are very unstable halides and they are covalent in nature. The covalent nature decreases and thallium halides are ionic in nature.

(e) Oxyacids

Among 13 group elements, only boron forms several oxyacids, all of which are obtained by adding one or more H_2O molecules to one or more B_2O_3 molecules as

$$B_2O_3 + 3H_2O \longrightarrow \underset{\text{orthoboric acid}}{2H_3BO_3} \quad \text{or } 2B(OH)_3$$

$$B_2O_3 + H_2O \longrightarrow \underset{\text{metaboric acid}}{2HBO_2}$$

$$2B_2O_3 + 3H_2O \longrightarrow \underset{\text{pyroboric acid}}{H_6B_4O_9}$$

$$3B_2O_3 + 2H_2O \longrightarrow \underset{\text{hexaboric acid}}{H_4B_6O_{11}}$$

$$4B_2O_3 + 3H_2O \longrightarrow \underset{\text{octaboric acid}}{H_6B_8O_{15}}$$

Sample **Problem 1** *The higher stability of* BCl_3 *as compared to* $TlCl_3$ *is due to* **[NCERT]**

(*a*) *absence of inert pair effect in* BCl_3
(*b*) *presence of inert pair effect in* BCl_3
(*c*) +3 *oxidation state of* B
(*d*) +3 *oxidation state of* Tl

Interpret (*a*) Boron exhibits only +3 oxidation state. So, it forms BCl_3, a stable compound. On moving down the group, the inert pair effect becomes more and more pronounced therefore, in thallium +1 oxidation state is more stable than +3 oxidation state. That's why BCl_3 is more stable than $TlCl_3$.

Sample **Problem 2** *The exhibition of highest coordination number depends on the availability of vacant orbitals in the central atom. Which of the following elements is not likely to act as central atom in* MF_6^{3-} ? **[NCERT Exemplar]**

(*a*) B (*b*) Al (*c*) Ga (*d*) In

Interpret (*a*) Because of the absence of *d*-orbitals B cannot exceed its covalency or coordination number more than 4. Thus, BF_6^{3-} does not exist.

Sample **Problem 3** *Which of the following oxides is acidic in nature?* **[NCERT Exemplar]**

(*a*) B_2O_3 (*b*) Al_2O_3 (*c*) Ga_2O_3 (*d*) In_2O_3

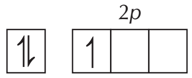
Interpret (*a*) Non-metallic oxides are generally acidic in nature and metallic character increases from B to In. Thus, B is non-metallic and hence, B_2O_3 is an acidic oxide.

Sample **Problem 4** *The geometry of a complex species can be understood from the knowledge of type of hybridisation of orbitals of central atom. The hybridisation of orbitals of central atom in* $[B(OH)_4]^-$ *and the geometry of the complex are respectively* **[NCERT Exemplar]**

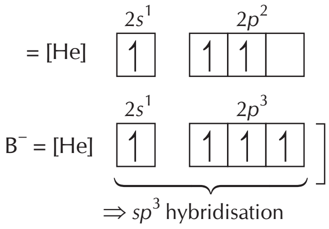
(*a*) sp^3, tetrahedral (*b*) sp^3, square planar
(*c*) sp^3d^2, octahedral (*d*) dsp^2, square planar

Interpret (*a*) In $[B(OH)_4]^-$, the central atom B have 3 valence electrons and one negative charge, thus it can form four σ bonds with $4OH^-$. Hence, its hybridisation is sp^3 and geometry is tetrahedral.

$_5B = [He]\, 2s^2 2p^1$



In first excited state



These four sp^3 hybridised orbitals overlap with four OH^- orbitals to form 4 σ bonds

$\Rightarrow sp^3$ hybridisation

11.2 Unique Behaviour of Boron

Owing to its extremely small size, high electron density, high electronegativity and non-avilability of *d*-electrons, *boron exhibits following anomalous properties*

1. Boron is a typical non-metal, while other members of the group are metals.
2. Its melting and boiling points are higher than the other members of the group.
3. It forms only covalent compounds while other members can form covalent as well as ionic compounds. The maximum covalency of B is four while that of Al is six.
4. Only boron exhibit allotropy and exists in crystalline as well as amorphous forms.
5. Its oxides and hydroxides have acidic nature while that of other members have amphoteric and basic nature.
6. Its hydrides are quite stable while that of other members are not so stable.
7. Like non-metals, it combines with metals to form metal borides (*e.g.*, Mg_3B_2) while other members form alloy with metals.
8. It does not decompose steam while other members do so.

Similarities with Silicon

Boron due to its small size and similar *e/m* ratio, shows resemblance with silicon, present diagonally opposite.

It shows the following similarities

1. Like Si, it also is a typical non-metal with high melting and boiling points and low atomic volumes.
2. It is a bad conductor of electricity and exhibits allotropy like Si.
3. Chlorides of both B and Si fumes in moist air and readily hydrolysed by water.

$$BCl_3 + 3H_2O \longrightarrow B(OH)_3 + 3HCl$$
$$SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 + 4HCl$$

4. Carbides of B and Si both are very hard and used as a abrasive.

11.3 Chemistry of Boron

Boron (B), the first member of 13th group, occurs in two isotopic forms *i.e.*, ^{10}B (19%) and ^{11}B (81%). The abundance of B in the earth crust is less than 0.001% by mass. B occurs mainly as the salts of boric acid.

Extraction of Boron

Ores of Boron

The important ores are

Borax : $Na_2B_4O_7 \cdot 10H_2O$
Colemanite : $Ca_2B_6O_{11} \cdot 5H_2O$
Panderinite : $Ca_2B_6O_{11} \cdot 3H_2O$
Boracite : $2Mg_3B_8O_{15} \cdot MgCl_2$
Kernite (Rasorite) : $Na_2B_4O_5(OH)_4$

Extraction Procedure

Boron is extracted from borax and colemanite minerals using following two steps :

(i) Preparation of B_2O_3 from the mineral
(ii) Reduction of B_2O_3

Step I **From borax** B_2O_3 is obtained by heating it with concentrated acids.

$$\underset{\text{borax}}{Na_2B_4O_7} + 2HCl \longrightarrow 2NaCl + \underset{\text{tetraboric acid}}{H_2B_4O_7}$$
$$Na_2B_4O_7 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2B_4O_7$$
$$H_2B_4O_7 + 5H_2O \longrightarrow \underset{\text{orthoboric acid}}{4H_3BO_3}$$
$$2H_3BO_3 \longrightarrow B_2O_3 + 3H_2O$$

From colemanite mineral, first borax is obtained which on heating with concentrated acids gives B_2O_3 as

$$\underset{\text{colemanite}}{Ca_2B_6O_{11}} + 2Na_2CO_3 \longrightarrow 2CaCO_3 + Na_2B_4O_7 + 2NaBO_2$$

$$\begin{tikzcd} 4NaBO_2 + CO_2 \arrow[r] & Na_2B_4O_7 + Na_2CO_3 \arrow[d, "\Delta"', "\text{acid}"] \\ & B_2O_3 \end{tikzcd}$$

Colemanite also gives B_2O_3 when SO_2 gas is passed in its suspension and the obtained H_3BO_3 is heated.

$$Ca_2B_6O_{11} + 11H_2O + 4SO_2 \longrightarrow 2Ca(HSO_3)_2 + 6H_3BO_3$$
$$2H_3BO_3 \xrightarrow{\Delta} B_2O_3 + 3H_2O$$

Step II B_2O_3 can be reduced by an electropositive metal, *e.g.*,

$$B_2O_3(s) + 6Na(s) \longrightarrow 2B(s) + 3Na_2O(s)$$
$$B_2O_3(s) + 6K(s) \longrightarrow 2B(s) + 3K_2O(s)$$
$$B_2O_3(s) + 3Mg(s) \longrightarrow 2B(s) + 3MgO(s)$$

The fused mass is stirred with iron rod to oxidise the unreacted sodium or potassium. The mass is then boiled with dil. HCl when insoluble boron powder is obtained. It is washed with water and made dry. **This is the amorphous variety of boron.**

Boron can also be obtained by the following methods.

1. Electrolytic reduction of fused borates or tetra-fluoroborates (KBF_4) in molten KCl/KF at 1073 K.
2. By reduction (hydrogenation) of a volatile boron compound with H_2 at high temperature on a heated tantalum filament as,

   $$2BCl_3(g) + 3H_2(g) \xrightarrow{1270\ K} 2B(s) + 6HCl(g)$$

   Boron obtained by this method is of high purity (almost 99.9%).
3. By thermal decomposition of boranes and boron halides at temperatures above than 900°C.

Physical Properties of Boron

Boron is a non-metallic element. It is poor conductor of electricity and is non-fusible under ordinary pressure. Its ionisation energy is highest among the group. It is an extremely hard refractory solid.

The phenomenon of existence of an element in different forms (which generally differ is number of atoms and physical properties) is called **allotropy.** Boron exists in two allotropic forms, called amorphous and crystalline forms. **Amorphous boron** is a brown powder of specific gravity 2.34. It melts at 2030°C and volatiles appreciably even at 1600°C. **Crystalline boron** exists in several different modifications. Atleast four allotrops of B may be obtained under different conditions. However, the transition between different forms is an extremely slow process. All crystalline **allotropes** have structure built up of B_{12} octahedral units as shown in the figure.

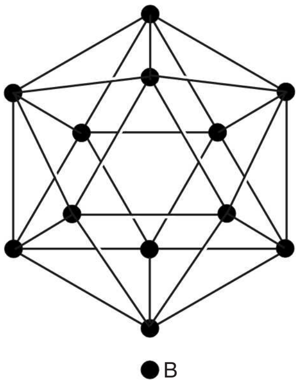


Fig. 11.4 Icosahedron arrangement of 12 B atoms in a crystalline variety

Chemical Properties of Boron

Boron reacts differently with different reagents.

Some of its characteristics reactions are as

(a) Action of Air

When heated in air at 700°C, boron forms boric anhydride with O_2 of air and boron nitride with N_2 of air as

$$4B + 3O_2 \longrightarrow 2B_2O_3$$
$$2B + N_2 \longrightarrow 2BN$$

Since, the compounds formed, form a protective layer over boron surface, these reactions do not proceed to completion.

(b) Action of Acids

B is not attacked by HCl but is oxidised by nitric acid and sulphuric acid as

$$B + 3HNO_3 \longrightarrow H_3BO_3 + 3NO_2$$
$$2B + 3H_2SO_4 \longrightarrow 2H_3BO_3 + 3SO_2$$

(c) Reaction with Alkalies

With fused alkali metal hydroxides, it forms borates and H_2 gas is evolved as

$$2B + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2$$

(d) Reaction with Metals

B combines with many metals on heating to give the corresponding borides as

$$3Mg + 2B \longrightarrow Mg_3B_2$$

(e) Reaction with Non-metals

B reacts with non-metals as

(i) Boron combines with N_2 at a temperature greater than 900°C to form boron nitride (BN).

(ii) When heated with S, it forms boron sulphide, B_2S_3.

(iii) On heating with C in an electric furnace, an extremely hard substance, called **boron carbide** (B_4C) is formed.

Boron carbide is one of the hardest materials known ranking third behind diamond and cubic boron nitride.

(iv) It also combines with halogens at high temperature to form covalent boron trihalides like BF_3, BCl_3 etc.

(f) Reaction with Water

B does not react with water, but reacts with steam at red heat liberating H_2 as

$$2B + 3H_2O \longrightarrow B_2O_3 + 3H_2\uparrow$$

(g) As a Reducing Agent

B is a powerful reducing agent, since it can replace C from CO_2, silicon from SiO_2 and N_2 from NO as

$$4B + 3CO_2 \longrightarrow 2B_2O_3 + 3C$$
$$4B + 3SiO_2 \longrightarrow 2B_2O_3 + 3Si$$
$$4B + 6NO \longrightarrow 2B_2O_3 + 3N_2$$

Uses of Boron

1. Boron is used for making bullet-proof vests and light composite material for aircrafts.
2. It is used in nuclear industry as protective shields and control rods.
3. It is used in steel industry to increase the hardness of steel.
4. It is used as a semiconductor for making electronic devices.
5. Many important compounds like borax, boric acid etc., are synthesized from it.
6. It is used as a deoxidiser in casting of iron.

11.4 Chemistry of Aluminium

Next to silica and oxygen, **Al is the third widely distributed element.** It is present to the extent of 7.3% of earth crust.

Extraction of Aluminium

Its important ores are bauxite, $Al_2O_3 \cdot H_2O$; cryolite Na_3AlF_6; corundum, Al_2O_3.

(a) Concentration of Ore

Bauxite is the principle ore of aluminium. Usually impurities like ferric oxide, silica and titanium (IV) oxide are associated with it. These are removed by one of the following methods

1. When bauxite contains Fe_2O_3 in excess, Baeyer's process is used

In this process, the ore is powdered and digested with a concentrated solution of sodium hydroxide in an autoclave under pressure at 130°C. By this, alumina present in the ore dissolves as sodium meta aluminate, whereas impurities being insoluble in NaOH, settle down.

Similarly, silica of the ore reacts with NaOH to form sodium silicate which is also present in the solution along with sodium meta aluminate. Solution is filtered leaving insoluble impurities behind. Now, the filtrate containing sodium meta-aluminate and sodium silicate is diluted and seeded with freshly prepared $Al(OH)_3$ solution which induces the precipitation of $Al(OH)_3$ leaving behind sodium silicate in solution.

$$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$$
$$NaAlO_2 + 2H_2O \longrightarrow Al(OH)_3 + NaOH$$

The precipitate is filtered, washed and ignited to obtain pure alumina.

2. If SiO_2 is in excess, Serpeck's process is used

In this method, the ore is mixed with coke and heated at 1800°C in a current of nitrogen. By this, alumina converts into AlN and SiO_2 is reduced into Si. Si being volatile, passes off as vapours. AlN on dilution induces the precipitation of aluminium hydroxide.

$$Al_2O_3 + 3C + N_2 \longrightarrow 2AlN + 3CO$$
$$SiO_2 + 2C \longrightarrow Si + 2CO$$
$$AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$$

Alumina is obtained by filtering, washing and igniting the precipitate.

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$$

3. In Hall's process

The bauxite ore is fused with sodium carbonate. The alumina present in the ore dissolves as sodium meta aluminate leaving behind Fe_2O_3 and SiO_2. The fused mass after extraction with water and filtration, is warmed to 58° and CO_2 is passed through it, $Al(OH)_3$ precipitates out.

$$Al_2O_3 \cdot 2H_2O \longrightarrow 2NaAlO_2 + CO_2 + 2H_2O$$
$$2NaAlO_2 + CO_2 + 3H_2O \longrightarrow 2Al(OH)_3 + Na_2CO_3$$

This precipitate, when filtered, washed and ignited gives pure alumina.

(b) Reduction of Alumina to Al Metal

Aluminium is obtained from alumina by electrolysis, called **Hall-Heroult process.** In this process, cathode and anode both are made up of carbon. The electrolyte used contains Na_3AlF_6 (80-85%), CaF_2 (5-7%), AlF_3 (5-7%), Al_2O_3 (2-8%), of which Al_2O_3 is recharged intermittently. When electricity is passed, Al is deposited at cathode while O_2 is liberated at anode which reacts with C electrode to produce CO and then CO_2.

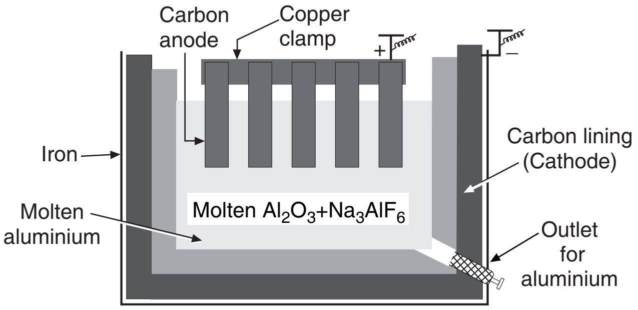


Fig. 11.5 Electrolysis of alumina

Caution Point *The electrolysis of pure alumina faces two difficulties : (i) Pure alumina is a bad conductor of electricity, (ii) The fusion temperature of pure alumina is about 2000°C and at this temperature when the electrolysis is carried of fused mass, the metal formed vaporises as the boiling point of aluminium is 1800°C.*

The above difficulties are overcome by using a mixture of alumina, cryolite (Na_3AlF_6) and fluorspar (CaF_2) in the ratio of 20 : 24 : 20. The fusion temperature of this mixture is 900°C and it is a good conductor of electricity.

The exact mechanism of the electrolysis is not yet known. Two concepts have been proposed.

First concept AlF_3 from cryolite ionises as,

$$AlF_3 \rightleftharpoons Al^{3+} + 3F^-$$

Al^{3+} ions are discharged at cathode and F^- ions at anode.

$$Al^{3+} + 3e^- \longrightarrow Al \qquad \text{(at cathode)}$$

$$2F^- \longrightarrow F_2 + 2e^- \qquad \text{(at anode)}$$

The liberated fluorine reacts with alumina to form AlF_3 and O_2. The oxygen attacks the carbon anodes to form CO and CO_2.

$$Al_2O_3 + 3F_2 \longrightarrow 2AlF_3 + \frac{3}{2}O_2$$

$$2C + O_2 \longrightarrow 2CO$$

$$C + O_2 \longrightarrow CO_2$$

Anodes are replaced frequently.

Second concept Alumina (Al_2O_3) ionises as,

$$Al_2O_3 \rightleftharpoons \underset{\text{cathode}}{Al^{3+}} + \underset{\text{anode}}{AlO_3^{3-}}$$

$$Al^{3+} + 3e^- \longrightarrow Al \text{ (at cathode)}$$

At anode AlO_3^{3-} is oxidised.

$$4AlO_3^{3-} \longrightarrow 2Al_2O_3 + 3O_2 + 12e^- \text{ (at anode)}$$

Thus, the overall chemical reaction taking place during electrolysis is

$$2Al_2O_3 \longrightarrow 4Al + 3O_2$$

Refining of Aluminium

The aluminium obtained by reduction process is about 98% pure. *In order to purify it, Hoope's electrolytic method is used.* The cell used for the refining contains three layers that differ in specific gravities. The upper most layer contains pure aluminium which acts as cathode, the middle layer contains a mixture of fluorides of Al, Na and Ba and acts as electrolyte while the lower layer contains impure aluminium which acts as anode. On electrolysis, pure Al is deposited at cathode from the middle layer and an equivalent quantity of Al is deposited to the lower layer. The aluminium obtained by this process is 99.98% pure.

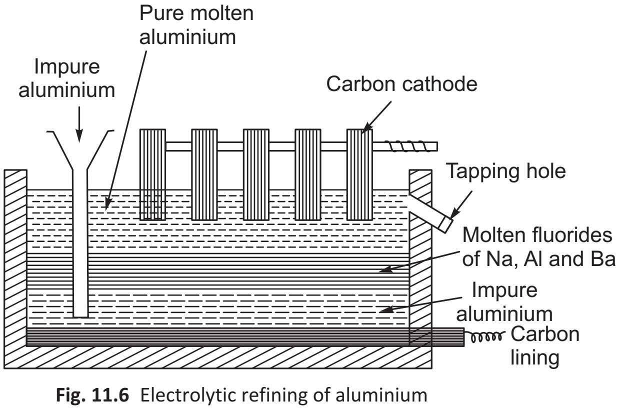


Fig. 11.6 Electrolytic refining of aluminium

Modern Method of Extraction of Al

When vapour of aluminium chloride is passed over fused oxide at 1000°C, aluminium monochloride is formed which on cooling disproportionates to give Al.

$$2Al_2O_3 + 2AlCl_3 \longrightarrow 6AlCl + 3O_2$$

$$3AlCl \longrightarrow AlCl_3 + 2Al$$

The $AlCl_3$ obtained is reused.

Physical Properties of Aluminium

Al is a bluish-white metal with a brilliant lusture which soon get destroyed due to the formation of oxide layer over it.

It is malleable and ductile in nature and can be rolled into sheets, foils and wires. Al is a very light metal (sp. gravity 2.7), good conductor of heat and electricity, melts at 659°C and boils at 2450°C. On a weight to weight basis, the electrical conductivity of Al is twice that of copper.

Chemical Properties of Aluminium

Aluminium is a very reactive metal but formation of oxide layer over its surface reduces its reactivity. Al shows following reactions

(a) With Air

Al is not affected by pure dry air but with moist air, a film of oxide is formed at the surface which protects the metal from further corrosion. It burns readily in oxygen giving out energy. The heat evolved in the oxidation of Al is used in **thermite process** for the reduction of oxides of Cr, Fe, Mn etc.

$$Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3 + \text{heat}$$

$$Fe_2O_3 + 2Al \longrightarrow 2Fe + Al_2O_3 + \text{heat}$$

$$3Mn_3O_4 + 8Al \longrightarrow 9Mn + 4Al_2O_3 + \text{heat}$$

Al also reduces oxides of non-metals as

$$3CO_2 + 4Al \longrightarrow 2Al_2O_3 + 3C$$

$$3SiO_2 + 4Al \longrightarrow 2Al_2O_3 + 3Si$$

(b) With Water

Pure water does not affect pure Al. However, impure form is readily corroded by water containing salts. It decomposes boiling water evolving hydrogen.

(c) With Alkalies

Al readily dissolves in alkalies evolving H_2 and forming the corresponding aluminates.

$$2Al + 2H_2O + 2NaOH \xrightarrow{\Delta} \underset{\substack{\text{sodium} \\ \text{meta aluminate}}}{2NaAlO_2} + 3H_2$$

The metal also dissolves in hot conc. solution of Na_2CO_3 as

$$2Al + Na_2CO_3 + 3H_2O \xrightarrow{\Delta} 2NaAlO_2 + CO_2 + 3H_2$$

(d) With Acids

The metal dissolves in dil. HCl and dil. H_2SO_4 solutions evolving H_2. With hot conc. H_2SO_4, SO_2 is given out. **Conc. HNO_3 has no reaction, the metal rendered passive due to surface oxidation.**

(e) With Halogen and Nitrogen

The metal gives halides and nitrides respectively on heating with halogens and nitrogen.

(f) Displacement Reactions

Al displaces Cu, Zn and Pb from the solutions of their salts as

$$3ZnSO_4 + 2Al \longrightarrow Al_2(SO_4)_3 + 3Zn$$
$$3CuSO_4 + 2Al \longrightarrow Al_2(SO_4)_3 + 3Cu$$

Uses of Aluminium

Aluminium is used

1. in manufacturing of household utensils, aeroplane parts, precision and surgical instruments etc.
2. in HNO_3 transportation and in construction of tank for chemical plants where HNO_3 is manufactured. (Since, it rendered passive to HNO_3).
3. as aluminium foil, in packing of different objects.
4. for the formation of alums which is used as mordants in dyeing and paints.
5. as a reducing agent.
6. as building material, refractory bricks and ultra-marine.
7. for sizing the paper.
8. in thermite welding processes.
9. in making alloys.

Some of the important alloys of Al *are tabulated below*

Table 11.3 **Important Alloys of Aluminium**

Alloy	Approx. composition	Uses
Magnalium	Al = 94.5%, Mg = 5.5%	Scientific apparatus, machined articles.
Duralumin	Al = 95%, Cu = 4% Mg = 0.5%, Mn = 0.5%	Aircraft parts, railroad cars, bos machinery.
Nickel alloy or Nickeloy	Al = 95%, Cu = 4%, Ni = 1%	Aircraft parts
γ-alloy	Al = 93%, Cu = 4%, Ni = 2%, Mg = 1%	Pistons and machinery parts.
Alnico	Steel = 77%, Ni = 2%, Al = 20%, Co = 1%	For making permanent magnets.
Artificial gold	Al = 10%, Cu = 90%	For making artificial ornaments, pots, paints.

Check Point 1

1. Why does boron not form tripositive ions?
2. Boron forms no compound in unipositive state while the compounds of thallium in unipositive state are quite stable, Explain, why?
3. Explain, why boron halides do not exist as dimers while $AlCl_3$ exists as Al_2Cl_6?
4. Cryolite is added to alumina during electrolysis process, why?
5. Melting point of gallium is lowest among the group. Give reason.
6. Ga and In are less electropositive than Tl, explain why?
7. BF_3 is a weaker Lewis acid as compared to BI_3, why?
8. In aqueous solution $AlCl_3$ does not exist as dimer. Explain.

11.5 Compounds of Elements of Group 13

Some of the important compounds of elements of this group are discussed below

Borax

Chemically borax is sodium tetraborate decahydrate ($Na_2B_4O_7 \cdot 10H_2O$). It is also called **tincal.** Since, borax contains the tetranuclear units $[B_4O_5(OH)_4]^{2-}$, its correct formula is $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$.

Methods of Preparation

1. It is prepared from colemanite, a mineral, by boiling the finely powered mineral with calculated quantity of sodium carbonate solution.

$$2Ca_2B_6O_{11} + 3Na_2CO_3 + H_2O \longrightarrow 3Na_2B_4O_7 + 3CaCO_3\downarrow + Ca(OH)_2$$

   The precipitate of calcium carbonate is removed by filtration and borax is crystallised from the filtrate.

2. It is obtained by neutralising a solution of the boric acid by soda ash.

$$Na_2CO_3 + 4H_3BO_3 \longrightarrow Na_2B_4O_7 + 6H_2O + CO_2$$

Physical Properties

Borax is a crystalline solid which exists in three forms

(i) Prismatic borax ($Na_2B_4O_7 \cdot 10H_2O$) is an ordinary form of borax and is obtained when a solution of the salt is crystallised at ordinary temperature.

(ii) Octahedral borax ($Na_2B_4O_7 \cdot 5H_2O$) is obtained when a solution of the salt is crystallised above 60°C. This is **jeweller's borax.**

(iii) Borax glass ($Na_2B_4O_7$) is anhydrous sodium tetraborate and is obtained by heating ordinary form of borax above its melting point until all the water of crystallisation is removed. It is a colourless glassy substance which absorbs moisture from the atmosphere and converts into prismatic borax.

Chemical Properties

(i) It is sparingly soluble in **cold water** but is readily soluble in hot water. Its aqueous solution is alkaline due to hydrolysis.

$$Na_2B_4O_7 + 7H_2O \rightleftharpoons \underset{\text{strong base}}{2NaOH} + \underset{\text{weak acid}}{4H_3BO_3}$$

(ii) It reacts **with conc. acid** like HCl, H_2SO_4 to form sparingly soluble boric acid as

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4H_3BO_3$$

(iii) When heated with NH_4Cl, it forms boron nitride.

$$Na_2B_4O_7 + 2NH_4Cl \longrightarrow 2NaCl + \underset{\text{boron nitride}}{2BN} + B_2O_3 + 4H_2O$$

(iv) On heating above its melting point, it loses its water of crystallisation and swells up to form a mass. On further heating, it melts into a liquid which then solidifies to form transparent glassy mass like bead, called the **borax bead.** This bead is employed in qualitative analysis for the detection of certain coloured radicals such as $Ni^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}$, etc.

When a salt, containing any of these ions, is heated with borax bead on a Pt wire, the salt decomposes to corresponding oxide which combines with B_2O_3 of glassy bead and form coloured meta borate. This test is called **borax bead test.**

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow{-10H_2O} Na_2B_4O_7 \xrightarrow{\Delta} \underbrace{\underset{\text{sodium meta borate}}{2NaBO_2} + \underset{\text{boric anhydride}}{B_2O_3}}_{\text{glassy mass}}$$

$$CoO + B_2O_3 \xrightarrow{\Delta} \underset{\text{blue}}{Co(BO_2)_2}$$

$$Cr_2O_3 + 3B_2O_3 \xrightarrow{\Delta} \underset{\text{green}}{2Cr(BO_2)_3}$$

Uses

Borax is used

1. in leather and match industries.
2. in making optical glass and heat resistant boro-silicate glassware.
3. as a preservative for food.
4. in borax bead test, for the detection of basic radicals.
5. as a flux in metallurgy.
6. as an antiseptic in the manufacture of medicinal soaps.

Structure

Borax contains the tetrahedral units, *i.e.*, $[B_4O_5(OH)_4]^{2-}$ and its structure can be shown as

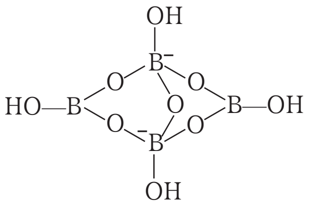


Fig. 11.5 Structure of $[B_4O_5(OH)_4]^{2-}$ ion

2. Orthoboric Acid or Boric Acid

Chemically it is H_3BO_3 or $B(OH)_3$.

Methods of Preparation

(i) It can be prepared from **borax** $(Na_2B_4O_7)$ or **colemenite** ore $(Ca_2B_6O_{11})$ through extraction directly.

(ii) Besides, it can also be prepared by the action of superheated water on boron nitride (BN) and boron sulphide (B_2S_3) as

$$BN + 3H_2O \longrightarrow H_3BO_3 + NH_3$$

$$B_2S_3 + 6H_2O \longrightarrow 2H_3BO_3 + 3H_2S$$

(iii) The acid can also be obtained by the hydrolysis of BCl_3 as

$$BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$$

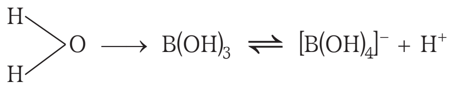
Physical Properties

It is seen as pearly white, needle like crystals with greasy feel. It is moderately soluble in water. The dissolution is accompanied by absorption of heat, *i.e.,* its solubility increases with increase in temperature.

Chemical Properties

Orthoboric acid exhibits the following chemical properties

(i) Boric acid is a weak acid and behaves as a monobasic Lewis acid. This is because in aqueous solution, it coordinates with a molecule of water to form a hydrated species, $\begin{matrix} H \\ H \end{matrix}\!\!>\!O \longrightarrow B(OH)_3$. B^{3+} ion pulls the σ-electron charge of the coordinated O-atom towards itself. The coordinated oxygen, in turn, pulls the σ-electron charge of the O—H bond of the attached water molecule towards itself. This facilitates the removal of H^+ ion from the O—H bond. Thus, the aqueous solution acts as a weak acid.



$$\begin{matrix} H \\ H \end{matrix}\!\!>\!O \longrightarrow B(OH)_3 \rightleftharpoons [B(OH)_4]^- + H^+$$

(ii) H_3BO_3 reacts with the aqueous solution of an alkali (*e.g.,* NaOH, KOH) and gives various types of polymeric metaborates like $NaBO_2 \cdot 2H_2O$, $NaB_3O_5 \cdot 2H_2O$, $Na_2B_4O_7 \cdot 10H_2O$, $KB_5O_8 \cdot 4H_2O$ etc., as

$$B(OH)_3 + NaOH(dil) \longrightarrow \underset{\text{sodium metaborate}}{NaBO_2 \cdot 2H_2O}$$

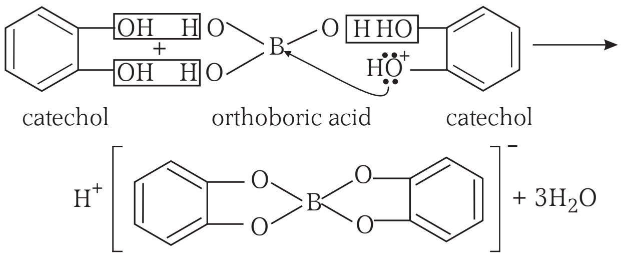
$$\text{or } Na^+[B(OH)_4]^-$$

$$5B(OH)_3 + KOH \longrightarrow KB_5O_8 \cdot 4H_2O + 4H_2O$$

The titration between $B(OH)_3$ and a strong alkali solution (*e.g.,* NaOH) is not possible, because sodium metaborate formed by reaction between $B(OH)_3$ and NaOH gets hydrolysed to regenerate $B(OH)_3$ and NaOH.

$$Na^+[B(OH)_4]^- \longrightarrow B(OH)_3 + NaOH$$

However, some quantity of polyhydroxy compounds like catechol, glycerol, mannitol, sugar etc., if added to the titration solution, a chelated complex compound is formed which makes H_3BO_3 *a strong acid by providing* H^+ *ions.*



chelated complex compound

The titration between $B(OH)_3$ and strong alkali solution, in the presence of polyhydroxy compound (with phenolphthalein indicator) makes the basis for the estimation of the acid and borax phenolphthalein test of glycerol.

(iii) When **heated to 100°C,** H_3BO_3 loses H_2O to give metaboric acid (HBO_2) which on being heated to 160°C, gives tetraboric acid ($H_2B_4O_7$). When $H_2B_4O_7$ is heated to redness, boron trioxide (B_2O_3) is obtained.

$$4H_3BO_3 \xrightarrow[-4H_2O]{100°C} 4HBO_2 \xrightarrow[-H_2O]{160°C} H_2B_4O_7 \xrightarrow[-H_2O]{\text{Red heat}} 2B_2O_3$$

On **heating below 100°C,** it gives pyroboric acid which on dilution further gives H_3BO_3 as

$$4H_3BO_3 \longrightarrow \underset{\text{pyroboric acid}}{H_6B_4O_9} + 3H_2O$$

$$H_6B_4O_9 + 3H_2O \longrightarrow 4H_3BO_3$$

(iv) When H_3BO_3 is treated **with sodium hydroperoxide** NaOOH, dihydrated sodium peroxyborate, $Na_2B_2O_6 \cdot 2H_2O$ is formed.

$$2B(OH)_3 + 2NaOOH \longrightarrow Na_2B_2O_6 \cdot 2H_2O + 2H_2O$$

(v) When H_3BO_3 or any borate is heated **with alcohol** (C_2H_5OH), in the presence of conc. H_2SO_4, volatile triethylborate, $(C_2H_5)_3BO_3$ (ester) is formed.

$$H_3BO_3 + 3C_2H_5OH \xrightarrow{\text{Conc. } H_2SO_4} (C_2H_5)_3BO_3 + 3H_2O$$

This ester burns with a green-edged flame. This property of the ester has been utilised for the identification of BO_3^{3-} radical.

(vi) When H_3BO_3 is heated **with CaF_2 and conc. H_2SO_4,** BF_3 (volatile) is obtained. If BF_3, produced as above, is brought near the Bunsen flame, a green flame is produced due to the burning of volatile BF_3. The formation of green flame, in this way, is used to detect BO_3^{3-} ion in the presence of Cu, given in a salt.

(vii) When H_3BO_3 is neutralised by soda ash, (Na_2CO_3), borax ($Na_2B_4O_7$) is obtained.

$$4H_3BO_3 + Na_2CO_3 \longrightarrow Na_2B_4O_7 + 6H_2O + CO_2$$

(viii) When H_3BO_4 is dissolved **in HF,** fluoroboric acid, $H[BF_4]$ (also called hydrofluoroboric acid) is obtained.

$$H_3BO_3 + 4HF \longrightarrow H^+[BF_4]^- + 3H_2O$$

(ix) When treated with acetic anhydride, $(CH_3CO)_2O$, H_3BO_3 gives boron acetate.

Uses

Boric acid is used

(i) as a preservative for milk and food stuffs.
(ii) as a mild antiseptic in aqueous solution, for washing eyes.
(iii) for preparing heat resistant borosilicate glass.
(iv) for the preparation of glazes in pottery.

Structure of Boric Acid

In solid state, boric acid has layer structure, *i.e.,* boric acid consists of a number of layers, which are linked together by van der Waals' forces and are at a distance of 318 pm from each other. Each layer is composed of various trigonal planar $B(OH)_3$ units. B atom, in each $B(OH)_3$ unit is linked with three OH groups, which are arranged at the corner of an equilateral triangle. The structure of one layer is shown in figure below, from which it may be seen that H-atom acts as a bridge between the two O-atoms, belonging to two different $B(OH)_3$ units.

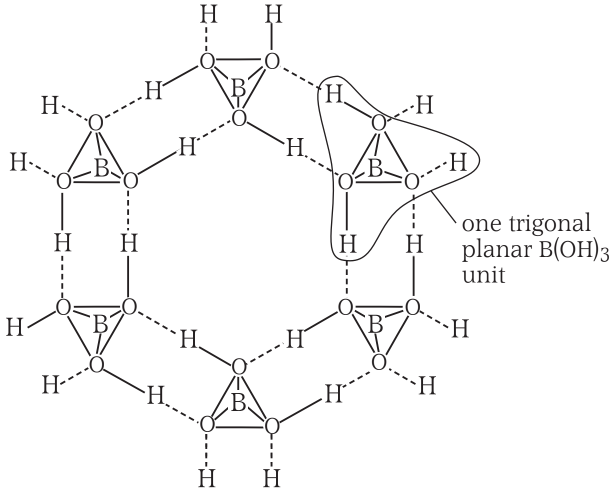


Fig. 11.7 Structure of boric acid

The dotted lines between O*-atom of one* B(OH)$_3$ *unit and H-atom of the other* B(OH)$_3$ *unit indicates hydrogen bonds.* It is due to the layer structure of boric acid which, in the solid state, consists of flakes, that are slippery to touch.

3. Diborane

Its formula is B_2H_6. It is the first member of B_nH_{n+4} series of boron hydrides because BH_3, which should be the first member, is known.

Methods of Preparation

Following methods are used for the preparation of diborane.

(i) By the reduction of boron trifluoride with $LiAlH_4$ in diethyl ether as

$$4BF_3 + 3LiAlH_4 \xrightarrow{\text{Diethyl ether}} 2B_2H_6 + 3LiF + 3AlF_3$$

(ii) By the oxidation of $NaBH_4$ with I_2 in DIGLYME (diethylene glycol methyl ether) as

$$2NaBH_4 + I_2 \xrightarrow{\text{DIGLYME}} B_2H_6 + 2NaI + H_2 \text{ (lab method)}$$

(iii) By the reaction of BF_3 with sodium hydride as

$$2BF_3 + 6NaH \xrightarrow{450\text{ K}} B_2H_6 + 6NaF \text{ (industrial method)}$$

(iv) By passing silent electric discharge through a mixture of hydrogen and BCl_3 vapour at a low pressure as

$$2BCl_3 + 6H_2 \xrightarrow[\text{discharge}]{\text{Silent electric}} B_2H_6 + 6HCl$$

Physical Properties

Diborane is a colourless, highly toxic gas with a boiling point of 180 K. It catches fire spontaneously on exposure to air and burns in oxygen releasing an enormous amount of energy as

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O + 1976 \text{ kJ/mol}$$

Most of the higher boranes are also spontaneously flammable in air.

Chemical Properties

Diborane shows the following chemical properties

(i) It gets **hydrolysed** readily as

$$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2\uparrow$$

(ii) It dissolves in strong alkali solutions giving metaborates and H_2 as

$$B_2H_6 + 2KOH + 2H_2O \longrightarrow 2KBO_2 + 6H_2\uparrow$$

(iii) It reacts slowly with active metals (Na, K, Ca and their amalgams). However, the reaction is faster in the presence of ether as

$$2B_2H_6 + 2Na \xrightarrow{\text{Ether}} NaBH_4 + \underset{\text{sodium polyborane}}{NaB_3H_8}$$

(iv) It reacts **with CO** at 100°C and 20 atm pressure to form the carbonyl H_3BCO as

$$B_2H_6 + 2CO \xrightarrow[20\text{ atm}]{100°\text{C}} 2H_3BCO$$

(v) It reacts **with halogens** under different conditions to form halo diboranes as

$$B_2H_6 + Cl_2 \xrightarrow[\text{explosive}]{25°\text{C}} \underset{\text{chloro diborane}}{B_2H_5Cl} + HCl$$

$$B_2H_6 + Br_2 \xrightarrow[\text{rapid}]{100°\text{C}} \underset{\text{bromo diborane}}{B_2H_5Br} + HBr$$

(vi) It reacts **with halogen acids** as

$$B_2H_6 + HCl \longrightarrow B_2H_5Cl + H_2\uparrow$$

(vii) It combines **with hydrides of alkali metals** to form complex hydrides as

$$B_2H_6 + 2NaH \longrightarrow 2Na[BH_4]$$

(viii) It adds to **alkanes** and **alkynes** in the presence of a Lewis base like THF (tetrahydro furan) or DIGLYME (diethylene glycol methyl ether) as

$$3RCH{=}CH_2 + BH_3 \xrightarrow[\text{DIGLYME}]{\text{THF or}} \underset{\text{trialkyl borane}}{(RCH_2CH_2)_3B}$$

$$3RC{\equiv}CH + BH_3 \xrightarrow[\text{DIGLYME}]{\text{THF or}} \underset{\text{trialkenyl borane}}{(R{-}CH{=}CH)_3B}$$

This reaction is called **hydroboration reaction** and has been of great synthetic utility in organic chemistry.

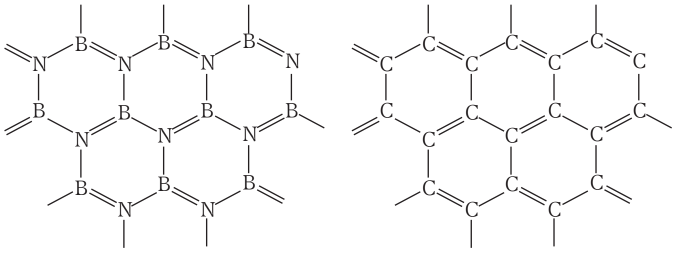
(ix) Diborane reacts **with NH_3** and the products formed depend upon the conditions of reaction as

(a) $B_2H_6 + 2NH_3 \xrightarrow{\text{Low temperature}} \underset{\text{diammoniate of diborane}}{B_2H_6\cdot 2NH_3}$

The compound $B_2H_6\cdot 2NH_3$ is ionic and exists as $[H_3N \longrightarrow BH_2 \longleftarrow NH_3]^+ [BH_4]^-$. It forms borazine on heating.

(b) $nB_2H_6 \xrightarrow[\text{at high temperature}]{\text{Excess } NH_3} \underset{\text{boron nitride}}{(BN)_n}$

Boron nitride is a white crystalline solid and resembles graphite in structure as shown below

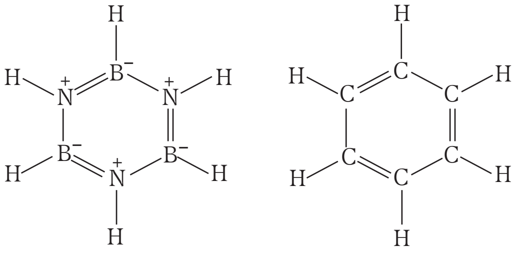


(a) Boron nitride (b) Graphite

Fig. 11.8 Similarity in the structure of boron nitride and graphite

$$\text{(iii) } 3B_2H_6 + 6NH_3 \xrightarrow{200°C} \underset{\substack{\text{borazine}\\ \text{or borazole}}}{2B_3N_3H_6} + 12H_2$$

Borazine or **borazole** can also be prepared by heating BCl_3 and NH_4Cl together or by treating $NaBH_4$ with NH_4Cl. Its structure is similar to that of benzene as shown below

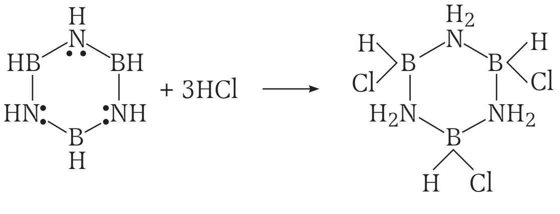


(a) Borazine (b) Benzene

Fig. 11.9 Similarity in the structure of borazine and benzene

Because of its similarity with benzene in structure, and some physical and chemical properties borazine is also called **inorganic benzene.**

However, in benzene the C═C bonds are non-polar and the nucleus is very resistant to addition reactions, whereas borazole nucleus is fairly reactive on account of its polarities. Thus, it readily adds three molecules of H_2O, CH_3OH, CH_3I or HCl, the more negative group generally attaches to boron atoms.



Borazole decomposes slowly on standing and undergoes hydrolysis at high temperatures.

$$B_3N_3H_6 + 9H_2O \longrightarrow 3B(OH)_3 + 3NH_3 + 3H_2$$

Uses

Diborane is used

1. as a reducing agent in organic reaction.
2. for the synthesis of a number of borohydrides like $LiBH_4$, $NaBH_4$ etc.
3. as a fuel for supersonic rockets.

Structure of Diborane

Boranes provide interesting examples of **electron deficient compounds.** The structure of diborane shows that the four terminal hydrogens along with two boron atoms lie in one plane. Two bridging hydrogens are seen to present above and below this plane. The four terminal B—H bonds are regular two centred two electron (2*c*–2*e*) bonds while two bridge bonds (B—H—B) are different and can be described in terms of three centred two electron (3*c*–2*e*) bonds as shown in the figure below.

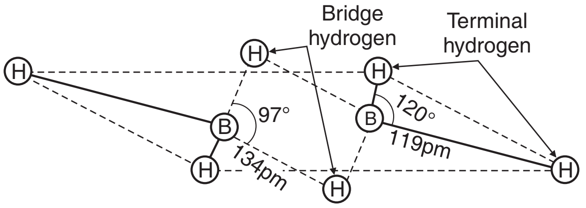


Fig. 11.10 Structure of B_2H_6

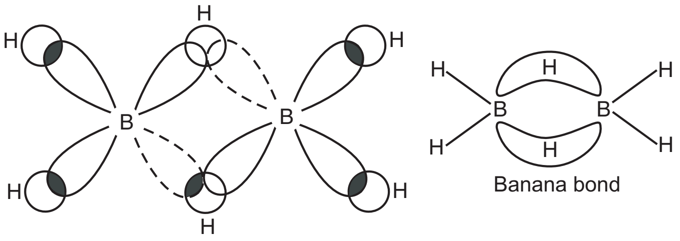


Fig. 11.11 Orbital picture of B_2H_6

According to molecular orbital theory, each B atom uses sp^3-hybrid orbitals for bonding. Out of $4sp^3$-hybrid orbitals one orbital is empty, *i.e.,* without any electron and is shown with broken lines in the figure. So, the involvement of one half-filled orbital of one B atom with one empty orbital of other B atom and half-filled orbital of hydrogen atom results in three centred (B—H—B) two electron (one contributed by one of the B atoms and other by hydrogen atom) electron deficient bridge bond. Such a bond is also called **banana bond** due to its banana like shape as shown in the figure below.

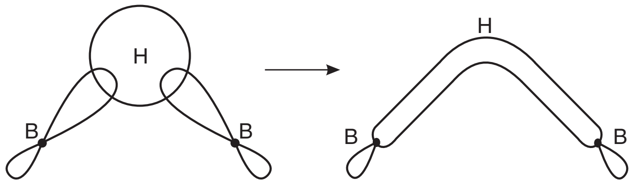


Fig. 11.12 Banana bond in diborane

The structure discussed above is supported by the following additional facts

1. **Heat capacity** measurements shown that the rotation of the two ends of the molecule against each other is very much hindered. This indicates that the bridge hydrogen atoms lie in a plane at right angles to the plane in which the rest of the molecule lies. In a molecule, like ethane (where bridge hydrogen atoms are absent) the hinderance of this type of rotation is very low.
2. Diborane cannot be methylated beyond $(CH_3)_4B_2H_2$. The hydrogens which cannot be methylated, evidently, are in a different environment. These are infact bridged hydrogens.

Boron Trifluoride

It is an electorn deficient compound of formula BF_3. It is generally used as a Lewis acid and catalyses many organic reactions.

Methods of Preparation

(i) BF_3 is obtained as a colourless gas by heating B_2O_3 or borax with calcium fluoride and conc. H_2SO_4 as

$$B_2O_3 + 3CaF_2 + 3H_2SO_4 \longrightarrow 3CaSO_4 + 3H_2O + 2BF_3$$

$$Na_2B_4O_7 + 6CaF_2 + 8H_2SO_4 \longrightarrow 2NaHSO_4 + 6CaSO_4 + 4BF_3 + 7H_2O$$

BF_3 is collected over Hg.

(ii) BF_3 can also be obtained by heating together B_2O_3, ammonium fluoroborate and concentrated sulphuric acid.

$$B_2O_3 + 6NH_4BF_4 + 6H_2SO_4 \longrightarrow 8BF_3 + 6NH_4HSO_4 + 3H_2O$$

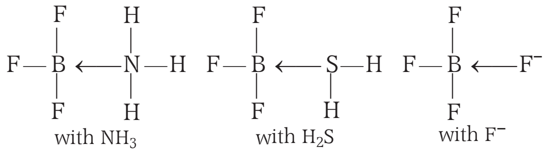
(iii) Pure BF_3 can also obtained by the thermal decomposition of diazonium tetrafluoroborate as

$$C_6H_5N_2BF_4 \xrightarrow{\Delta} C_6H_5F + N_2 + BF_3$$

Physical and Chemical Properties

(i) BF_3 is a colourless pungent gas (mp −127.1°C and bp −99.9°C) which strongly fumes in moist air and possesses a pungent smell. It is exceedingly soluble in water that's why it is collected over Hg.

(ii) BF_3, being an electron deficient compound, can accept a lone pair of electrons, thus behaves as Lewis acid, *e.g.*, with NH_3, H_2S and F^-, it can form complexes like



Due to its electron accepting tendency, it is used as a catalyst in a number of organic reactions.

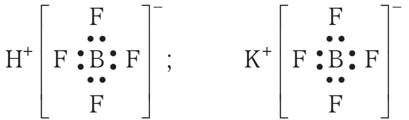
(iii) BF_3 combines with water forming two hydrates, *i.e.*, $BF_3 \cdot H_2O$ (mp 10.18°C) and $BF_3 \cdot 2H_2O$ (mp 6.36°C). It gets hydrolysed in aqueous solutions yielding boric acid and hydrofluoroboric acid as

$$BF_3 + 3H_2O \longrightarrow H_3BO_3 + 3HF$$

If we take BF_3 in excess, it is dissolved in HF to give hydrofluoroboric acid $H[BF_4]$ as

$$BF_3 + HF \longrightarrow H[BF_4]$$

Fluoroboric acid forms definite salts, known as fluoroborates or borofluorides, *e.g.*, KBF_4, in which boron is tetracovalent (as in the acid also).



fluoroboric acid potassium borofluoride

On strong heating, these salts decompose into BF_3 and metal fluoride.

$$KBF_4 \xrightarrow{\Delta} KF + BF_3$$

Sample **Problem 5** *In the following reaction sequence Z is*

$$Z + 3LiAlH_4 \longrightarrow X + 3LiF + 3AlF_3$$

$$X + 6H_2O \longrightarrow Y + 6H_2$$

$$X + 3O_2 \xrightarrow{\Delta} B_2O_3 + 3H_2O$$

[NCERT Exemplar]

(*a*) *boron trifluoride* (*b*) *boron trichloride*
(*c*) *diborane* (*d*) *Both* (*a*) *and* (*b*)

Interpret (*a*) $4BF_3 + 3LiAlH_4 \longrightarrow \underset{\substack{\text{diborane} \\ (X)}}{2B_2H_6} + 3LiF + 3AlF_3$

$$\underset{(X)}{B_2H_6} + 6H_2O \longrightarrow \underset{\text{orthoboric acid}}{2H_3BO_3} + 6H_2$$

$$\underset{(X)}{B_2H_6} + 3O_2 \xrightarrow{\Delta} B_2O_3 + 3H_2O$$

Sample **Problem 6** *A compound X of boron reacts with* NH_3 *on heating to give another compound Y which is called inorganic benzene. The compound X can be prepared by treating* BF_3 *with lithium aluminium hydride. The compounds X and Y are represented by the formulae.* **[NCERT Exemplar]**

(*a*) $B_2H_6, B_3N_3H_6$ (*b*) $B_2O_3, B_3N_3H_6$
(*c*) $BF_3, B_3N_3H_6$ (*d*) $B_3N_3H_6, B_2H_6$

Interpret (*a*) $B_3N_3H_6$ or borazene is called inorganic benzene. It is obtained by heating diborane with NH_3.

$$3B_2H_6 + 6NH_3 \longrightarrow \underset{\text{inorganic benzene}}{2B_3N_3H_6} + 12H_2$$

Diborane is also prepared by treating BF_3 with $LiAlH_4$

$$4BF_3 + 3LiAlH_4 \longrightarrow 2B_2H_6 + 3LiF + 3AlF_3$$

Hot Spot 2

ALUMINIUM Chloride

It is also an important topic of this chapter for JEE Main examination. Question based on preparation and properties are generally asked. The nature of question is easy to moderate.

Methods of Preparation

$AlCl_3$ is prepared by dissolving Al in excess of HCl. It is deposited as the crystals of $Al_2Cl_6 \cdot 12H_2O$. This hydrate on heating decomposes to give alumina as

$$Al_2Cl_6 \cdot 12H_2O \xrightarrow{\Delta} Al_2O_3 + 6HCl + 9H_2O$$

So, for preparing anhydrous $AlCl_3$, Al is heated in a steam of dry chlorine or hydrogen chloride gas as

$$2Al + 3Cl_2 \longrightarrow 2AlCl_3$$

This reaction is extremely exothermic.

$$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2$$

Anhydrous $AlCl_3$ can also be formed when

1. A mixture of Al_2O_3 and C is strongly heated in dry chlorine gas as

$$Al_2O_3 + 3Cl_2 + 3C \longrightarrow 2AlCl_3 + 3CO$$

2. A mixture of CO and Cl_2 is passed over heated Al_2O_3 as

$$Al_2O_3 + 3CO + 3Cl_2 \longrightarrow 2AlCl_3 + 3CO_2$$

AlI_3, when reacts with CCl_4, also gives $AlCl_3$.

$$4AlI_3 + 3CCl_4 \longrightarrow 4AlCl_3 + 3CI_4$$

Properties

1. $AlCl_3$ is white in its pure form and sublimes at 183°C. It is extremely hygroscopic and fumes strongly in moist air due to the formation of HCl as

$$2AlCl_3 + 6H_2O \longrightarrow 2Al(OH)_3 + 6HCl$$

2. It exists as a monomer above 800°C with sp^2-hybridisation, trigonal planar structure and three pure covalent bond. However, below 400°C, it exists as a dimer with sp^3 hybridisation (three pure covalent and one co ordinate bond). In solid state also, $AlCl_3$ exists as a dimer and is non-conducting.
3. When dissolved in water, it changes into hydrated aluminium chloride which is ionic in nature.

$$Al_2Cl_6 + 12H_2O \longrightarrow 2AlCl_3 \cdot 6H_2O$$

4. Aluminium chloride forms addition compounds with the molecules capable of donating lone pair of electrons, *e.g.*, like NH_3, phosphine, $COCl_2$ etc.

$$Al_2Cl_6 + 12NH_3 \longrightarrow 2(AlCl_3 \cdot 6NH_3)$$

5. When sodium hydroxide is added to the solution of aluminium chloride drop by drop, a white gelatinous precipitate appears which dissolves in excess of sodium hydroxide forming sodium meta-aluminate.

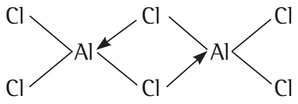
$$AlCl_3 + 3NaOH \longrightarrow Al(OH)_3 + 3NaCl$$
$$Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$$

Uses

$AlCl_3$ is a strong Lewis acid and readily forms adducts with Lewis base. It is, therefore, use as a catalyst in 'organic chemistry' and also used in the manufacture of dyes, drugs and pharmaceuticals.

Structure

The structure of Al_2Cl_6 can be represented as



The dimeric formula exists in non-polar solvents such as benzene but due to higher heat of hydration, it changes into $[Al(H_2O)_6]^{3+}$ and $3Cl^-$ ions in aqueous solution.

Sample Problem 7 *Which of the following is obtained when aluminium oxide and carbon is strongly heated in dry chlorine gas?*

(a) *Aluminium chloride*
(b) *Hydrated aluminium chloride*
(c) *Anhydrous aluminium chloride*
(d) *None of the above*

Interpret (c) When aluminium oxide and carbon are heated in the presence of dry chlorine gas they result in the formation of anhydrous aluminium chloride.

$$Al_2O_3 + 3Cl_2 + 3C \longrightarrow \underset{\text{anhydrous}}{2AlCl_3} + 3CO$$

Alums

The name *alum*, is given to all double salts with the formula $(M')_2SO_4 \cdot (M'')_2(SO_4)_3 \cdot 24H_2O$.

where, M' = univalent basic radicals like Na^+, K^+, NH_4^+, Ag^+ etc.

M''' = trivalent metal like Al^{3+}, Cr^{3+}, Fe^{3+}, Co^{3+} etc.

Some common examples include $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$, *potash alum* or *common alum*; $Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$, *sodium alum*, $(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$, *ammonium alum*, $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$, *chrome alum*.

Methods of Preparation

Common alum is potash alum, $KAl(SO_4)_2 \cdot 12H_2O$ and is prepared

(i) **From alunite or alum stone** Alunite is boiled with dilute sulphuric acid and filtered. The filtrate is mixed with a requisite amount of potassium sulphate and crystallized.

$$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 4Al(OH)_3 + 6H_2SO_4 \longrightarrow K_2SO_4 + 3Al_2(SO_4)_3 + 12H_2O$$

$$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \longrightarrow 2[KAl(SO_4)_2 \cdot 12H_2O]$$

(ii) **From bauxite** Bauxite is dissolved in sulphuric acid, treated with calculated amount of potassium sulphate and crystallized.

(iii) **From pyrites shale $Al_2O_2 \cdot xSiO_2 + FeS_2$.** It is also known as alum shale which is aluminium silicate mixed with iron sulphide. It is roasted in excess of air when ferrous sulphide gives ferrous sulphate and sulphuric acid and the latter then reacts with alumina to form aluminium sulphate.

$$2FeS_2 + 2H_2O + 7O_2 \longrightarrow 2FeSO_4 + 2H_2SO_4$$

$$Al_2O_3 \cdot xSiO_2 + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + xSiO_2 + 3H_2O$$

Ferrous sulphate is removed by fractional crystallization and potassium sulphate added to the mother liquor when potash alum crystallizes out. Being an ionic compound it does not contain discrete molecules and is usually represented as $KAl(SO_4)_2 \cdot 12H_2O$.

Properties

All the alums are **isomorphous,** form mixed crystals in all proportions. Each alum has different melting point. These are usually much more soluble in hot water than in cold water. On heating, alum loses its water of crystallisation and swells up leaving behind a porous mass, called the **burnt alum.**

Uses

It is used in purification of water, water proofing of textiles and in dyeing and paper industry. It is also employed as a styptic to arrest bleeding.

Pseudoalums

These are the double sulphate of divalent ions and trivalent ions. These have general formula,

$$MSO_4 \cdot (M'')_2(SO_4)_3 \cdot 24H_2O$$

Here, M = bivalent metal

M'' = trivalent metal.

Pseudoalums are not isomorphous with alums.

Some examples are

$$MnSO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$$
$$FeSO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$$

Check Point 2

1. Why BF_3 is collected over Hg?
2. Anhydrous aluminium chloride fumes is moist air. Give reason.
3. Why is boric acid slippery to touch?
4. Why borazine gives addition reaction but benzene does not?
5. Anhydrous aluminium chloride is covalent while hydrated aluminium chloride is not. Explain, why?
6. Why does boron trifluoride behave as a Lewis acid?
7. Alum is used in setting muddy water. Give reason.

Elements of Group 14 (or IVA) and their Compounds

11.6 Elements of Group 14 (or IVA)

The group 14 (IVA) contains 5 elements namely **carbon** (C), **silicon** (Si), **germanium** (Ge), **tin** (Sn) and **lead** (Pb). Carbon is an essential constituent of all organic matter while silicon is an important constituent of inorganic matter.

Occurrence

Carbon is the 17th most abundant element and is found both in native and combined state.

Silicon occurs most abundantly, next only to oxygen, up to 26% in earth crust as silica and silicates. Ge occurs rather sparsely. Sn occurs chiefly as SnO_2 while lead occurs mainly as PbS.

Electronic Configuration

General electronic configuration of elements of this group is ns^2p^2 (where, n = 2, 3, 4, ...)

Table 11.4 **Electronic Configuration of Elements of Group 14**

Element	Electronic configuration
$_6C$	[He] $2s^2 2p^2$
$_{14}Si$	[Ne] $3s^2 3p^2$
$_{32}Ge$	[Ar] $3d^{10}, 4s^2 4p^2$
$_{50}Sn$	[Kr] $4d^{10}, 5s^2 5p^2$
$_{82}Pb$	[Xe] $4f^{14}, 5d^{10}, 6s^2 6p^2$

Although they have same number of valence electron, yet these are known to exhibit a variation in properties. This is because, they differ in configuration of penultimate shell.

Trends in Physical Properties of Elements of Group 14

(a) Molar Volumes and Atomic Radius

Molar volumes and atomic radius increase down the group. Their atomic radii are smaller than the corresponding elements of group 13 due to increase in effective nuclear charge.

(b) Melting and Boiling Points

The melting and boiling points of first member *i.e.,* carbon are exceedingly high. The values decrease as we move from carbon to lead. The melting point of Sn and Pb are relatively low because the *M—M* bonds are weaker. They do not use all the four outer electrons for metallic bonding.

(c) Ionisation Energy

Ionisation energy of C is very high and decreases sharply as we move from carbon to silicon. It is because there is an appreciable increase in the size of Si atom. After Si the decrease is regular but not so much and not very sharp from Si to Sn due to appearance of *d*-electrons in them. However, a marginal increase is seen between Sn and Pb. This is because of the further appearance of *f*-electrons in Pb due to which, there is a marginal increase in atomic radius which increases the ionisation energy marginally.

The *d*-electrons and *f*-electrons show very less or almost no screening due to very less electrons density in them. This constant or almost constant screening effect is responsible for such a gradation seen in ionisation energy.

(d) Metallic or Electropositive Character

First two members of the group are non-metals (C and Si); the middle one is semi-metal (Ge) while Sn and Pb are metals. The metallic or electropositive character increases down the group.

$$\underbrace{\text{C}\qquad\text{Si}}_{\text{non-metals}}\qquad\underset{\text{metalloid}}{\text{Ge}}\qquad\underbrace{\text{Sn}\qquad\text{Pb}}_{\text{metals}}$$

The change from non-metallic to metallic character is due to less effective nuclear charge and increased number of available orbitals with increase in the size of the atom.

(e) Electronegativity

C is the most electronegative element of the group. While on moving down the group electronegativity decreases upto Si and then remains constant. Such a different trend in electronegativity is due to the fact that *d*-orbitals are filled up in the case of Ge and Sn while in the case of Pb *f*-orbitals are filled up.

(f) Covalency

Carbon, due to the absence of *d*-orbitals, cannot expand its valence shell and thus, its maximum covalency is four. Other members, however, have vacant *d*-orbital and thus, can expand their covalency beyond four. They form pentacoordinated and hexacoordinated complex. *e.g.,* SiF_4 can combine with $2F^-$ ions.

$$SiF_4 + 2F^- \longrightarrow [SiF_6]^{2-}$$

but $[CF_6]^{2-}$ does not exist.

The physical properties, described above, are summarised in the following table

Table 11.5 **Physical Properties of Elements of Group 14**

Property	Carbon	Silicon	Germanium	Tin	Lead
Atomic number	6	14	32	50	82
Molar mass ($g\ mol^{-1}$)	12.00	28.086	72.59	118.89	207.19
Density ($g\ cm^{-3}$)	3.52	2.49	5.35	7.30	11.34
Atomic radius (Å)	0.77	1.17	1.22	1.41	1.44
Molar volume ($cm^3\ mol^{-1}$)	3.4	11.4	13.6	16.3	18.27
Melting point (°C)	4100	1410	937.5	231.8	327.4
Boiling point (°C)	4833	2680	2830	2270	1725
Electronegativity	2.5	1.8	1.8	1.8	1.8
Ionisation enthalpy ($kJ\ mol^{-1}$)					
$\Delta_i H_1$	1086	786	761	708	715
$\Delta_i H_2$	2352	1577	1537	1411	1450
$\Delta_i H_3$	4620	3228	3300	2942	3081
$\Delta_i H_4$	6220	4354	4409	3929	4082
Oxidation states (stable)	+4	+4	+2, +4	+2, +4	+2, +4

(g) Catenation

The ability of like atoms to link together, through covalent bond is called catenation. Carbon exhibits the remarkable property of catenation. The tendency of catenation depends upon the strength of element-element bond which is described in terms of bond energy. The bond energy values for different elements of this group are given as :

Table 11.6 **Bond Energies of Elements of Carbon Family**

Bond	Bond energy (kJ/mol)
C—C	354
Si—Si	222
Ge—Ge	167
Sn—Sn	155

The table shows that bond energy is maximum in case of carbon and minimum in case of Sn. Thus, we can say the tendency of catenation decreases down the group as

$$C > Si > Ge > Sn > Pb.$$

The reason for greater tendency of carbon for catenation than other elements may further be explained by the fact that C—C bonds energy is approximately of the same value as the energies of bonds between carbon and other elements. On the other hand Si—Si bond is weaker than the bonds between silicon and other elements.

C—C	83 kcal/mol	Si—Si	54 kcal/mol
C—O	86 kcal/mol	Si—O	88 kcal/mol
C—Cl	81 kcal/mol	Si—C	186 kcal/mol

Thus, carbon forms a number of compounds in which large number of carbon atoms are linked together in the form of straight chains, branched chains or closed rings. The property of catenation is responsible for a very large number of compounds of carbon.

Although Sn and Pb have hardly any tendency for catenation.

(h) Allotropy

It is the tendency of an element to exist in different forms. Almost all members of this group show allotropy, *e.g.,* carbon exists in crystalline forms *e.g.,* diamond and graphite and microcrystalline forms *e.g.,* coal, coke, charcoal, carbon black etc. Microcrystalline forms were previously regarded as amorphous. [Amorphous = Without definite structure, Gr. Morpha = form.] All the microcrystalline forms have finely divided graphite structure.

Si also exists in two allotropic forms, *i.e.,* grey crystalline form and brown amorphous powder. These forms differ in particle size and content of impurities. The amorphous variety fuses on strong heating and solidifies on cooling to give the crystalline form.

Germanium exists in two crystalline forms, while tin exists in three solid forms namely grey tin, white tin and rhombic tin. Grey tin is stable below 18°C, white tin above 18°C and rhombic tin above 161°C. Out of these, white tin is the most common form of tin as it shows the stability at room temperature.

$$\text{Grey} \overset{18^\circ\text{C}}{\rightleftharpoons} \text{White} \overset{161^\circ\text{C}}{\rightleftharpoons} \text{Rhombic}$$

The densities of the three forms are 5.74, 7.32 and 6.55 g/cc respectively. White tin is not only the heaviest but also the most stable form. The conversion of white tin into grey tin takes place very slowly at 18°C (transition temperature). However, if the temperature is low as −50°C and a small amount of grey tin is also present, the conversion becomes very rapid. This conversion is known as **tin pest or tin disease.**

Hot Spot 3

OXIDATION STATE

and Nature of Compounds

Stability of oxidation state and finding oxidising and reducing agent on this basis is also a Hot Topic of this chapter for JEE Main examination. The nature of question is direct and level is easy.

All the elements in common, have the oxidation state of +4. C shows only +4 oxidation state but other elements also show +2 oxidation state. **The stability of +2 oxidation state increases down the group due to inert pair effect.** Thus, Pb^{2+} exists as stable ion and is much more stable and common than Pb^{4+} ions. Similarly owing to their small sizes, the M^{4+} ions of Pb have more covalent character than the electrovalent in their compounds. (The covalent nature in the compounds of Pb^{4+} ions can be explained on the basis of high polarisation produced by such ions).

Thus, the stability of ions of this group follow the following order

$$Ge^{2+} < Sn^{2+} < Pb^{2+}$$

$$Ge^{4+} > Sn^{4+} > Pb^{4+}$$

The compounds of Ge^{2+} are unstable while compounds of Ge^{4+} are stable. Thus, the compounds of Ge^{2+} get oxidised into Ge^{4+} easily and act as a reducing agent.

$$\underset{\substack{\text{less stable}\\\text{(reducing agent)}}}{Ge^{2+}} \xrightarrow{-2e} \underset{\text{more stable}}{Ge^{4+}}$$

The compounds of Sn^{2+} are less stable than Sn^{4+}. Thus, Sn^{2+} compounds also act as reducing agents. In the case of lead, Pb^{2+} compounds are more stable than Pb^{4+} compounds. The Pb^{4+} compounds, thus, act as oxidising agents.

$$\underset{\substack{\text{less stable}\\\text{(oxidising agent)}}}{Pb^{4+}} + 2e \longrightarrow \underset{\text{more stable}}{Pb^{2+}}$$

Sample Problem 8 *The most commonly used reducing agent is* [**NCERT** Exemplar]

(*a*) $AlCl_3$ (*b*) $PbCl_2$ (*c*) $SnCl_4$ (*d*) $SnCl_2$

Interpret (*d*) Sn^{4+} is more stable than Sn^{2+} thus, Sn^{2+} have a great tendency to get converted into Sn^{4+} by losing two electrons hence, it is used as reducing agent.

Trends in Chemical Properties of Elements of Group 14

(a) Reactivity

The elements of this group are relatively less reactive but reactivity increase down the group. Lead often appears more unreactive than expected. This is partly due to surface coating of the oxide and partly due to the high overpotential for the reduction of H^+ to H_2 at a lead surface.

(b) Reaction with Water

C, Si and Ge do not react with water while Sn reacts with steam and forms SnO_2 and H_2.

$$Sn(s) + 2H_2O(g) \xrightarrow{\Delta} SnO_2(g) + 2H_2(g)$$

Lead also remains unaffected due to the formation of a protective film of lead oxide over its surface.

(c) Hydrides

All the elements of this group form covalent hydrides. The number of stable hydrides and *the ease of their formation decreases down the group. Owing to which their tendency to act as reducing agent increases down the group.* Hydrides of different elements of the groups are discussed one by one.

Carbon forms a number of hydrides which are known as **hydrocarbons.** We study them completely in 'organic chemistry'.

Hydrides of silicon are similar to those of carbon but are less stable and much less in number. These are called **silanes** and have the general formula Si_nH_{2n+2}. Silanes up to $n = 8$ are known. The first two members are colourless gases while 3rd and subsequent members are liquids. SiH_4 is stable at room temperature and the thermal stability of silanes decreases with increasing chain length.

Some important facts related to silanes are as follows

(i) Silanes are produced by the action of acids on metallic silicides as

$$Mg_2Si + 4HCl \longrightarrow 2MgCl_2 + SiH_4$$

Actually in this reaction a mixture of silanes is obtained with the composition SiH_4(40%), Si_2H_6 (30%), Si_3H_8(12%), Si_4H_{10}(10%) and others 8%.

(ii) Silanes are much less stable than corresponding alkanes and their structure is analogous to that of alkanes. Infact they are spontaneously inflammable and explosive in air. The lower silanes decompose more easily than the higher ones, *e.g.,* SiH_4 decomposes spontaneously when comes in contact with air as

$$SiH_4 + 2O_2 \longrightarrow SiO_2 + 2H_2O$$

(iii) They decompose slowly when brought in contact with water as

$$SiH_4 + 3H_2O \longrightarrow H_2SiO_3 + 4H_2$$

(iv) These are soluble in strong alkali solutions in the presence of air and evolve hydrogen as

$$SiH_4 + 2NaOH + \frac{1}{2}O_2 \longrightarrow Na_2SiO_3 + 3H_2\uparrow$$

(v) Silanes, being oxidised easily, have strong reducing properties. They reduce permangnate to Mn (II), Hg (II) to Hg (I) or even Hg (0); Fe (III) to Fe (II) and copper (II) to copper hydride.

(vi) With Cl_2 and Br_2, they react with violent explosion even at ordinary temperatures. But treatment of SiH_4 with HCl or HBr at 100°C in the presence of $AlCl_3$ as a catalyst results in substitution of hydrogen atoms by chlorine or bromine as

$$SiH_4 + HCl \xrightarrow{AlCl_3} \underset{\text{halo (chloro) silane}}{SiH_3Cl} + H_2\uparrow$$

The hydrides of Ge are called **germanes** and have the general formula $[Ge_nH_{2n+2}]$. Germanes upto $n = 5$ are known. Three hydrides are more commonly known *i.e.,* monogermane (GeH_4), digermane (Ge_2H_6) and trigermane (Ge_3H_8).

Some points related to germanes are as follows

(i) These are prepared in the same way as silanes and the mixture contains mono, di and trigermanes. From the mixture individual germanes can be separated by fractional distillation.

(ii) First two germanes are colourless gases while higher members are liquids. These are less volatile and less reactive than corresponding silanes, *e.g.,* in comparison to SiH_4, the GeH_4 does not ignite when brought in contact with air. Also unlike silanes, they are not attacked by water.

(iii) Monogermane unlike monosilane is not attacked by 30% NaOH or KOH. Digermane, however, evolves hydrogen under these conditions. At higher temperatures these decompose to give germanium and hydrogen.

Two hydrides of tin namely **monostannane** (SnH_4) and **distannane** (Sn_2H_6) are known.

Important points related to stannanes are as follows

(i) SnH_4 is obtained as a gas by reducing tin (IV) chloride with ethereal $Li[AlH_4]$. It is also formed by the action of atomic hydrogen on metallic Sn or by the action of $SnCl_2$ with $NaBH_4$.

(ii) The melting point and boiling point of SnH_4 are −146°C and −52°C respectively. It is not so stable and decomposes slowly even at room temperature into Sn and hydrogen. Decomposition is easier above 145°C. It is resistant to dilute aqueous acids and alkalies.

There is some doubt about the existence of lead hydride although it is claimed that it is formed in minute quantities as a gas when a lead magnesium alloy is dissolved in dilute acids.

(d) **Halides**

The elements of group 14 form MX_4 and MX_2 type halides (where, X = F, Cl, Br, I).

All the tetrahalides (*i.e.,* MX_4) have covalent nature and are sp^3 hybridised. The thermal stability of halides of different elements with a common halogen decreases with increasing atomic number. The thermal stability of tetrahalides of the same element decreases with increase in molecular mass of the tetrahalide.

$$CX_4 > SiX_4 > GeX_4 > SnX_4 > PbX_4$$
$$CF_4 > CCl_4 > CBr_4 > CI_4$$

Other facts related to tetrahalides of element of this group are as follows

(i) The tetrafluorides of C, Si and Ge are gases while the tetrafluorides of Sn and Pb are solids. The last two are more ionic in character than the first three.

(ii) All the tetrachlorides of group 14th elements are liquids with $PbCl_4$ having lesser tendency to become liquid. CCl_4 is used for preparing freons such as $CFCl_3$, CF_2Cl_2 which are used in refrigeration.

(iii) CBr_4 is a solid, while tetrabromides of Si, Ge and Sn are liquids.

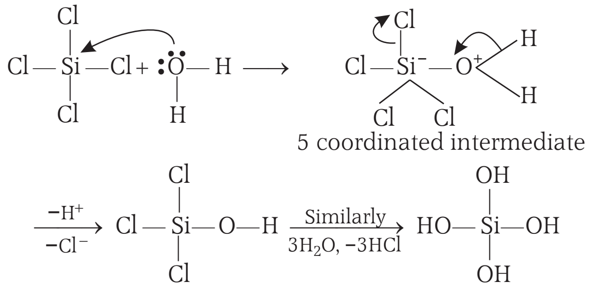
(iv) The tetraiodides of first four elements are solids. However $PbBr_4$ and PbI_4 are unknown.

[Non-existence of $PbBr_4$ and PbI_4 can be explained on the basis of strong oxidising nature of Pb^{4+}. The ions Br^- and I^- are reducing agents, *i.e.,* in the presence of these ions, Pb^{4+} ions are reduced to Pb^{2+} ions.

$$Pb^{4+} + 2Br^- \longrightarrow Pb^{2+} + Br_2$$
$$Pb^{4+} + 2I^- \longrightarrow Pb^{2+} + I_2]$$

(v) *The tetrahalides of* C *are not hydrolysed by water under normal conditions* (due to the absence of *d*-orbitals) while the tetrahalides of other elements are readily hydrolysed due to the availability of empty *d*-orbitals in them.

The mechanism of hydrolysis of $SiCl_4$ is as



Infact hydrolysis of SiF_4 ultimately yields H_2SiF_6 (fluorosilicic acid).

$$3SiF_4 + 2H_2O \longrightarrow SiO_2 + \underset{\text{fluorosilicic acid}}{2H_2SiF_6}$$

Fluorosilicic acid is a strong acid and exists largely in ionised state as

$$H_2SiF_6 + 2H_2O \longrightarrow 2H_3O^+ + [SiF_6]^{2-}$$

(GeF_4 also undergoes hydrolysis in the same manner).

(vi) The tetrahalides of carbon do not form complexes because of the unavailability of empty *d*-orbitals while tetrahalides of other elements form the complexes like $[SiF_6]^{2-}$, $[GeF_6]^{2-}$, $[SnCl_6]^{2-}$. These ions involve sp^3d^2 hybridisation with octahedral structure.

$SnCl_4$ on hydrolysis produces complex acidic compound $H_2[SnCl_3(OH)_3]$ as

$$SnCl_4 + 3H_2O \longrightarrow H_2[SnCl_3(OH)_3] + HCl$$

Carbon does not form dihalides while silicon along with Ge, Sn *and* Pb *form dihalides of* MX_2 *type. These dihalides are more ionic than covalent in character*. These dihalides can be prepared as

$$SiCl_4 + Si \xrightarrow[1100°C]{\text{above}} 2SiCl_2$$

$$GeX_4 + Ge \xrightarrow{\Delta} \underset{\substack{\text{(strong}\\ \text{reducing agent)}}}{2GeX_2}$$

$$SnCl_4 + Sn \xrightarrow{\Delta} \underset{\text{anhydrous}}{2SnCl_2}$$

($SnCl_2$ on reaction with weak alkali followed by dehydration in the absence of air, gives SnO).

$$Pb(NO_3)_2 + 2HF \longrightarrow \underset{\text{ppt.}}{PbF_2\downarrow} + 2HNO_3$$

The stability of dihalides increases on moving down the group. Thus, $PbCl_2 > PbCl_4$ (stability)

Lead dihalides are sparingly soluble in cold water that's why these are obtained differently from other dihalides.

Some trihalides of C, Si and Ge are also known, *e.g.,* $CHCl_3$, $SiHCl_3$, $GeHCl_3$. Lead and tin do not form such compounds.

Sample **Problem 9** *Consider the following statements*

I. *Lead (II) chloride reacts with* Cl_2 *to give* $PbCl_4$
II. *Lead (IV) chloride is highly unstable towards heat*
III. PbI_4 *exists.*

The incorrect statement(s) is/are **[NCERT]**

(a) *II and III only*
(b) *III only*
(c) *I and III only*
(d) *I and II only*

Interpret (c)

(i) Due to inert pair effect, Pb is more stable in +2 state than in +4 oxidation state. Therefore, lead (II) chloride does not react with Cl_2 to give lead (IV) chloride.

(ii) Lead (IV) chloride on heating decomposes to give lead (II) chloride and Cl_2 because lead in +2 oxidation state is more stable than in +4 oxidation state.

$$PbCl_4(l) \longrightarrow PbCl_2(s) + Cl_2(g)$$

(iii) Due to strong oxidising power of Pb^{4+} ion and reducing power of I^- ion, PbI_4 does not exist.

(e) Oxides

14th group elements form two types of oxides, namely, **monoxides** of formula MO, *e.g.,* CO, SiO, GeO, SnO and PbO and **dioxides** of formula MO_2, *e.g.,* CO_2, SiO_2, GeO_2, SnO_2 and PbO_2. The dioxides of Ge and Sn are amphoteric while that of Pb are weakly basic, thus, acidic character of dioxides decreases and basic character increases while moving down the group. *Lead also forms* Pb_3O_4 *which infact is a mixed oxide of* PbO *and* PbO_2 *i.e.,* $2PbO \cdot PbO_2$.

Among monoxide CO is neutral, GeO is acidic, SnO and PbO are amphoteric.

CO_2 is a gas and SiO_2 is a hard solid with a very high melting point. It is due to the fact that smaller atom of C (radius 0.77 Å) does not permit the oxygen to combine with another C-atom while fairly large atom of silica (1.17 Å) permits the sharing of single oxygen atom between two Si atoms as shown below

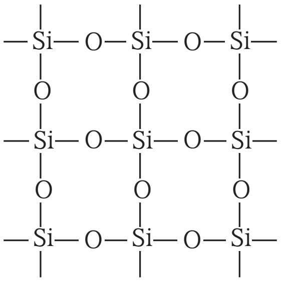


Fig. 11.13 Structure of SiO_2

11.7 Unique Behaviour of Carbon

The size of carbon is smallest among the group but it has high electronegativity and ionisation enthalpy. Moreover, in it, d-orbitals are also not present. Due to these reasons, its properties are quite different from other members of the group.

Some such properties are

(i) The melting and boiling points of carbon are very high as compared to other members of the group.

(ii) It has maximum tendency of catenation.

(iii) It has a high tendency of formation of $p\pi$ - $p\pi$ multiple bonds either with its own atoms (*e.g.,* $C{=}C$, $C{\equiv}C$) or with other atoms such as O, N, S (*e.g.,* $C{=}O, C{\equiv}N, C{=}S$ etc.) while other members do not have this tendency as their atomic orbitals are too large. (Other members have a tendency of $d\pi$ - $p\pi$ bonding.)

(iv) Maximum covalency of carbon is four while other members can expand their covalency upto 6.

(v) Carbon remains unaffected by alkalies while other members reacts with alkali as

$$Si + 2NaOH + \frac{1}{2}O_2 \longrightarrow \underset{\text{sodium silicate}}{Na_2SiO_3} + H_2$$

Similarities with Si

In the following characteristics carbon exhibits resemblence with silicon.

(i) Carbon is the essential constituent of the animal and vegetable kingdom (organic); silicon is the essential constituent of the mineral kingdom (inorganic) entering into the composition of all rocks, mountains, river beds, etc.

(ii) Both of these elements, as seen earlier, possess an electronic configuration ending with ns^2, np^2 grouping and show a tetracovalence.

(iii) They are both typical non-metals and form oxides, hydrides, etc. The higher oxides of both these elements are acidic in nature.

(iv) Carbon and silicon atoms possess a remarkable property of joining with one another in large numbers forming the long chains and rings.

(v) There is a marked similarity between the compounds for carbon and silicon as shown in the table given below

Table 11.7 **Similarity between the Compounds of C and Si**

	Compounds	Carbon	Silicon
(i)	Dioxides	CO_2, acidic formed by burning carbon in air of oxygen.	SiO_2, acidic, formed by burning silicon in air or oxygen
(ii)	Acids	H_2CO_3 (carbonic acid), $(COOH)_2$ (oxalic acid)	H_2SiO_3 (*meta*-silicic acid) $(SiOOH)_2$ (silico-oxalic acid)
(iii)	Hydrides	CH_4 methane C_2H_6 ethane	SiH_4 silico-methane Si_2H_6 Silico-ethane
(iv)	Halides	CCl_4, CI_4	$SiCl_4$, SiI_4
(v)	Other compounds	$CHCl_3$ (chloroform) $CHBr_3, CHI_3$, etc.	$SiHCl_3$ (silico-chloroform) $SiHBr_2, SiHI_3$, etc.

Points of Difference with Si

In spite of the similarity of formulae, the elements and their compounds show important dissimilarities which are as follows.

(i) Carbon dioxide is a gas while silica is a hard solid

(ii) Carbon tetrachloride and chloroform are stable liquids while the corresponding compounds of silicon are not so stable and are easily hydrolysed.

(iii) Similar is the case with the hydrides; those of carbon, *e.g.*, $CH_4C_2H_6$ are very stable while those of silicon, *e.g.*, SiH_4 are easily decomposed by the common reagents, *e.g.*, alkalies, silver nitrate, etc.

(iv) Oxalic acid, $(COOH)_2$ is much more stable than silico-oxalic acid $(SiOOH)_2$.

(v) The maximum covalence of carbon is four while that of silicon is six. Whereas carbon does not melt at all, silicon does melt at high temperature.

(vi) Silicon is a bad conductor of electricity while some varieties of carbon are good conductors.

Allotropes of Carbon

Carbon shows allotropism due to the property of catenation and $p\pi$- $p\pi$ bond formation. It exists in two allotropic forms.

11.8 Crystalline Forms of Carbon

These allotropes have well defined crystal structures. Diamond, graphite and fullerens are crystalline forms of carbon.

(a) Diamond

It is the purest form of carbon and hardest substance known with very high refractive index (2.417) and a very high density (3.15 g/cm^2 at 25°C). It is transparent to X-rays. It is a three dimensional giant molecule of carbon in which C-atoms (sp^3-hybridised) are arranged tetrahedrally by utilising their sp^3 hybrid orbitals. The C—C bond distance is 1.54 Å. Each C-atom seemes to lie at the centre of a regular tetrahedron and is linked to four surrounding C-atoms lying at the corners of the tetrahedron through strong covalent bonds as shown in the figure below.

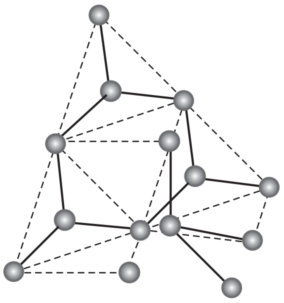


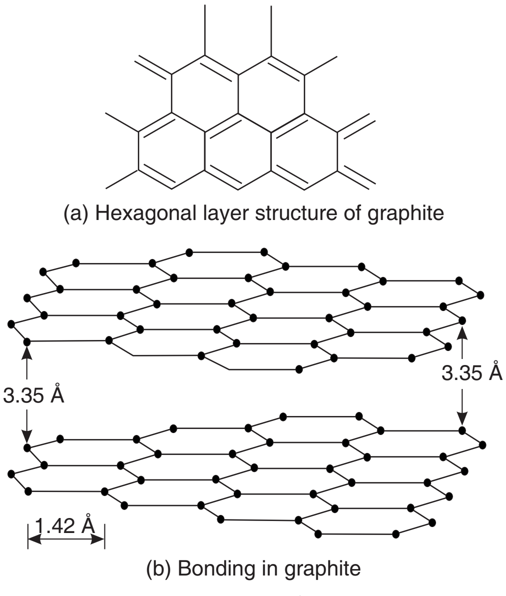
Fig. 11.14 Structure of diamond

Due to high strength of covalent bonds holding numerous C-atoms together, diamond is very hard and have high density. Since breaking of diamond requires breaking of strong covalent bonds, the melting point of C is unusually high (highest in the Periodic Table) being close to 3500°C. It is a bad conductor of electricity but a very good conductor of heat. Lattice vibrations are responsible for the high thermal conductivity of diamond.

Diamond is used as a gem stone on account of reflection and refraction of light. Impure diamonds (black) are used in knives for cutting glass and rock borers.

(b) Graphite

Unlike diamond, graphite, has a two dimensional structure. In this case, only 3 of the 4 valence electrons of C participate in bonding. Thus, hybridisation is sp^2 having 3 covalent bonds with 3 other C-atoms in the same plane. The 4th electron of C does not participate in the bonding, remains free and is responsible for electrical conductivity of graphite. In fact, the structure of graphite is two dimensional, sheet like consisting a number of hexagonal rings fused together as shown in the figure below


(a) Hexagonal layer structure of graphite

(b) Bonding in graphite

Fig. 11.15 Structure of graphite

The sheet or layers are held together by relatively weak van der Waals' forces. The C—C bond distance is 1.42 Å. The distance between two successive layers is 3.36 Å. This structure is less compact than that of diamond and since the bonding between layers involve only the van der Waals' forces (weak forces) hence, these layers can slide over each other. This gives softness, greasiness and lubricating character to graphite.

Graphite is thermodynamically more stable than diamond and its free energy of formation is 1.9 kJ less than diamond.

$$\text{Graphite} \xrightarrow[\text{50000–60000 atm.}]{1600^\circ\text{C}} \text{Diamond}$$

When graphite is heated with vapours of K, Rb, Cs at 300°C, it forms C_8M. Graphite is diamagnetic but C_8M is paramagnetic.

Uses

Graphite is used

(i) for lining and marking electrodes of electric furnaces.
(ii) in making refractory crucibles.
(iii) in making lead pencils.
(iv) as a moderator in nuclear reactor.
(v) as a lubricant in machinery.

(c) Fullerene

These are the recently discovered allotropes of carbon and called fullerene (or Buckminster fullerenes) due to their resemblance (in structure) with geodesic domes, designed and built by the American architect Robert Buckminster Fuller. *The credit of the discovery of fullerenes goes to HW kroto, RF curl and RE smalley.* Fullerenes are large cage like spheroidal molecules with general formula C_{2n} (where $n \geq 30$). Two important member are C_{60} and C_{70}. C_{60} fullerene looks like a soccer ball (so called bucky ball) and contains 20 six membered and 12 five membered rings of carbon atoms. Six membered rings are fused with both six membered as well as five membered rings while five membered rings are attached only with six membered rings. Each carbon atom in the structure, form three σ bonds with other three carbon atoms and the fourth electron remains free. These free electrons delocalise and provide some aromatic character to the molecule. C_{70}, On the other hand, have rugby ball like structure. It consists of 12 five membered and 25 six membered rings.

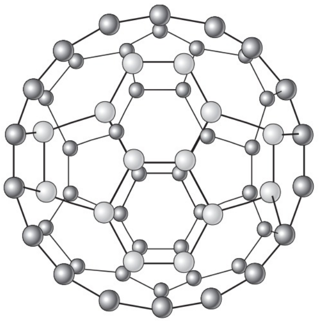


Fig. 11.16 Structure of C_{60}, Buckminster fullerene

Fullerene are prepared from graphite as

$$\text{Graphite} \xrightarrow[\text{He or Ar}]{\text{Electric arc}} \text{vaporised C} \xrightarrow{\text{Condense}} \text{fullerene}$$

soot (C_{60} mainly + C_{70} little)

Fullerenes act as wonderful lubricants and the alkali compounds of C_{60} are used as super conducting substance at the temperature range of 10-40 K.

Microcrystalline Forms

Coke, coal, charcoal, lamp black, gas carbon etc., belong to this category.

(a) Coal

It is formed by the slow carbonisation of vegetable matter buried underneath the earth centuries ago, in limited supply of air under high temperature and pressure. Peat (60% C), lignite (70% C), bituminous (78% C) and anthracite (90% C) are different varities of coal. Out of these, bituminous is the most common and anthracite is purest variety.

(b) Coke

It is a greyish black hard solid and is obtained by destructive distillation of coal.

(c) Charcoal

Depending upon the source from which it is obtained, charcoal can be animal charcoal, wood charcoal, sugar charcoal, and activated charcoal. Wood charcoal adsorbs colouring matter and odoriferous gases, thus used in decolourising sugar solutions and in gas masks.

(d) Lamp Black or Carbon Black

It is the most pure amorphous form, contains about 98-99% carbon. Lamp black is used for making printer ink, black paint, varnishes and carbon papers.

(e) Gas Carbon

It is scraped from the walls of retort used for destructive distillation of coal.

The physical characteristics of the various forms of carbon are summarised below

Table 11.8 **Physical Properties of Allotropes of Carbon**

S. No.		Crystalline forms			Microcrystalline forms			
	Property	Diamond	Graphite	Fullerene	Coal	Charcoal	Animal charcoal	Lamp black
1.	**Colour**	Colourless transparent	Grey	—	Black	Black	Black	Black
2.	**Carbon content**	100%	95–97%	—	60-90%	68-85%	8-10%	98-99%
3.	**Density** (g cm^{-3})	3.51	2.25	—	—	1.4-1.7	—	—
4.	**Hardness**	Hardest substance	Soft marks the paper	Medium	Hard mass	Soft	Soft	Soft
5.	**Electrical Conductivity**	Bad conductor	Good conductor	Good conductor	Bad conductor	Bad conductor	Bad conductor	Bad conductor

Check Point 3

1. Explain, why silicon shows a higher covalency than carbon?
2. Graphite is a conductor of electricity but diamond is not. Explain.
3. The tendency of catenation decreases down the 14 group. Explain, why?
4. Sn(II) is a reducing agent whereas Pb(II) is not. Explain.

11.9 Oxides of Carbon

Carbon forms two oxides. Carbon monoxide and carbon dioxide, which are described ahead.

Carbon Monoxide, CO

It is found in small amounts in volcanic gases, chimney gases, exhaust gases of internal combustion engines and coal gas.

Methods of Preparation

Carbon monoxide is obtained by burning C in limited supply of oxygen. Pure CO can be obtained by heating HCOOH with H_2SO_4 where, H_2SO_4 acts as dehydrating agent.

It is also prepared by

1. By heating carbonates of Ca, Ba or Mg with Zn

$$MgCO_3 + Zn \longrightarrow MgO + ZnO + CO$$

2. By heating potassium ferrocyanide with conc. H_2SO_4.

$$\begin{aligned}
K_4Fe(CN)_6 + 3H_2SO_4 &\longrightarrow 2K_2SO_4 + FeSO_4 + 6HCN \\
6HCN + 12H_2O &\longrightarrow \underset{\text{formic acid}}{6HCOOH} + 6NH_3 \\
6NH_3 + 3H_2SO_4 &\longrightarrow 3(NH_4)_2SO_4 \\
6HCOOH &\xrightarrow{H_2SO_4} 6CO + 6H_2O \\
\hline
K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O &\longrightarrow 2K_2SO_4 + FeSO_4 + 6CO \\
&\qquad + 3(NH_4)_2SO_4
\end{aligned}$$

Manufacture Carbon monoxide is obtained in the form of water gas and producer gas when air (moist) is passed over a bed of white hot coke. The following reactions may occur.

$$\begin{aligned}
2C + O_2 &\longrightarrow 2CO_2 \\
C + O_2 &\longrightarrow CO_2 \\
C + H_2O &\longrightarrow \underbrace{CO + H_2}_{\text{water gas}}
\end{aligned}$$

Carbon dioxide is reduced by passing the mixture over heated charcoal.

$$CO_2 + C \longrightarrow 2CO$$

The CO produced, always consists of N_2, H_2, CO_2, etc.

Properties

1. It is a colourless and odourless gas.
2. It is slightly soluble in water.
3. Its density is nearly equal to the density of air.
4. It is highly poisonous in nature. One part in 100 parts of air causes death in few minutes. *The poisonous nature of* CO *is due to the fact that it combines with haemoglobin (a red colouring matter of blood which is carrier of oxygen) to form carboxy-haemoglobin which is not capable to absorb oxygen and as a result of this, suffocation takes place.*
5. It is an essential constituent of gaseous fuels like water gas, producer gas etc.
6. CO is highly combustible gas and produces CO_2 on combustion, alongwith a large amount of heat.

$$CO + \frac{1}{2}O_2 \longrightarrow CO_2 + \text{heat}$$

7. It is a good reducing agent and reduces metal oxides to metals as

$$Fe_2O_3 + 3CO \xrightarrow{823\ K} 2Fe + 3CO_2$$

8. It gives phosgene when reacts with Cl_2 in sunlight.
9. It forms metal carbonyls with transition metals like Ni, Fe, Co, etc.

Uses

It is used

1. as industrial fuels, as water gas and producer gas
2. as reducing agent in many metallurgical processes.
3. in the purification of Ni by Mond's process.

Structure

The structure of CO can be represented as

$$C \underset{\leftarrow}{=} O$$

Two pairs of electrons are considered to be shared between carbon and oxygen. Oxygen also donates a lone pair to carbon resulting to a co-ordinate bond. The properties of CO can be explained satisfactorily if we consider CO as the resonance hybrid of following three structures.

$$C{=}\overset{..}{\underset{..}{O}} \longleftrightarrow \overset{-}{C}{\equiv}\overset{+}{O}\!: \longleftrightarrow :\!\overset{+}{C}{-}\overset{..}{\underset{..}{O}}\!:^{-}$$

Carbon Dioxide, CO_2

CO_2 is present in atmosphere to the extent of 0.03–0.05 per cent. It comes to the atmosphere from animal breathing, decay of vegetable matter, burning of carbon and carbonous matter, etc. It is also utilised by plants in photosynthesis. Thus, a carbon dioxide cycle is operating in nature and the proportion of CO_2 in the atmosphere remains about the same. It is found in combined state in the form of carbonates.

Methods of Preparation

CO_2 is obtained by burning C in air (excess). In laboratory, it can be prepared by the action of cold dilute HCl on $CaCO_3$ (marble).

Properties

1. CO_2 is colourless gas with a faint pungent smell and slight acidic taste. It dissolves in water forming H_2CO_3 as

   $$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

   H_2CO_3 is a weak acid and dissolves in alkalies to form salts as

   $$H_2CO_3 + 2NaOH \longrightarrow Na_2CO_3 + 2H_2O$$

2. It turns lime water milky which disappears, if CO_2 is passed for a long time due to the formation of soluble calcium bicarbonate.
3. It reacts with liquid NH_3 at 473 K and 220 atm, and gives ammonium carbonate which subsequently decomposes to give urea.
4. **Solid CO_2 is commonly called "dry ice".** It is a soft white snow like compound with specific gravity 1.53 and m.p. −56.6°C at 5.2 atm pressure. It is produced by evaporating liquid CO_2 at 20°C and 70 atm pressure to a pressure less than 5.2 atm.

Uses

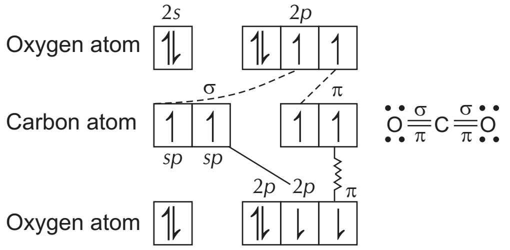
1. It is used as a refrigerant under the commercial name **Drikold.**
2. It is also used as a substitute of ice in cold drinks and in ice cream preparation.
3. In hospitals, it is used for surgical operations of sores.
4. Carbogen (a mixture of 95% O_2 and 5% CO_2) is used for artifical respiration.
5. CO_2 is also used as a fire extinguisher.

Structure

Structure of CO_2 is considered as resonance hybrid of following three structures

$$O{=}C{=}O \longleftrightarrow \overset{-}{O}{-}C{\equiv}\overset{+}{O} \longleftrightarrow \overset{+}{O}{\equiv}C{-}\overset{-}{O}$$

The formation of the molecule can be explained on the basis of hybridisation. Carbon is *sp*-hybridised. The hybrid orbitals form sigma bonds with *p*-orbitals of each oxygen atoms. The unhybridised two *p*-orbitals of carbon atom form two π-bonds with two oxygen atoms.



11.10 Compounds of Silicon

Silicon forms several compounds, some important of these are

1. Silicon Tetrachloride

Its chemical formula is $SiCl_4$.

Methods of Preparation

$SiCl_4$ is prepared by heating Si or SiC with Cl_2.

$$Si(s) + 2Cl_2(g) \xrightarrow{\Delta} SiCl_4(l)$$

$$SiC(s) + 4Cl_2(g) \xrightarrow{\Delta} SiCl_4(l) + CCl_4(l)$$

Properties and Uses

1. It is a volatile liquid with boiling point 330.57 K.
2. On hydrolysis, it gives silicic acid $Si(OH)_4$ which on further heating form silica gel.

$$\underset{}{SiCl_4 + 2H_2O} \xrightarrow{\Delta} \underset{\text{silicic acid}}{Si(OH)_4} \xrightarrow{\Delta} \underset{\text{silica gel}}{SiO_2 \cdot xH_2O}$$

(Silica gel being very porous is used as a catalyst in petroleum industry and as an adsorbent in column chromatography).

3. On reduction, it gets converted into Si. The silicon so obtained is ultrapure and is used for making transistors, computer chips and solar cells.

2. Silica

SiO_2 is commonly called as silica. It occurs in earth's crust as crystalline quartz, tridymite and crystabollite. Amorphous veriety flint is also found.

Methods of Preparation

1. It is obtained by heating silicon in oxygen as

$$Si + O_2 \longrightarrow SiO_2$$

2. Pure SiO_2 is prepared in its amorphous forms as a white powder by reacting $SiCl_4$ or SiF_4 with water as

$$SiCl_4 + 2H_2O \longrightarrow SiO_2 + 4HCl$$
$$SiF_4 + 2H_2O \longrightarrow SiO_2 + 4HF$$

The latter method is normally less used as SiO_2 further reacts with HF to form H_2SiF_6 (fluorosilicic acid).

Properties

1. SiO_2 is insoluble in water and in all acids except HF with which it reacts to form SiF_4 as

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

If we take HF in excess, SiF_4 further reacts with it to form fluorosilicic acid as

$$SiF_4 + 2HF \longrightarrow H_2SiF_6$$

2. SiO_2 *melts in oxyhydrogen flame above* 1875 *K to colourless glass, called quartz glass.* It has remarkably low coefficient of expansion. Red hot quartz when plunged into water does not shatter to pieces. Owing to this property quartz glass is used for the manufacture of chemical apparatus and optical instruments. It specific gravity is 2.65.
3. Three crystalline modification of SiO_2 are **quartz, cristobalite** and **tridymite** of which quartz and cristobalite are important. quartz is used as a **piezoelectric material** (crystal oscillators and transducers). The specific gravity of cristobalite is 2.25 while that of tridymite is 2.32.
4. SiO_2 is acidic and dissolves in hot conc. alkalies to form sodium silicate as

$$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$$

5. It acts as a powerful acid anhydride and combines with bases and many metallic oxides to form silicates as,

$$SiO_2 + Na_2O \longrightarrow Na_2SiO_3$$
$$SiO_2 + CaO \longrightarrow CaSiO_3$$

6. It also reacts with carbonates of many metals at high temperatures forming silicates with liberation of CO_2 as

$$SiO_2 + Na_2CO_3 \longrightarrow Na_2SiO_3 + CO_2$$
$$SiO_2 + CaCO_3 \longrightarrow CaSiO_3 + CO_2$$

7. When heated with carbon in an electric furnace, it is reduced to **carborundum** or **silicon carbide** as

$$SiO_2 + 3C \longrightarrow SiC + 2CO$$

Uses

It is used

1. as an adsorbent in column chromatography.
2. as a catalyst in petroleum industry.
3. on mixing with $(NH_4)_2CoCl_4$, as a humidity detector.
4. as Kieselguhr, in filtration plants and as an inert support or filler.

3. Silicates

Silicates are minerals of silicon and occur in earth's crust in the form of numerous silicate minerals and clays. Mica, asbestos, cement, bricks, tiles, porcelains, glass, pottery etc., are made from silicates. All silicates involve Si—O bonds of two types

(i) Terminal Si—O bonds in which oxygen is bonded to a silicon and not other atom.
(ii) Bridging Si—O—Si bonds in which oxygen is bonded to two silicon atoms.

The basic building unit of all silicates is the tetrahedral SiO_4^{4-} ion. The three dimensional tetrahedral structure is represented by a planar structure for convenience

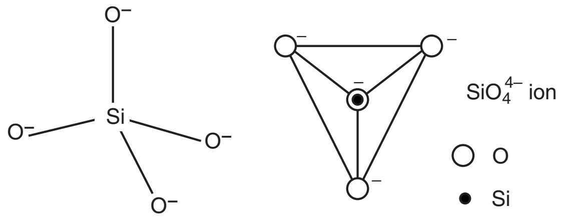


Fig. 11.17 Structure of SiO_4^{4-} ion

Generally the silicates have complex structures but they mainly differ in

1. number of oxygen atoms shared between SiO_4^{4-} tetrahedron.
2. geometric arrangement of tetrahedron.
3. the number, type and arrangement of metallic cations.

On the basis of the way, the SiO_4^{4-} *tetrahedral units are linked together, the silicates minerals are classified into following types*

(a) Orthosilicates

They contain discrete SiO_4^{4-} units in which oxygen atoms are found to associate only with metal ions *e.g.,* **zircon** ($ZrSiO_4$), **wellimite** (Zn_2SiO_4) and **phenacite** (Be_2SiO_4).

(b) Pyrosilicates

Two SiO_4^{4-} tetrahedrons share a corner oxygen atom. They contain $[Si_2O_7]^{6-}$ ions as discrete units. These are also called **island structures.** These silicates are not very common.

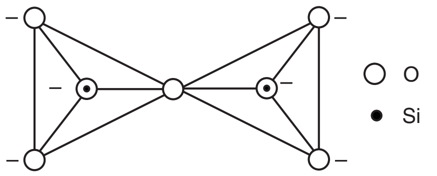


Fig. 11.18 $Si_2O_7^{6-}$ (Anion of pyrosilicate)

e.g., **thorteveitite** ($Sc_2Si_2O_7$) and **hemimorphite** $[Zn_4(OH)_2Si_2O_7]$.

(c) Cyclic Silicates

Two oxygen atoms of each tetrahedron are shared to form a ring with general formula $[SiO_3]_n^{2n-}$. The ring may be

(i) Three membered ring in which discrete units are $[Si_3O_9]^{6-}$ *e.g.,* **wollastonite** $Ca_3Si_3O_9$, **bentonite** $BaTi[Si_3O_9]$.

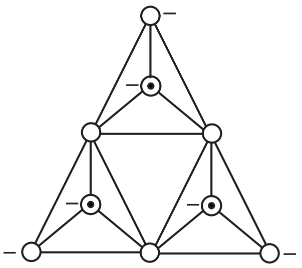


Fig. 11.19 $Si_3O_9^{6-}$ ion (Anion of three membered cyclic silicate)

(ii) Six membered ring in which discrete units are $[Si_6O_{18}]^{12-}$ *e.g.,* **beryl** ($Be_3Al_2Si_6O_8$)

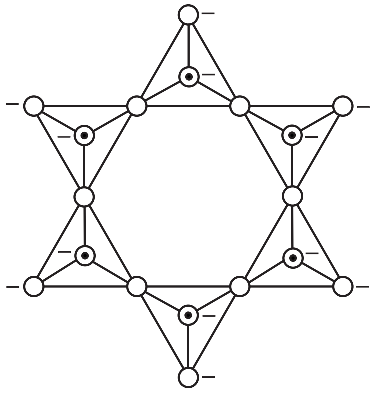


Fig. 11.20 $Si_6O_{18}^{12-}$ ion (Anion of six membered cyclic silicates)

(d) Chain Silicates

Two oxygen atoms per tetrahedron are shared to form an extensively long chain. The primary units is $[SiO_3]^{2-}$ and the simple formula is $[SiO_3]_n^{2n-}$. Two types of chain silicates may be formed.

(i) **Single chain silicates,** in which $[SiO_3]_2^{4-}$ combine to form a chain like polymer, these are also called pyroxenes, *e.g.,* **diopside** $[CaMg(SiO_3)_2]$.

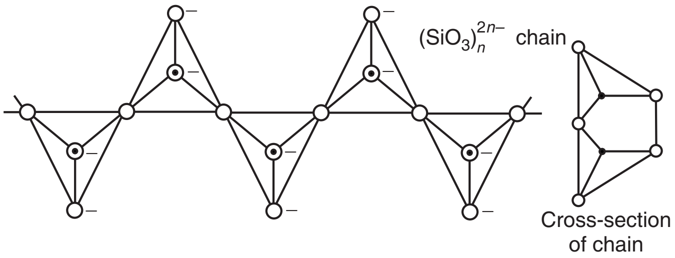


Fig. 11.21 Single chain silicates

(ii) **Double chain silicates,** in which $[Si_4O_{11}]^{6-}$ are primary units. Two simple chains are joined together through the third oxygen atom of SiO_4 tetrahedra. These structures are known as **amphiboles**. Some tetrahedra share three oxygen *e.g.,* **termolite** $Ca_2Mg_5(Si_4O_{11})_2(OH)_2$, **asbestos** $CaMg_3O(Si_4O_{11})$.

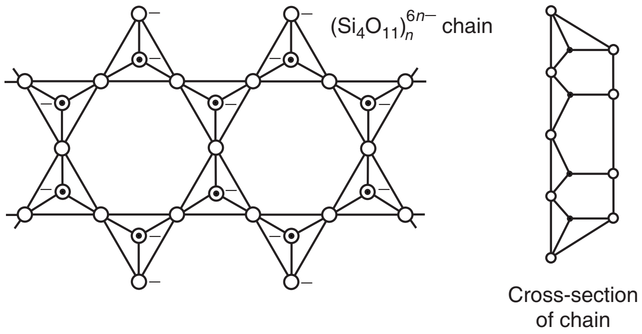


Fig. 11.22 Double chain silicates

(e) Sheet Silicates

Three oxygen atoms per tetrahedron are shared to form an infinite plane sheet, containing $[Si_2O_5]_n^{2n-}$. *e.g.,* **kaolinite** $[Al(OH)_4Si_2O_5]$, talc $[Mg_3(OH)_2(Si_2O_5)_2]$.

Mica minerals too belong to this category and have a variety of compositions.

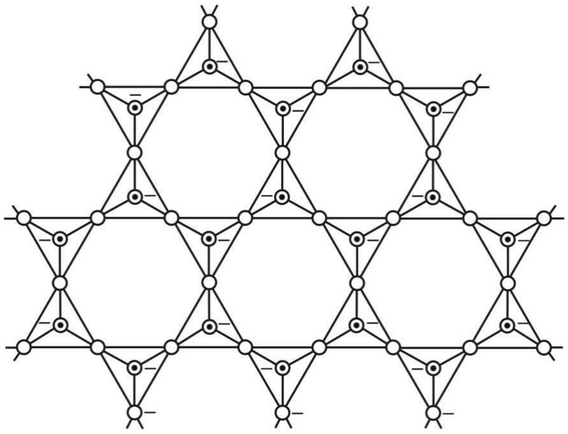


Fig. 11.23 $(Si_2O_5)_n^{2n-}$ sheet

(f) Three Dimensional Silicates

All the four oxygen atoms are shared in each tetrahedron to form an infinite three dimensional structure. Each oxygen atom is bonded to two silicon atoms. Each silicon atom (sp^3 hybridised) is surrounded tetrahedrally by four oxygen atoms and each oxygen atom is linked covalently to two silicon atoms. Various forms of silica occur in three dimensional silicate structure, have general formula $(SiO_3)_n^{2n-}$. These silicates are neutral.

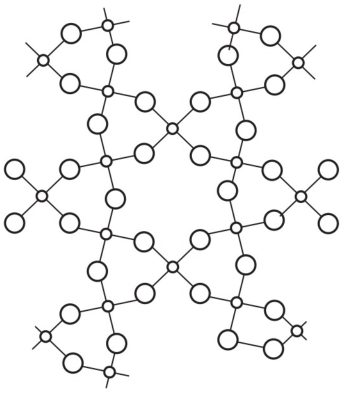
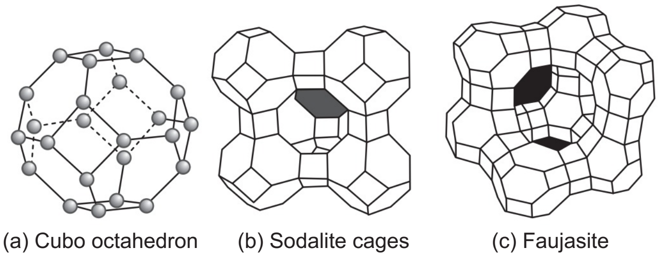


Fig. 11.24 Three dimensional structure of silica

Zeolites

These are microporous aluminosilicate having general formula $M_{x/n}[AlO_2]_x[SiO_2]_y \cdot mH_2O$. Aluminosilicates are obtained by substituting some of the silicon atoms in a three dimensional network silicate by Al^{3+} ions. The negative charge carried by aluminosilicate framework is neutralised by exchangeable cations of valence n, while m water molecules fill the voids. The **cubo** octahedron shown in figure (a) is the building block of zeolites and also called the **sodalite cage.** The sodalite cages are linked to each other through four membered rings to produce two or three dimensional network of inter connected channels and cavities. As a consequence of such packing, the zeolites are highly porous. When sodalite cages are linked through double six-membered rings, Faujasite is obtained.



(a) Cubo octahedron (b) Sodalite cages (c) Faujasite

Fig. 11.25 The three dimensional structure of zeolites

Uses

Zeolites are used as molecular seives and can separate molecules of different sizes. They are also used extensively as catalyst due to their porous structure.

Hot Spot 4

SILICONES

It is again an important topic for JEE Main examination. The questions are generally based on "the preparation of silicones." The level of question is average.

Silicones are organo-silicon polymers containing ...... O–Si–O ...... linkages. These may be linear silicones, cyclic silicones and cross-linked silicones.

Preparation

These are prepared by the hydrolysis of alkyl or aryl derivatives of $SiCl_4$ like $RSiCl_3$, R_2SiCl_2 and R_3SiCl followed by polymerisation of obtained product. Thus, this method consists of the following steps

Step I **To prepare alkyl or aryl derivatives of silicon tetrachloride.** Examples of such derivatives are $RSiCl_3$, R_2SiCl_2 and R_3SiCl where R is an alkyl (*e.g.,* CH_3, C_2H_5 etc.,) or aryl (*e.g.,* C_6H_5) group. These derivatives are prepared by the following methods

1. **Methyl chlorosilanes** [like $(CH_3)SiCl_3$, $(CH_3)_2SiCl_2$ and $(CH_3)_3SiCl$] are prepared by heating methyl chloride, CH_3Cl with Si, catalysed by Cu, at 300°C. This reaction gives a mixture of methyl chlorosilanes.

$$2CH_3Cl + Si \xrightarrow[300°C]{Cu} (CH_3)\underbrace{SiCl_3 + (CH_3)_2SiCl_2 + (CH_3)_3SiCl}_{\substack{\text{Mixture of methyl chlorosilanes}\\ \text{+ other compounds}}}$$

2. Alkyl chlorosilanes can also be obtained by the action of Grignard reagent on $SiCl_4$.

$$RMgCl\text{ (Grignard reagent)} + SiCl_4 \longrightarrow RSiCl_3 + MgCl_2$$
$$2RMgCl + SiCl_4 \longrightarrow R_2SiCl_2 + 2MgCl_2$$
$$3RMgCl + SiCl_4 \longrightarrow R_3SiCl + 3MgCl_2$$

3. Phenyl chlorosilane, $(C_6H_5)SiCl_3$ is obtained by heating C_6H_6 with $HSiCl_3$ at 230-300°C in the presence of a catalyst like BF_3, BCl_3 or $AlCl_3$.

$$C_6H_6 + HSiCl_3 \xrightarrow[\text{Catalyst}]{\Delta} (C_6H_5)SiCl_3 + H_2$$

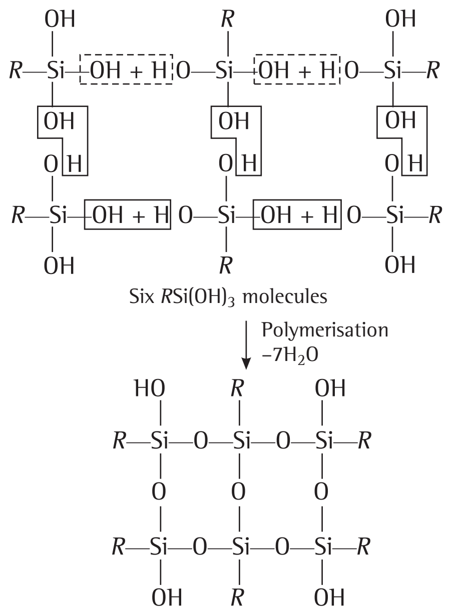
Step II **To prepare alkyl or aryl hydroxy derivatives of silicon tetrachloride** (called silanols or silandiols) These silanols are obtained by the hydrolysis of $RSiCl_3$, R_2SiCl_2 and R_3SiCl respectively, *e.g.*,

$$RSiCl_3 + 3H\cdot OH \xrightarrow{\text{Hydrolysis}} RSi(OH)_3 + 3HCl$$

$$R_2SiCl_2 + 2H\cdot OH \xrightarrow{\text{Hydrolysis}} R_2Si(OH)_2 + 2HCl$$

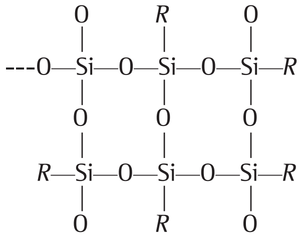
Step III **To allow the alkyl or aryl hydroxy derivatives to undergo polymerisation** The type of silicon obtained depends on the nature of alkyl or aryl hydroxy derivative and the way in which the hydroxy derivative undergoes polymerisation. For example

1. When many molecules of alkyl trihydroxy silane, $RSi(OH)_3$ undergoes polymerisation, a cross-linked two dimensional silicone is obtained as



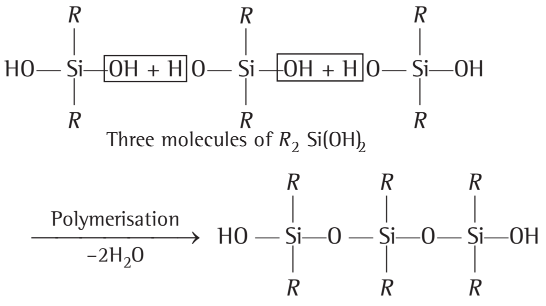
Six $RSi(OH)_3$ molecules

Since, an active OH group is present at each end of the chain, polymerisation continues on both the ends and hence, the length of the chain increases. The increase in the length of the chain produce cross-linked silicone as shown below



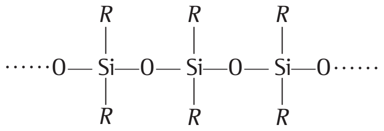
Two dimensional cross-linked silicone

2. When many molecules of dialkyldihydroxysilane, $R_2Si(OH)_2$ undergo polymerisation, a straight chain (linear) or cyclic (ring) silicone is obtained.



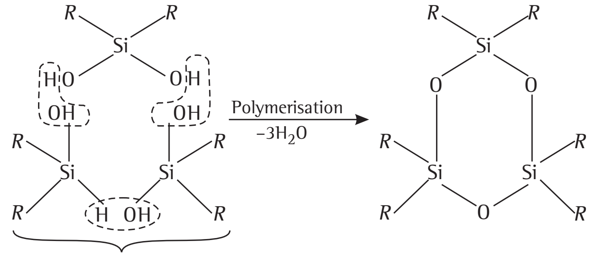
Three molecules of $R_2Si(OH)_2$

Since an active OH group is present at each end of the chain, polymerisation continues and hence, the length of the chain increases and gives rise to the formation of long chain silicon, as shown below



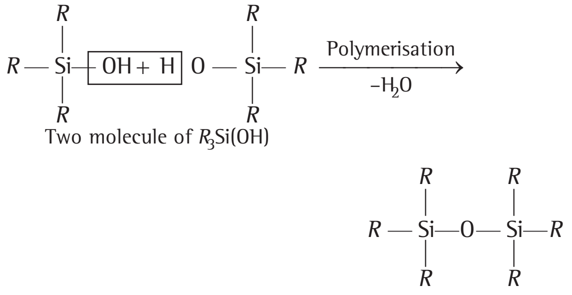
$$\cdots\cdots O-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O\cdots\cdots$$

Linear or straight chain silicone (thermoplastic polymer)



Three molecules of $R_2Si(OH)_2$ **cyclic trimer**

3. When two molecules of trialkyl monohydroxysilane, $R_3Si(OH)$ undergo polymerisation, a straight chain silicon (dimer) is obtained.



Two molecule of $R_3Si(OH)$

straight chain silicon, $R_3Si–O–SiR_3$ (dimer)
(It is a siloxane)

Properties and Uses

Important properties and uses of silicones are as follows

1. They have high **thermal stability** in the absence of air and withstand temperature up to 250–300°C.
2. They remain unaffected by most of the chemical reagents, such as weak acids, alkalies and salt solution. Thus, **silicones are chemically inert.**
3. Many of low molecular weight silicones dissolve in solvents like C_6H_6, ether and CCl_4.
4. They do not become too viscous on cooling and are, therefore, used for low temperature lubrication.
5. They are water repellent, ***i.e.,*** they are not wetted by water and are, therefore, used in making waterproof cloth and paper by exposing cloth or paper to the silicone vapours.
6. **All silicones have good insulating properties and can with stand high temperature without charring.** It is due to these properties that silicones are used as insulating materials for electric motors and other electric appliances.
7. They are non-toxic.

Sample **Problem 10** *Silicon has a strong tendency to form polymers like silicones. The chain length of silicone polymer can be controlled by adding* **[NCERT Exemplar]**

(*a*) $MeSiCl_3$
(*b*) Me_2SiCl_2
(*c*) Me_3SiCl
(*d*) Me_4Si

Interpret (*c*) The product obtained by the hydrolysis of Me_3SiCl contains only one —OH group which when subjected to polymerisation makes the polymer incapable for further polymerisation, thus, controls the chain length.

Check Point 4

1. CO_2 is a gas while SiO_2 is a solid. Explain.
2. Why are zeolites used as catalyst?
3. Why carbon monoxide is a poisonous gas?
4. Solid CO_2 is also called dry ice, why?
5. Silicon are used as insulating materials. Give reason.

WORKED **OUT**

Examples

Example 1 *In the following reaction sequence,*

$$\text{Metal }(A) + N_2 \xrightarrow{\Delta} (B) \xrightarrow{-H_2O} (C) + (D)$$

white ppt (C) is formed and gas (D) is evolved. White ppt (C) dissolves in NaOH *solution, while gas (D) gives white fumes in* HCl. *Metal A is*

(a) B
(b) Al
(c) Ga
(d) C

Solution (b) $\underset{(A)}{2Al} + N_2 \longrightarrow \underset{(B)}{2AlN}$

$$AlN + 3H_2O \longrightarrow \underset{(C)}{Al(OH)_3} + \underset{(D)}{NH_3}$$

Example 2 *A certain salt (X) gives the following tests :*

(i) *Its aqueous solution is alkaline to litmus.*
(ii) *On strong heating, it swells to give a glassy bead.*
(iii) *When concentrated sulphuric acid is added to a hot concentrated solution of (X), white crystal of Z separate out. The salt (Z) is* **[NCERT]**

(a) H_3BO_3
(b) $Na_2B_4O_7$
(c) $NaBO_2$
(d) B_2O_3

Solution (a) (X) is borax, $Na_2B_4O_7 \cdot 10H_2O$ as its aqueous solution is weakly alkaline, it gives a glassy bead on strong heating. The reactions are as follows :

(i) $Na_2B_4O_7 + 7H_2O \rightleftharpoons \underset{\text{strong}}{2NaOH} + \underset{\text{weak}}{4H_3BO_3}$

Due to the presence of a strong base (NaOH), the aqueous solution is alkaline to litmus.

(ii) $Na_2B_4O_7 \cdot 10H_2O \xrightarrow[\text{swells}]{\Delta} Na_2B_4O_7 + 10H_2O$

$$\longrightarrow 2NaBO_2 + \underset{\text{glassy bead}}{B_2O_3}$$

(iii) $Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + \underset{Z}{4H_3BO_3}$

Example 3 *Compound X on reduction with* $LiAlH_4$ *gives a hydride (Y) containing 21.72% hydrogen along with other products. The compound (Y) reacts with air explosively resulting in boron trioxide. Compound X and Y are respectively.*

(a) $BCl_3 \cdot B_2H_6$
(b) $B_2H_6 \cdot BCl_3$
(c) $BF_3 \cdot Al_2O_6$
(d) $B_2H_6 \cdot BF_3$

Solution (a) $\underset{(X)}{4BCl_3} + 3LiAlH_4 \longrightarrow \underset{(Y)}{2B_2H_6} + 3AlCl_3 + 3LiCl$

$$\text{Percentage of hydrogen in } B_2H_6 = \frac{6}{27.62} \times 100 = 21.72$$

$$B_2H_6 + 3O_2 \xrightarrow{\text{Explosion}} B_2O_3 + 3H_2O$$

Example 4 *An inorganic compound 'A' shows the following reactions.*

(i) *It is white solid, exists as dimer and fumes in wet air.*
(ii) *It sublimes at 180°C and forms monomer if heated to 400°C.*
(iii) *Its aqueous solution turns blue litmus to red and gives a white precipitate with* $AgNO_3$ *solution, which is soluble in* NH_4OH
(iv) *Addition of* NH_4OH *and* NaOH *separately to the solution of 'A' gives a gelatinous precipitate which in however soluble in excess of* NaOH.

The compound 'A' is

(a) $Al(OH)_3$
(b) Al_2Cl_6
(c) Al_2O_3
(d) $Al_2(SO_4)_3$

Solution (b) Compound 'A' is Al_2Cl_6.

(i) Al_2Cl_6 is a white solid, exists as dimer and fumes in wet air.
(ii) It sublimes at 180°C and converts into $AlCl_3$ at 400°C.
(iii) Its aqueous solution is acidic, so it turns blue litmus to red.

$$Al_2Cl_6 + 6H_2O \longrightarrow \underset{\text{weak base}}{2Al(OH)_3} + \underset{\text{strong acid}}{6HCl}$$

It gives a white ppt with $AgNO_3$ which is soluble in NH_4OH.

(iv) $AlCl_3 + 3NaOH \longrightarrow \underset{\text{white ppt}}{Al(OH)_3} + 3NaCl$

$$Al(OH)_3 + \underset{\text{excess}}{NaOH} \longrightarrow \underset{\text{soluble}}{NaAlO_2} + 2H_2O$$

But in case of NH_4OH, the ppt. of $Al(OH)_3$ does not dissolve in excess of NH_4OH.

Example 5 *An inorganic salt 'A' is a strong reducing agent. Its hydrolysis in water gives a white turbidity (B). Aqueous solution of 'A' gives a white ppt (C) with* NaOH. *'A' reduces auric chloride to produce purple of cassius. 'A' also reduces iodine and gives chromyl chloride test. Inorganic salt 'A' is*

(a) $SnCl_4$
(b) $SnCl_2$
(c) Na_2SnO_2
(d) $Sn(OH)Cl$

Solution (*b*) $\underset{(A)}{SnCl_2} + H_2O \longrightarrow \underset{(B)}{Sn(OH)Cl} + HCl$

$$SnCl_2 + 2NaOH \longrightarrow \underset{(C)}{Sn(OH)_2} + 2NaCl$$

$$Sn(OH)_2 + 2NaOH \longrightarrow Na_2SnO_2 + 2H_2O$$

$$3SnCl_2 + 2AuCl_3 \longrightarrow 3SnCl_4 + 2Au$$

$$SnCl_2 + 2HCl + I_2 \longrightarrow SnCl_4 + 2HI$$

Example 6 *A red coloured oxide* (*X*) *on treatment with conc.* HNO$_3$ *gives a compound* (*Y*). (*Y*) *with* HCl *produces a chloride* (*Z*) *which is insoluble in cold water but soluble in hot water.* (*Z*) *can also be formed by treating* (*X*) *with conc.* HCl. *Compound X, Y and Z are*

(*a*) $Pb_3O_4 \cdot PbO_2 \cdot PbCl_2$
(*b*) $Mn_3O_4, MnO_2, MnCl_2$
(*c*) $Fe_3O_4, Fe_2O_3, FeCl_3$
(*d*) Fe_3O_4, FeO, $FeCl_2$

Solution (*a*) Compound *X*, *Y* and *Z* are Pb_3O_4, PbO_2 and $PbCl_2$.

$$\underset{(X)}{Pb_3O_4} + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + \underset{(Y)}{PbO_2} + 2H_2O$$

$$PbO_2 + 4HCl \longrightarrow \underset{(Z)}{PbCl_2} + 2H_2O + Cl_2$$

$PbCl_2$ is insoluble in cold water but soluble in hot water.

$$\underset{(X)}{Pb_3O_4} + 8HCl \longrightarrow 3PbCl_2 + 4H_2O + Cl_2$$

Example 7 *A white crystalline compound 'A' swells up on heating and gives violet coloured flame on bunsen flame. Its aqueous solution gives following reactions.*

(*i*) *A white ppt with* BaCl$_2$ *in the presence of* HCl
(*ii*) *It gives white ppt when treated with excess of* NH$_4$OH. *The ppt dissolves in* NaOH *and reappears on boiling with conc solution of* NH$_4$Cl
(*iii*) *It gives yellow ppt with cobalt nitrite solution.*

The compound A is

(*a*) *Potash alum*
(*b*) *Borax*
(*c*) *Diborane*
(*d*) *Aluminium sulphate*

Solution (*a*) Compound '*A*' is **potash alum**.

$$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$$

It swells on heating due to evolution of water molecule.

It gives violet colour to the flame due to potassium salt.

(i) The solution consists of sulphate ion which combine with Ba^{2+} ion to form white ppt of BaSO$_4$.

(ii) $$Al_2(SO_4)_3 + 6NH_4OH \longrightarrow \underset{\text{ppt}}{2Al(OH)_3} + 3(NH_4)_2SO_4$$

$$Al(OH)_3 + NaOH \longrightarrow \underset{\text{soluble}}{NaAlO_2} + 2H_2O$$

$$NaAlO_2 + NH_4Cl + H_2O \longrightarrow \underset{\text{ppt.}}{Al(OH)_3} + NaCl + NH_3$$

(iii) Potassium salt gives yellow ppt with cobalt nitrite solution.

$$2K_2SO_4 + Na_4[Co(NO_2)_6] \longrightarrow \underset{\text{yellow ppt.}}{K_4[Co(NO_2)_6]} + 2Na_2SO_4$$

Example 8 *The metallic salt XY is soluble in water. When the solution is treated with* NaOH *solution, a white precipitate 'A' is formed. This precipitate is soluble in excess of* NaOH *solution to form a compound 'B'. When this solution is boiled with solid* NH$_4$Cl, *a precipitate of a compound 'C' is formed. An aqueous solution of XY upon treatment with* BaCl$_2$ *solution gave a white precipitate (O).*

The metallic salt XY is

(*a*) Al_2Cl_6
(*b*) $Al_2(SO_4)_3$
(*c*) Alum
(*d*) $BaSO_4$

Solution (*b*) Metallic salt *XY* is $Al_2(SO_4)_3$.

$Al_2(SO_4)_3$ is soluble in water.

When $Al_2(SO_4)_3$ is treated with NaOH, a white ppt of $Al(OH)_3$ is formed which is soluble in excess of NaOH.

$$\underset{XY}{Al_2(SO_4)_3} + 6NaOH \longrightarrow \underset{'A'}{2Al(OH)_3} + 3Na_2SO_4$$

$$Al(OH)_3 + \underset{\text{(excess)}}{NaOH} \longrightarrow \underset{\substack{(B)\\ \text{soluble}}}{NaAlO_2} + 2H_2O$$

The solution when boiled with solid NH$_4$Cl gives white ppt of Al(OH)$_3$.

$$NaAlO_2 + NH_4Cl + H_2O \longrightarrow \underset{\text{white ppt}}{Al(OH)_3} + NaCl + NH_3\uparrow$$

The salt reacts with BaCl$_2$ to give white ppt of BaSO$_4$.

$$Al_2(SO_4)_3 + 3BaCl_2 \longrightarrow Al_2Cl_6 + 3BaSO_4$$

Example 9 *Aluminium trifluoride is treated with anhydrous* HF *and then with* NaF. *When gaseous* BF$_3$ *is passed through the solution obtained, a precipitate is formed, which is of*

[NCERT]

(*a*) $Na_3[AlF_6]$
(*b*) $Na[BF_4]$
(*c*) AlF_3
(*d*) $H_3[AlF_6]$

Solution (*c*) Anhydrous HF is a covalent compound and is strongly H-bonded. Therefore, it does not give F$^-$ ions and hence AlF$_3$ does not dissolve in HF. NaF is an ionic compound. It contains F$^-$ ions which combine with electron deficient AlF$_3$ to form the soluble complex.

$$3NaF + AlF_3 \longrightarrow \underset{\substack{\text{sodium hexafluoroaluminate (III)}\\ \text{(soluble complex)}}}{Na_3[AlF_6]}$$

Boron due to its small size and higher electronegativity has greater tendency to form complexes than aluminium. Hence, precipitation of AlF$_3$ takes place when BF$_3$ is passed through Na$_3$[AlF$_6$] solution.

$$Na_3[AlF_6] + 3BF_3 \longrightarrow \underset{\substack{\text{sodium tetrafluoroborate (III)}\\ \text{(soluble complex)}}}{3Na[BF_4]} + AlF_3(s)$$

Start **Practice** *for* JEE Main

Round I (Topically Divided Problems)

Elements of Group 13

1. The most abundant metal in the earth crust is
(a) Na (b) Al
(c) Ca (d) Fe

2. The element which exists in liquid state for a wide range of temperature and can be used for measuring high temperature is **[NCERT Exemplar]**
(a) B (b) Al
(c) Ga (d) In

3. Which of the following is the electron deficient molecule?
(a) PH_3 (b) C_2H_6
(c) SiH_4 (d) B_2H_6

4. BF_3 exists but BH_3 doesn't because of the absence of **[NCERT Exemplar]**
(a) back bonding in BF_3
(b) back bonding in BH_3
(c) *d* orbital in B
(d) None of the above

5. Ionisation enthalpy ($\Delta_i H_1 \text{kJ mol}^{-1}$) for the elements of Gorup 13 follows the order. **[NCERT Exemplar]**
(a) $B > Al > Ga > In > Tl$ (b) $B < Al < Ga < In < Tl$
(c) $B < Al > Ga < In > Tl$ (d) $B > Al < Ga > In < Tl$

6. Which gas is liberated when Al_4C_3 is hydrolysed?
(a) CH_4 (b) C_2H_2
(c) C_2H_6 (d) CO_2

7. Alumina is
(a) acidic (b) amphoteric
(c) basic (d) None of these

8. AlI_3, when react with CCl_4, gives
(a) $AlCl_3$ (b) Cl_4
(c) Al_4C_3 (d) Al_2O_3

9. BCl_3 exists as monomer whereas $AlCl_3$ dimerises through halogen bridging. This is because of the **[NCERT Exemplar]**
(a) small size of B atom as compare to Al
(b) absence of *d* orbital in B atom
(c) $p\pi$-$p\pi$ back bonding in $AlCl_3$
(d) $p\pi$-$p\pi$ back bonding in BCl_3

10. Which of the following is a Lewis acid? **[NCERT Exemplar]**
(a) $AlCl_3$ (b) $MgCl_2$
(c) $CaCl_2$ (d) $BaCl_2$

11. In electrolysis of aluminium oxide which of the following is added to accelerate the process?
(a) Silica (b) Silicate
(c) Cryolite (d) Nickel

12. In purification of bauxite by Hall's process, bauxite ore is
(a) fused with Na_2CO_3
(b) heated with NaOH solution at 50°C
(c) heated with $NaHCO_3$
(d) fused with coke and heated at 1800°C in a current of nitrogen

13. Purification of aluminium done by electrolytic refining is known as
(a) Hoope's process (b) Serpeck's process
(c) Hall's process (d) Baeyer's process

14. The function of fluorspar in the electrolytic reduction of alumina dissolved in fused cryolite (Na_3AlF_6) is
(a) to decrease the rate of oxidation of carbon at the anode
(b) to lower the temperature of the melt and to make the fused mixture very conducting
(c) as a catalyst
(d) None of the above

15. Aluminium vessels should not be washed with materials containing washing soda since
(a) washing soda reacts with aluminium to form soluble aluminate
(b) washing soda reacts with aluminium to form insoluble aluminium oxide
(c) washing soda is expensive
(d) washing soda is easily decomposed.

16. In extraction of aluminium the electrolyte is
(a) fused cryolite with felspar
(b) pure alumina in molten state
(c) fused cryolite with fluorspar
(d) pure alumina with bauxite and molten cryolite

17. When Al is added to KOH solution,
(a) hydrogen is evolved (b) oxygen is evolved
(c) ozone is evolved (d) no reaction takes place

18. Which one of the following is correct statement?
(a) The hydroxide of aluminium is more acidic than that of boron.
(b) The hydroxide of boron is basic, while that of aluminium is amphoteric
(c) The hydroxide of boron is acidic, while that of aluminium is amphoteric
(d) The hydroxide of boron and aluminium are amphoteric

19. Boron when heated with carbon forms
(a) B_4C (b) BC_4 (c) B_4C_3 (d) B_2C_3

20. In the aluminothermic process, Al acts as a/an
(a) solder (b) oxidising agent
(c) reducing agent (d) flux

21. Which of the following oxides is strongly basic?
(a) Tl_2O (b) B_2O_3
(c) Al_2O_3 (d) Ga_2O_3

22. Aluminium alloys are used for making aircraft bodies because **[NCERT]**
(a) they are tough
(b) they are light
(c) they are resistant towards corrosion
(d) All of the above

23. Concentrated HNO_3 can be transported in aluminium container. This is because **[NCERT]**
(a) Al is a less reactive metal
(b) Al becomes passive by conc HNO_3
(c) Al is a cheap metal
(d) All of the above

24. When hydrated alumina is treated with aqueous NaOH solution, it gives **[NCERT]**
(a) $Al(OH)_3$ (b) pure alumina
(c) $NaAlO_2$ (d) $NaAlO_3$

25. In III A group Tl (thalium) shows +1 oxidation state while other members show +3 oxidation state, why?
(a) Presence of lone pair of electron in Tl
(b) Large ionic radius of Tl ion
(c) Inert pair effect
(d) None of the above

26. In aqueous solution, GaCl disproportionates to
(a) $GaCl_2$ and $GaCl_3$ (b) Ga and $GaCl_3$
(c) $GaCl_2$ and Ga (d) $GaCl_3$ and $GaCl_5$

27. Which is true for an element R present in III group of the Periodic Table?
(a) It has oxidation state of +4
(b) It is gas at room temperature
(c) It forms R_2O_3
(d) It forms RX_2

28. A non-metallic element of group 13, used in making bullet proof vests is extremely hard solid of black colour. It can exist in many allotropic forms and has unusually high melting point. Its trifluoride acts as **[NCERT Exemplar]**
(a) Lewis base (b) Lewis acid
(c) Bronsted acid (d) Bronsted base

29. Which metal is protected by a layer of its own oxide?
(a) Fe (b) Au
(c) Ag (d) Al

Compounds of Elements of Group 13

30. The structure of BF_3 is
(a) planar triangular (b) pyramidal
(c) tetrahedral (d) T-shaped

31. BF_3 acts as Lewis acid as it is **[NCERT]**
(a) electron deficient (b) electron precise
(c) electron rich (d) interstitial compound

32. Which of the following is known as inorganic benzene?
(a) Borazine (b) Phosphonitrilic acid
(c) Boron nitride (d) *p*-dichlorobenzene

33. In the structure of diborane **[NCERT Exemplar]**
(a) all hydrogen atoms lie in one plane and boron atoms lie in a plane perpendicular to this plane.
(b) 2 boron atoms and 4 terminal hydrogen atoms lie in the same plane and 2 bridging hydrogen atoms lie in the perpendicular plane.
(c) 4 bridging hydrogen atoms and boron atoms lie in one plane and two terminal hydrogen atoms lie in a plane perpendicular to this plane.
(d) all the atoms are in the same plane

34. Boron nitride has the structure of the type
(a) graphite type
(b) diamond type
(c) Both diamond and graphite type
(d) NaCl type

35. A compound (A) of boron reacts with NMe_3 to give an adduct (B) which on hydrolysis gives a compound (C) and hydrogen gas. Compound (C) is an acid. The adduct (B) is **[NCERT Exemplar]**
(a) $B_3N_3H_6$ (b) $2BH_3 \cdot NMe_3$
(c) $BH_3 \cdot 2NMe_3$ (d) $2BH_3 \cdot NMe_3$

36. In diborane the two H—B—H angles are nearly
(a) 95°, 120° (b) 60°, 120°
(c) 120°, 180° (d) 95°, 150°

37. Which of the following compounds are formed when BCl_3 is treated with water?
(a) B_2O_3 + HCl (b) B_2H_6 + HCl
(c) H_3BO_3 + HCl (d) None of these

38. $B(OH)_3 + NaOH \rightleftharpoons NaBO_2 \cdot 2H_2O$ or $Na[B(OH)_4]$
How can this reaction is made to proceed in forward direction?
(a) Addition of *cis*-1, 2 diol
(b) Addition of borax
(c) Addition of *trans*-1, 2 diol
(d) Addition of Na_2HPO_4

39. The product obtained when boric acid is red heated is **[NCERT]**
(a) metaboric acid (b) tetraboric acid
(c) boron trioxide (d) boron metal

40. The shapes of BF_3 and $[BH_4^-]$ are respectively **[NCERT]**
(a) planar, tetrahedral (b) tetrahedral, planar
(c) planar, planar (d) tetrahedral, tetrahedral

41. Which of the following statements about H_3BO_3 is not correct?
(a) It is prepared by acidifying an aqueous solution of borax
(b) It has a layer structure in which planar BO_3 units are joined by hydrogen bonds
(c) It does not act as proton donor but acts as Lewis acid by accepting hydroxyl ion
(d) It is a strong tribasic acid

42. Boric acid is an acid because its molecule **[NCERT Exemplar]**
(a) contains replaceable H^+ ion
(b) gives up a proton
(c) accepts OH^- from water releasing proton
(d) combines with proton from water molecule

43. $AlCl_3$ is
(a) anhydrous and ionic
(b) covalent and basic
(c) anhydrous and covalent
(d) coordinate and acidic

44. Alum are used as mordant in dyeing because
(a) dye is adsorbed on $Al(OH)_3$ which is deposited on fibre in the hydrolysis process
(b) dye is adsorbed on KOH formed due to hydrolysis
(c) Both (a) and (b)
(d) None of the above

45. Which of the following is not true about potash alum?
(a) Its aqueous solution is basic
(b) It is used in dyeing industries
(c) On heating it melts to give water of crystallization
(d) Its empirical formula is $KAl(SO_4)_2 \cdot 12H_2O$

46. Aluminium hydroxide is soluble in excess of sodium hydroxide forming the ion
(a) AlO_2^{3+} (b) AlO_2^-
(c) AlO_2^{3-} (d) AlO_3^-

47. In the reaction $B_2O_3 + C + Cl_2 \longrightarrow A + CO$. The A is
(a) CCl_2 (b) BCl_3 (c) BCl_2 (d) B_2Cl_2

Elements of Group 14

48. Which of the following elements is a metalloid?
(a) C (b) Ge
(c) Bi (d) Sn

49. Thermodynamically the most stable form of carbon is
(a) diamond (b) graphite
(c) fullerenes (d) coal

50. Elements of group 14
(a) exhibit oxidation state of + 4 only
(b) exhibit oxidation state of + 2 and + 4
(c) form M^{2-} and M^{4+} ions
(d) form M^{2+} and M^{4+} ions

51. Catenation *i.e.*, linking of similar atoms depends on size and electronic configuration of atoms. The tendency of catenation in Group 14 elements follows the order: **[NCERT Exemplar]**
(a) C > Si > Ge > Sn (b) C >> Si > Ge ≈ Sn
(c) Si > C > Sn > Ge (d) Ge > Sn > Si > C

52. Formation of in-numberable compounds of carbon is due to its
(a) high reactivity
(b) catenation tendency
(c) covalent and ionic tendency
(d) different valency

53. Percentage of lead in lead pencil is

(a) 20
(b) 80
(c) 70
(d) zero

54. In which of the following the inert pair effect is most prominent?

(a) Si
(b) Ge
(c) Pb
(d) C

55. The different layers in graphite are held together by

(a) metallic bonding
(b) covalent bonding
(c) ionic bonding
(d) van der Waals' forces

56. Which of the following statement is correct with respect to the property of elements in the carbon family with an increase in the atomic number? Their

(a) atomic size decreases
(b) stability of +2 oxidation state increases
(c) metallic character decreases
(d) ionization energy increases

57. A tetravalent element forms monoxide and dioxide with oxygen. When air is passed over heated element (1273 K), producer gas is obtained. Monoxide of the element is a powerful reducing agent and reduces ferric oxide to iron. Identify the element. **[NCERT Exemplar]**

(a) Lead
(b) Carbon
(c) Tin
(d) Silicon

58. Because of the lack of which of the following tendency, Si does not form a graphite like structure but carbon does? **[NCERT Exemplar]**

(a) $p\pi$-$d\pi$ bonding
(b) $p\pi$-$p\pi$ bonding
(c) d-orbital
(d) Small size

59. The hybridisation of carbon in CO_3^{2-}, diamond and graphite are respectively **[NCERT]**

(a) sp^2, sp^2, sp^3
(b) sp^2, sp^3, sp^2
(c) sp^2, sp^3, sp^3
(d) sp^3, sp^3, sp^2

60. Diamond is used as abrasive because of its **[NCERT]**

(a) transparent nature
(b) high refractive index
(c) three dimensional network structure
(d) sp^3 hybridisation

61. Monosilane on coming in contact with air burns with a luminous flame producing vortex rings. These rings are of

(a) SiO_2
(b) SiO
(c) Si
(d) H_2SiO_3

62. What is the number of free electrons present on each carbon atom in graphite?

(a) Zero
(b) 3
(c) 2
(d) 1

63. Quartz is extensively used as a piezoelectric material as it contains **[NCERT Exemplar]**

(a) Pb
(b) Si
(c) Ti
(d) Sn

64. The product obtained when silicon dioxide is treated with HF is **[NCERT]**

(a) SiF_4
(b) H_2SiF_4
(c) H_2SiF_6
(d) None of these

65. Carborundum is obtained when silica is heated at high temperature with

(a) carbon
(b) carbon monoxide
(c) carbon dioxide
(d) calcium carbonate

66. PbO is

(a) acidic
(b) amphoteric
(c) basic
(d) neutral

67. Lead pipes are corroded quickly by

(a) dil. H_2SO_4
(b) acetic acid
(c) conc. H_2SO_4
(d) water

Compounds of Elements of Group 14

68. Dry ice is **[NCERT Exemplar]**

(a) solid NH_3
(b) solid SO_2
(c) solid CO_2
(d) solid N_2

69. CO behaves as

(a) Lewis acid
(b) Lewis base
(c) amphoteric oxide
(d) None of these

70. CO_2 in water behaves as

(a) weak dibasic acid H_2CO_3
(b) weak monobasic acid HO—COOH
(c) weak diacid base $CO(OH)_2$
(d) weak monoacid base HO—COOH

71. Sodium oxalate on heating with conc. H_2SO_4 gives

(a) CO only
(b) CO and CO_2
(c) CO_2 only
(d) SO_2 and SO_3

72. Name of the structure of silicates in which three oxygen atoms of $[SiO_4]^{4-}$ are shared is

(a) pyrosilicate
(b) sheet silicate
(c) linear chain silicate
(d) three dimensional silicate

73. Silicones have the general formula

(a) $(SiO_4)^{4-}$
(b) SiO_6^{7-}
(c) $(SiO_3)_n^{-2n}$
(d) $(R_2SiO)_n$

74. When silicon is heated with CH_3Cl at higher temperature in the presence of Cu, **[NCERT]**
(a) $CH_3SiCl_3 + (CH_3)_2 SiCl_2$ obtained
(b) $(CH_3)_3 SiCl$ is obtained
(c) $(CH_3)_4 Si$ is obtained
(d) a mixture of all of the above is obtained

75. If the starting material for the manufacture of silicones is $RSiCl_3$, the product obtained is **[NCERT]**
(a) silicone rubber
(b) silicone oils
(c) cross-linked silicone
(d) linear chain silicone

Miscellaneous

76. Which of the following has highest density?
(a) Pb (b) B (c) Cu (d) Fe

77. Which of the following form dimeric halides?
(a) Al (b) Mg (c) In (d) Ca

78. The hardest substance amongst the following is
(a) Be_2C (b) tritonium
(c) B_4C (d) graphite

79. Which metal burns in air at high temperature with the evolution of much heat?
(a) Cu (b) Pb (c) Hg (d) Al

Round II (Mixed Bag)

Only One Correct Option

1. An aqueous solution of borax is
(a) neutral (b) amphoteric
(c) basic (d) acidic

2. The type of hybridisation of boron in diborane is
(a) sp (b) sp^2
(c) sp^3 (d) dsp^2

3. Identify compound Z in the following reaction sequence.

$$A + 2HCl + 5H_2O \longrightarrow 2NaCl + X$$

$$X \xrightarrow[370\text{ K}]{\Delta} HBO_2 \xrightarrow[>370\text{ K}]{\Delta} Z$$

[NCERT Exemplar]
(a) Borax (b) Orthoboric acid
(c) Metaboric acid (d) Boron trioxide

4. The B—F bond length in BF_3 is shorter than that in BF_4^-. This is because of **[NCERT]**
(a) resonance in BF_3 but not in BF_4^-
(b) $p\pi$-$p\pi$ back bonding in BF_4^- but not in BF_3
(c) $p\pi$-$p\pi$ back bonding in BF_3 but not in BF_4^-
(d) $p\pi$-$d\pi$ back bonding in BF_3 but not in BF_4^-

5. When aqueous solution of borax is acidified with hydrochloric acid, a white crystalline solid is formed which is soapy to touch. The nature of the solid is **[NCERT Exemplar]**
(a) acidic
(b) basic
(c) neutral
(d) depends upon the nature of solvent

6. The order of acidic strength of boron trihalides is
(a) $BF_3 < BCl_3 < BBr_3 < BI_3$
(b) $BI_3 < BBr_3 < BCl_3 < BF_3$
(c) $BCl_3 < BBr_3 < BI_3 < BF_3$
(d) $BBr_3 < BCl_3 < BF_3 < BI_3$

7. Boric acid is used in carom boards for smooth gliding of pawns because
(a) H_3BO_3 molecules are loosely chemically bonded and hence soft
(b) its low density makes it fluffy
(c) it can be powdered to a very small grain size
(d) H-bonding in H_3BO_3 give it a layered structure

8. When BCl_3 is treated with water, it hydrolysis and forms $[B(OH)_4]^-$ only whereas $AlCl_3$ in acidified aqueous solution forms $[Al(H_2O)_6]^{3+}$ ion. The hybridisation of boron and aluminium in these species is respectively. **[NCERT Exemplar]**
(a) sp^3, sp^3d (b) sp^3, sp^3d^2
(c) sp^3d, sp^3d^2 (d) sp^2, sp^3d^2

9. A mixture of dilute NaOH and aluminium pieces is used to open drain because **[NCERT]**
(a) the gas obtained creates higher pressure
(b) they react explosively
(c) they creates fire
(d) the given statement is not true

10. Graphite is used as lubricant because of its **[NCERT]**
(a) layered structure
(b) weak van der Waals' forces between the layers
(c) strong covalent bonding between the layers
(d) tendency to exist in solid form

11. When CO is heated with ZnO, **[NCERT]**
(a) Zn is obtained
(b) CO_2 is obtained
(c) Both (a) and (b)
(d) None of the above

12. Excessive CO_2 content is responsible for global warming. This is because of its **[NCERT]**
(a) higher wavelength IR trapping nature
(b) lower wavelength IR trapping nature
(c) UV wave trapping nature
(d) heating effect

13. In SiF_6^{2-} and $SiCl_6^{2-}$ which one is known and why?
(a) SiF_6^{2-} because of small size of F
(b) SiF_6^{2-} because of large size of F
(c) $SiCl_6^{2-}$ because of small size of Cl
(d) $SiCl_6^{2-}$ because of large size of Cl

14. Aluminium oxide is not reduced by chemical reactions since
(a) aluminium oxide is reactive
(b) reducing agents contaminate
(c) aluminium oxide is highly stable
(d) the process pollutes the environment

15. Anodising can be done by electrolysing dilute H_2SO_4 with Al as anode, this result in
(a) the formation of protective oxide layer
(b) the formation of $Al_2(SO_4)_3$ and SO_2 gas
(c) the formation of AlH_3 and SO_2 gas
(d) the formation of $Al(HSO_3)$ and H_2 gas

16. Solid CO_2 is known as dry ice, because
(a) it evaporates at 40°C
(b) it melts at 0°C
(c) its boiling points is more than 199°C
(d) it evaporates at – 78°C without melting

17. Which one of the following statements about the zeolite is false?
(a) They are used as cation exchangers
(b) Some of the SiO_4^{4-} units are replaced by AlO_4^{5-} and AlO_6^{9-} ions in zeolite
(c) They have open structure which enables them to take up small molecules
(d) Zeolites are aluminosilicates having three dimensional structures

18. Alzeimer's disease is caused due to Al interaction with internal organs of the body if food is contaminated with Al. This disease
(a) induces senility in young persons
(b) causes memory loss
(c) Both (a) and (b)
(d) None of the above

19. Carbon suboxide, C_3O_2 has
(a) bent structure
(b) trigonal planar structure
(c) linear structure
(d) distorted tetrahedral structure

20. Suppose you have to determine the percentage of carbon dioxide in a sample of a gas available in a container. Which is the best absorbing material for the carbon dioxide?
(a) Heated copper oxide
(b) Cold, solid calcium chloride
(c) Cold, solid calcium hydroxide
(d) Heated charcoal

21. When carbon monoxide is passed over solid caustic soda heated to 200°C, it forms
(a) Na_2CO_3 (b) CH_3COONa
(c) $NaHCO_3$ (d) HCOONa

22. For purification of alumina, the modern processes most useful when (i) the impurity present is a lot of iron oxides and (ii) the impurity present is a lot of silica, are
(a) for (i) Hall's process; for (ii) Baeyer's process
(b) for (i) Serpeck's process; for (ii) Baeyer's process
(c) for (i) Hall's process; for (ii) Serpeck's process
(d) for (i) Baeyer's process; for (ii) Serpeck's process

23. The stability of hydrides of carbon family is in the order
(a) $CH_4 > SiH_4 > GeH_4 > SnH_4 > PbH_4$
(b) $CH_4 < SiH_4 < GeH_4 < SnH_4 < PbH_4$
(c) $CH_4 > SnH_4 > GeH_4 > SiH_4 > PbH_4$
(d) None of the above

24. Lead pipes are not suitable for drinking water because
(a) a layer of lead dioxide is deposited over pipes
(b) lead forms basic lead carbonate
(c) lead reacts with water containing air to form $Pb(OH)_2$
(d) lead reacts with air to form litharge

25. When metal *X* is treated with sodium hydroxide, a white precipitate (*A*) is obtained, which is soluble in excess of NaOH to give soluble complex (*B*). Compound (*A*) is soluble in dilute HCl to form compound (*C*). The compound (*A*) when heated strongly gives (*D*), which is used to extract metal. Compound *D* is **[NCERT]**
(a) aluminium hydroxide
(b) sodium aluminate
(c) aluminium chloride
(d) alumina

More than One Correct Option

26. The reason for small radius of Ga compared to Al is **[NCERT Exemplar]**

(a) poor screening effect of *d* and *f* orbitals
(b) increase in nuclear charge
(c) presence of higher orbitals
(d) higher atomic number

27. The linear shape of CO_2 is due to **[NCERT Exemplar]**

(a) sp^3 hybridisation of carbon
(b) sp hybridisation of carbon
(c) $p\pi$-$p\pi$ bonding between carbon and oxygen
(d) sp^2 hybridisation of carbon

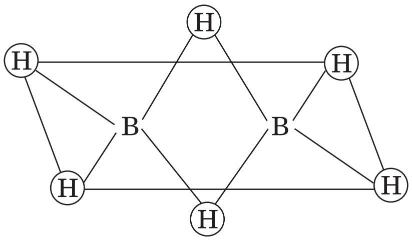
28. Me_3SiCl is used during polymerisation of organo silicones because **[NCERT Exemplar]**

(a) the chain length of organo silicone polymers can be controlled by adding Me_3SiCl
(b) Me_3SiCl blocks the end terminal of silicone polymer
(c) Me_3SiCl improves the quality and yield of the polymer
(d) Me_3SiCl acts as a catalyst during polymerisation

29. Which of the following statements are correct? **[NCERT Exemplar]**

(a) Fullerenes have dangling bonds
(b) Fullerenes are cage-like molecules
(c) Graphite is thermodynamically most stable allotrope of carbon
(d) Graphite is slippery and hard and therefore used as a dry lubrication in machines

30. Which of the following statements are correct? Answer on the basis of figure **[NCERT Exemplar]**



(a) The two birdged hydrogen atoms and the two boron atoms lie in one plane;
(b) Out of six B—H bonds two bonds can be described in terms of 3-centre-2-electron bonds.
(c) Out of six B—H bonds four B—H bonds can be described in terms of 3-centre-2-electron bonds
(d) The four terminal B—H bonds are two centre-two electron regular bonds.

Assertion and Reason

Directions (Q. Nos. 31 to 36) *Each of these questions contains two statements : Statement* I (*Assertion*) *and Statement* II (*Reason*). *Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes* (*a*), (*b*), (*c*), (*d*) *given below*

(a) Statement I is true; Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true; Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

31. Statement I BF_3 is a useful organic catalyst for Friedel-Crafts reaction.

Statement II It is covalent, gaseous and hydrolysed by water.

32. Statement I Calcium carbide on hydrolysis gives acetylene.

Statement II Calcium carbide contains C^{4-} anions.

33. Statement I If aluminium atoms replace a few silicon atoms in three dimensional network of silicon dioxide, the overall structure acquires a negative charge.

Statement II Aluminium is trivalent while silicon is tetravalent. **[NCERT Exemplar]**

34. Statement I GeO, SnO and PbO are more basic and ionic than the corresponding GeO_2, SnO_2 and PbO_2.

Statement II GeO is acidic while SnO and PbO are amphoteric.

35. Statement I Si—Si bonds are weaker than Si—O bonds.

Statement II Silicon forms double bonds with itself.

36. Statement I Silicons are water repelling in nature.

Statement II Silicons are organosilicon polymers, which have $\left(R_2SiO \right)$ as repeating unit. **[NCERT Exemplar]**

Comprehension Based Questions

Directions (Q. Nos. 37 to 39) Boric oxide B_2O_3 reacts with water to form boric acid. The net ionisation reaction of boric acid when dissolves in water is

$$B(OH)_3(aq) + 2H_2O(l) \longrightarrow H_3O^+(aq) + [B(OH)_4]^-(aq)$$

Boric acid is quite toxic and slippery. The solution of the salt are generally quite complex because they contain polymers of the borate anions as well as the simple anion $[B(OH)_4]^-$, BO_3^{3-} and BO_4^{5-}. Borates hydrolyse in water to give basic solution and this is why borane is used in some cleaning agents.

37. Which of the following statements is/are correct?
(a) Boric acid is Lewis base
(b) Hybridisation of boron in boric acid is sp^3
(c) Boric acid molecule held together by hydrogen bonding
(d) All of the above

38. The oxidation number of boron in $NaBO_3 \cdot 4H_2O$ is
(a) +1
(b) +2
(c) +3
(d) +4

39. Boric acid is slippery due to
(a) banana bonds
(b) hydrogen bonds
(c) van der Waals' forces
(d) None of these

Directions (Q. Nos. 40 to 42) Like halides of boron, halides of aluminium do not show back bonding because of increase in size of aluminium. Actually aluminium atoms complete their octets by forming dimers. Thus, chloride and bromide of aluminium exist as dimers, both in the vapour state and in polar solvents like benzene while the corresponding boron halides exists as monomer. In boron trihalides the extent of back bonding decreases with increase in size of halogens and thus, Lewis acid character increases.

40. Which of the following reaction is incorrect?
(a) $BCl_3 + 3EtOH \longrightarrow B(OEt)_3 + 3HCl$
(b) $BF_3 + 2H_2O \longrightarrow [BF_3OH]^- + H_3O^+$
(c) $BF_3 + F^- \longrightarrow BF_4^-$
(d) $BCl_3 + 2C_5H_5N \longrightarrow Cl_3B(C_2H_5N)_2$

41. Which statements about anhydrous aluminium chloride is correct?
(a) It is a strong Lewis base
(b) It is not easily hydrolysed
(c) It exists as $AlCl_3$ molecule
(d) It sublimes at 100°C

42. The dimeric structure of aluminium chloride disappears when
(a) it dissolves in water
(b) it dissolves in benzene
(c) it reacts with R_3N
(d) Both (a) and (c)

Directions (Q. Nos. 43 to 45) The heavier elements of group 13 and 14 besides their group oxidation state exhibit another oxidation state which is two units lower than the group oxidation state. The stability of lower oxidation state increases on moving down the group due to inert pair effect.

43. Which of the following statements is incorrect?
(a) Boron exhibits +3 oxidation state only
(b) In Ga +3 oxidation state is more stable than +1 oxidation state
(c) In Sn +2 oxidation state is more stable than +4 oxidation state
(d) In Tl +1 oxidation state is more stable than +3 oxidation state

44. The strongest oxidising agent among the given is
(a) SiO_2
(b) GeO_2
(c) SnO_2
(d) PbO_2

45. Inert pair is not exhibit by
(a) Pb
(b) Bi
(c) Tl
(d) B

Previous Years' Questions

46. Boron can't form which one of the following anions? **[AIEEE 2011]**
(a) BF_6^{3-}
(b) BH_4^-
(c) $B(OH)_4^-$
(d) BO_2^-

47. The bond dissociation energy of B—F in BF_3 is 646 kJ mol^{-1} whereas that of C—F in CF_4 is 515 kJ mol^{-1}. The correct reason for higher B—F bond dissociation energy as compared to that of C—F is **[AIEEE 2009]**
(a) smaller size of B-atom as compared to that of C-atom
(b) stronger σ-bond between B and F in BF_3 as compared to that between C and F in CF_4
(c) significant $p\pi$ - $p\pi$ interaction between B and F in BF_3 whereas there is no possibility of such interaction between C and F in CF_4
(d) lower degree of $p\pi$ - $p\pi$ interaction between B and F in BF_3 than that between C and F in CF_4

48. Among the following substituted silanes the one which will give rise to crosslinked silicone polymer on hydrolysis is **[AIEEE 2008]**
(a) R_4Si
(b) $RSiCl_3$
(c) R_2SiCl_2
(d) R_3SiCl

49. Which one of the following is the correct statement? **[AIEEE 2008]**
(a) Boric acid is a protonic acid
(b) Beryllium exhibits coordination number of six
(c) Chlorides of both beryllium and aluminium have bridged chloride structures in solid phase
(d) $B_2H_6 \cdot 2NH_3$ is known as 'inorganic benzene'

50. The stability of dihalides of Si, Ge, Sn and Pb increases steadily in the sequence **[AIEEE 2007]**
(a) $GeX_2 < SiX_2 < SnX_2 < PbX_2$
(b) $SiX_2 < GeX_2 < PbX_2 < SnX_2$
(c) $SiX_2 < GeX_2 < SnX_2 < PbX_2$
(d) $PbX_2 < SnX_2 < GeX_2 < SiX_2$

51. A metal, M forms chlorides in its +2 and +4 oxidation states. Which of the following statements about these chlorides is correct? **[AIEEE 2006]**

(a) MCl_2 is more volatile than MCl_4
(b) MCl_2 is more soluble in anhydrous ethanol than MCl_4
(c) MCl_2 is more ionic than MCl_4
(d) MCl_2 is more easily hydrolysed than MCl_4

52. Which of the following oxides is amphoteric in character? **[AIEEE 2005]**

(a) SnO_2
(b) SiO_2
(c) CO_2
(d) CaO

53. In silicon dioxide **[AIEEE 2005]**

(a) there are double bonds between silicon and oxygen atoms
(b) silicon atom is bonded to two oxygen atoms
(c) each silicon atom is surrounded by two oxygen atoms and each oxygen atom is bonded to two silicon atoms
(d) each silicon atom is surrounded by four oxygen atoms and each oxygen atom is bonded to two silicon atoms

54. Heating of an aqueous solution of aluminium chloride to dryness will give **[AIEEE 2005]**

(a) $Al(OH)Cl_2$
(b) Al_2O_3
(c) Al_2Cl_6
(d) $AlCl_3$

55. The structure of diborane (B_2H_6) contains **[AIEEE 2005]**

(a) four $2c-2e^-$ bonds and four $3c-2e^-$ bonds
(b) two $2c-2e^-$ bonds and two $3c-3e^-$ bonds
(c) two $2c-2e^-$ bonds and four $3c-2e^-$ bonds
(d) four $2c-2e^-$ bonds and two $3c-2e^-$ bonds

56. Aluminium chloride exists as dimer, Al_2Cl_6 in solid state as well as in solution of non-polar solvents such as benzene. When dissolved in water, it gives **[AIEEE 2004]**

(a) $Al^{3+} + 3Cl^-$ (b) $[Al(H_2O)_6]^{3+} + 3Cl^-$
(c) $[Al(OH)_6]^{3-} + 3HCl$ (d) $Al_2O_3 + 6HCl$

57. The soldiers of Napolean army while at Alps during freezing winter suffered a serious problem as regards to the tin buttons of their uniforms. White metallic tin buttons got converted to grey powder. This transformation is related to **[AIEEE 2004]**

(a) a change in the crystalline structure of tin
(b) an interaction with nitrogen of the air at very low temperatures
(c) a change in the partial pressure of oxygen in the air
(d) an interaction with water vapour contained in the humid air

58. Graphite is a soft solid lubricant extremely difficult to melt. The reason for this anomalous behaviour is that graphite **[AIEEE 2003]**

(a) is a non-crystalline substance
(b) is an allotropic form of diamond
(c) has molecules of variable molecular masses like polymers
(d) has carbon atoms arranged in large plates of rings of strongly bound carbon atoms with weak interplate bonds

59. Alum is widely used to purify water since **[AIEEE 2002]**

(a) it forms complex with clay particles
(b) it coagulates the mud particles
(c) it exchanges Ca^{2+} and Mg^{2+} ions present in hard water
(d) its sulphate ion is water purifier

Answers

Round I

1. (b)	**2.** (c)	**3.** (d)	**4.** (b)	**5.** (d)	**6.** (a)	**7.** (b)	**8.** (a)	**9.** (b)	**10.** (a)
11. (c)	**12.** (a)	**13.** (a)	**14.** (b)	**15.** (a)	**16.** (d)	**17.** (a)	**18.** (c)	**19.** (a)	**20.** (c)
21. (a)	**22.** (d)	**23.** (b)	**24.** (c)	**25.** (c)	**26.** (b)	**27.** (c)	**28.** (b)	**29.** (d)	**30.** (a)
31. (a)	**32.** (a)	**33.** (b)	**34.** (a)	**35.** (b)	**36.** (a)	**37.** (c)	**38.** (a)	**39.** (c)	**40.** (a)
41. (d)	**42.** (c)	**43.** (c)	**44.** (a)	**45.** (a)	**46.** (b)	**47.** (b)	**48.** (b)	**49.** (b)	**50.** (b)
51. (a)	**52.** (b)	**53.** (d)	**54.** (c)	**55.** (d)	**56.** (b)	**57.** (b)	**58.** (b)	**59.** (b)	**60.** (c)
61. (a)	**62.** (d)	**63.** (b)	**64.** (c)	**65.** (a)	**66.** (b)	**67.** (b)	**68.** (c)	**69.** (b)	**70.** (a)
71. (b)	**72.** (b)	**73.** (d)	**74.** (d)	**75.** (c)	**76.** (a)	**77.** (a)	**78.** (c)	**79.** (d)	

Round II

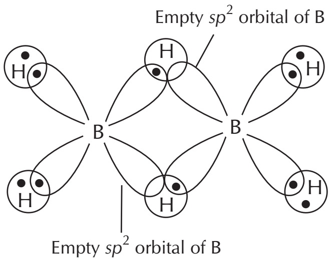
1. (c)	**2.** (c)	**3.** (d)	**4.** (c)	**5.** (a)	**6.** (a)	**7.** (d)	**8.** (b)	**9.** (a)	**10.** (b)
11. (d)	**12.** (a)	**13.** (a)	**14.** (c)	**15.** (a)	**16.** (d)	**17.** (b)	**18.** (c)	**19.** (c)	**20.** (c)
21. (d)	**22.** (d)	**23.** (a)	**24.** (c)	**25.** (d)	**26.** (a,b)	**27.** (b,c)	**28.** (a,b)	**29.** (b,c)	**30.** (b,d)
31. (b)	**32.** (c)	**33.** (a)	**34.** (d)	**35.** (c)	**36.** (b)	**37.** (c)	**38.** (c)	**39.** (b)	**40.** (d)
41. (d)	**42.** (d)	**43.** (c)	**44.** (d)	**45.** (d)	**46.** (a)	**47.** (c)	**48.** (b)	**49.** (c)	**50.** (c)
51. (c)	**52.** (a)	**53.** (d)	**54.** (b)	**55.** (d)	**56.** (b)	**57.** (a)	**58.** (d)	**59.** (d)	

the Guidance

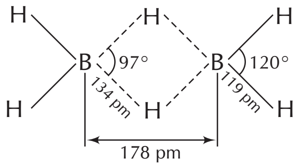
Round I

2. Gallium, Ga because of its unusual structure, exists as Ga_2 molecules and thus has low melting point. It exists as liquid upto 2000°C and hence, used in high temperature thermometry.

3. B_2H_6



4. Boron fluoride exists as BF_3. Due to its small size, B atom cannot coordinate to 4 larger fluoride ions and hence, cannot form the dimeric molecule. On the other hand, boron hydride exists as B_2H_6. This is due to the fact that hydrogen atom in BH_3 has no electron to form $p\pi$-$p\pi$ back bonding. Thus, boron possesses incomplete octet and BH_3 is dimerised to form B_2H_6 molecule with covalent and three centre bonds.



Structure of diborane, B_2H_6

5. Because of its small size and lowest shielding effect, IE is highest for boron and decreases from B to Tl, But not in a regular manner. IE of Ga is greater than that of Al because of poor shielding of 10*d* electrons, while IE of Tl is higher than that of In because of the poor shielding effect of 14*f* electrons present in the inner energy shell. Thus, the correct order is

$$B > Al < Ga > In < Tl$$

6. $Al_4C_3 + 12H_2O \longrightarrow 3CH_4 + 4Al(OH)_3$

7. Alumina is amphoteric oxide, which reacts with acid as well as base.

8. AlI_3, on reaction with CCl_4, gives $AlCl_3$.

$$4AlI_3 + 3CCl_4 \longrightarrow 4AlCl_3 + 3CI_4$$

9. Due to the absence of *d*-orbitals, BCl_3 does not dimerise but in $AlCl_3$, Al contains empty *d*-orbital so it is capable to undergo dimerisation.

10. $AlCl_3$ being electron deficient have a tendency to accept a electron pair, thus acts as Lewis acid.

Note In $MgCl_2$, $CaCl_2$ and $BaCl_2$, octet of all the atoms are complete by the transfer of electrons, thus these cannot act as Lewis acid.

11. Cryolite is added to lower the melting point of alumina and to increase the electrical conductivity.

12. In Hall's process

$$Al_2O_3 \cdot 2H_2O + Na_2CO_3 \longrightarrow 2NaAlO_2 + CO_2 + 2H_2O$$

$$2NaAlO_2 + 3H_2O + CO_2 \xrightarrow{333\text{ K}} 2Al(OH)_3 \downarrow + Na_2CO_3$$

$$2Al(OH)_3 \xrightarrow{1473\text{ K}} Al_2O_3 + 3H_2O$$

15. $2Al + Na_2CO_3 + 3H_2O \xrightarrow{\Delta} 2NaAlO_2 + CO_2 + 2H_2$

17. $2KOH + 2Al + 2H_2O \longrightarrow 2KAlO_2 + 3H_2$

18. $B(OH)_3 \Rightarrow H_3BO_3$ boric acid

$Al(OH)_3 \Rightarrow$ amphoteric

19. It form boron carbide. The molecular formula of boron carbide is $B_{12}C_3$.

$$4B + C \xrightarrow{\Delta} B_4C$$

20. In alumino thermic process, aluminium reduces Fe_2O_3 or Cr_2O_3 to respective metals and acts as a reducing agent.

$$Fe_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Fe$$

21. As we move down the group, the basic nature of the oxides of group 13 elements increases. Tl_2O in aqueous solution gives TlOH which is as strong a base as alkali metal hydroxides.

22. Aluminium alloys such as duralumin is light, tough and resistant to corrosion and hence, it is used in making aircraft body.

23. Al reacts with conc. HNO_3 to form a protective layer of aluminium oxide on its surface which prevents it from further reaction.

$$2Al(s) + 6HNO_3\text{ (conc.)} \longrightarrow \underset{\substack{\text{alumina} \\ \text{(a passive protective layer)}}}{Al_2O_3(s)} + 6NO_2(g) + 3H_2O(l)$$

Therefore, Al becomes passive that's why aluminium containers can be used to transport conc. HNO_3.

24. Alumina dissolves to form sodium meta-aluminate.

$$\underset{\substack{\text{hydrated alumina} \\ \text{or bauxite}}}{Al_2O_3 \cdot 2H_2O\ (s)} + 2NaOH(aq) \xrightarrow{\text{Heat}} \underset{\substack{\text{sodium} \\ \text{meta aluminate}}}{2NaAlO_2} + 3H_2O$$

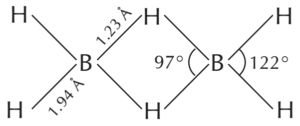
28. The given characteristics are of B and BF_3 because of the presence of electron deficient boron atom, acts as Lewis acid.

29. The thin protective layer of oxide, Al_2O_3 is formed which protects the metal from further attack of air and water and thus, Al is stable in air.

31. BF_3 being electron deficient, is a strong Lewis acid. It reacts with Lewis bases easily to complete the octet around boron.

$$\underset{\text{Lewis acid}}{F_3B} + \underset{\text{Lewis base}}{:NH_3} \longrightarrow F_3B \leftarrow NH_3$$

33. The structure of diborane is as



In this structure, four terminal H atoms along with the two B atoms lie in one plane and two bridging H atoms lie above and below the plane.

35. Since, compound '*A*' of boron reacts with NMe_3 to form an adduct '*B*'. Thus, compound '*A*' is a Lewis acid. Since, adduct '*B*' on hydrolysis gives an acid '*C*' and hydrogen gas, therefore, '*A*' is B_2H_6 and '*C*' is boric acid.

$$\underset{\text{diborane }(A)}{B_2H_6} + 2NMe_3 \longrightarrow \underset{\text{adduct }(B)}{2BH_3 \cdot NMe_3}$$

$$BH_3 \cdot NMe_3 + 3H_2O \longrightarrow \underset{\text{boric acid }(C)}{H_3BO_3} + NMe_3 + 3H_2$$

37. BCl_3 is completely hydrolysed by water yielding boric acid and hydrochloric acid.

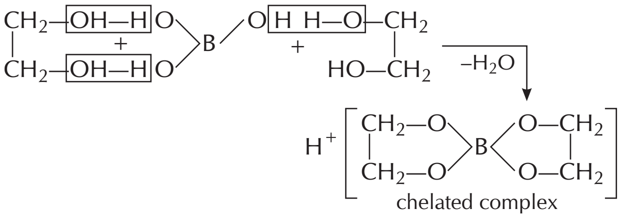
$$BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$$

38. $B(OH)_3 + NaOH \rightleftharpoons NaBO_2 \cdot H_2O$ or $Na^+[B(OH)_4]^-$

This reaction is reversible reaction because sodium metaborate, $Na^+[B(OH)_4]^-$ formed by the reaction between $B(OH)_3$ and NaOH gets hydrolysed to regenerate $B(OH)_3$ and NaOH.

$$Na^+[B(OH)_4]^- \xrightarrow[\text{hydrolysis}]{} NaOH + B(OH)_3$$

If, some quantity of polyhydroxy compounds like *cis*-1,2-diol, catechol, glycerol etc., is added to the reaction mixture the $B(OH)_3$ combines with such polyhydroxy compounds to give chelated complex compound. Due to complex compound formation, stability increases and due to higher stability of complex, reaction moves in forward direction.



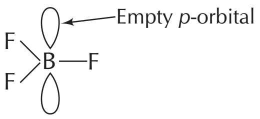
chelated complex compound

39. Boric acid, on heating loses water in three different stages at different temperatures ultimately giving boron trioxide.

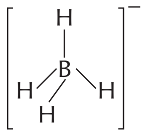
$$\underset{\text{boric acid}}{H_3BO_3} \xrightarrow{370\text{ K}} \underset{\text{metaboric acid}}{HBO_2} + H_2O$$

$$\underset{\text{metaboric acid}}{4HBO_2} \xrightarrow[-H_2O]{410\text{ K}} \underset{\text{tetraboric acid}}{H_2B_4O_7} \xrightarrow{\text{Red heat}} \underset{\text{boron trioxide}}{2B_2O_3} + H_2O$$

40. In BF_3, boron is sp^2-hybridised as it contains three bond pairs and, therefore, BF_3 molecule is trigonal planar in shape. On the other hand, in $[BH_4]^-$ boron is sp^3-hybridised because of the presence of four bond pairs and hence, $[BH_4]^-$ species is tetrahedral in shape.

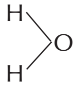


BF_3 sp^2-hybridised
(trigonal planar shape)



$[BH_4]^-$,sp^3-hybridised
(tetrahedral shape)

41. H_3BO_3 *i.e.,* $B(OH)_3$ is weak mono-basic acid.

42. H_3BO_3, because of the presence of electron deficient B atom, in aqueous medium coordinates with a water molecule to form hydrated species  $H_2O \longrightarrow B(OH)_3.B^{3+}$ ion pulls the σ electron density of coordinated O atom towards itself, which in turn pulls the σ electron density of the O—H bond of attached water molecule towards itself. This facilitates the removal of H^+. Thus, H_3BO_3 behaves as weak Lewis acid.

49. Thermodynamically the most stable form of carbon is graphite.

50. Due to inert pair effect, elements of group 14 exhibit oxidation states of +2 and +4.

51. Since the *E*—*E* (where, $E = C, Si, Ge, Sn$) bond energy decreases with increase in the size, the catenation tendency follows the similar order, as it depends upon the *E*—*E* bond strength.

52. Generally IV group element shows catenation tendency and carbon has more catenation power, so forms a large number of compounds.

54. The inert pair effect is most prominent in Pb because from top to bottom number of shells increases.

55. Graphite has two dimensional sheet like structure in which the various layers are held together by weak van der Waals' forces.

56. In carbon family stability of +2 oxidation state increases on moving down the group in the Periodic Table with an increase in atomic number due to screening effect.

57. Producer gas is a mixture of CO and N_2, therefore, the tetravalent element is carbon and its monoxide and dioxide are CO and CO_2 respectively.

$$2C(s) + \underbrace{O_2(s) + 4N_2(g)}_{\text{air}} \xrightarrow{1273\text{ K}} \underbrace{2CO(g) + 4N_2(g)}_{\text{producer gas}}$$

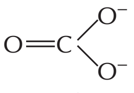
The carbon monoxide is a strong reducing agent and reduces ferric oxide to iron.

$$Fe_2O_3(s) + 3CO(g) \xrightarrow{\Delta} 2\,Fe(s) + 3CO_2(g)$$

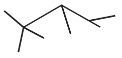
58. In graphite, C is sp^2 hybridised. Carbon due to its smallest size and highest electronegativity among group 14 elements has strong tendency to form $p\pi$-$p\pi$ multiple bonds. While silicon due to its larger size and less electronegativity has poor ability to form $p\pi$-$p\pi$ multiple bonds. That's why the silicon does not form a graphite like structure.

59. Hybridisation depends upon the number of σ bonds, so count the number of σ bonds formed by C. If number of bonds is 4, the hybridisation is sp^3, if σ bonds are 3, hybridisation is sp^2 and if σ bonds are 2, hybridisation is sp.

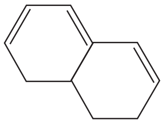
The state of hybridisation of carbon in CO_3^{2-}, diamond and in graphite is sp^2, sp^3 and sp^2 respectively.



CO_3^{2-}



diamond



graphite

60. In diamond, each sp^3 hybridised carbon atom is linked to four other carbon atoms. It has three dimensional network of carbon atoms. It is very difficult to break extended covalent bonding and therefore diamond is a hardest substance on the earth. That's why it is used as an abrasive.

61. Monosilane (e.g., SiH_4) on coming in contact with air burns with a luminous flame producing vortex ring. These rings are of silica.

$$SiH_4 + 2O_2 \longrightarrow SiO_2 + 2H_2O$$

62. Graphite has a two dimensional structure. In this case only three of the four valence electrons of each carbon atom are involved in bonding. Thus, each carbon atom makes use of sp^2-hybrid orbitals. Hence, the fourth valency of each carbon atom remains unsatisfied *i.e.,* the fourth valency electron remains unpaired or free. This free electron can easily move from one carbon atom to another under the influence of applied potential. So, in structure of graphite only one electron is free on each carbon atom.

63. Quartz is the amorphous form of silicon (Si).

64. When SiO_2 reacts with HF, silicon tetrafluoride is formed which dissolves in excess HF to from hydrofluorosilicic acid.

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O;$$
$$SiF_4 + 2HF \longrightarrow H_2SiF_6$$

65. Silica on heating with carbon at high temperature gives carborundum (silicon carbide).

$$SiO_2 + 3C \xrightarrow{\Delta} \underset{\text{carborundum}}{SiC} + 2CO$$

Carborundum is very hard substance.

66. It react with alkali as well as acid, so amphoteric.

67. Organic acids dissolve lead in the presence of oxygen.

$$Pb + 2CH_3COOH + \frac{1}{2}O_2 \longrightarrow Pb(CH_3COO)_2 + H_2O$$

68. Because of its snow like appearance and very low melting point (–56.6°C at 5.2 atm pressure), solid CO_2 is commonly known as 'dry ice' or 'drikold'.

70. $CO_2 + H_2O \longrightarrow H_2CO_3$

71. Sodium oxalate react with conc. H_2SO_4 to form CO and CO_2 gas.

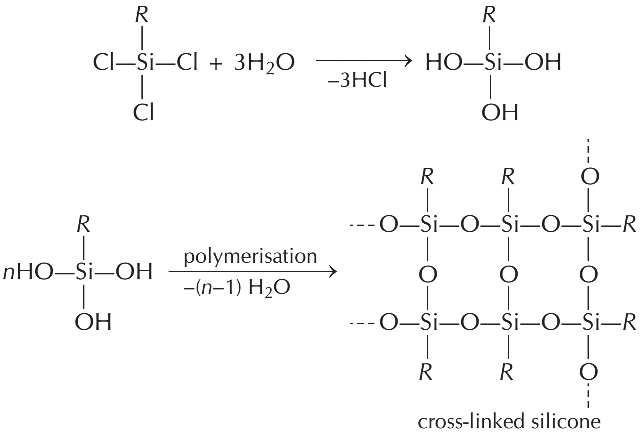
72. Sheet silicates are formed when three oxygen atoms (bridging O-atoms) of each $(SiO_4)^{4-}$ unit are shared. Hence, the general formula of sheet silicates is $(Si_2O_5)^{2n-}$.

73. Silicones are organosilicon compounds having the general formula $(R_2SiO)_n$ which contains repeated R_2SiO units held by Si—O—Si linkages.

74. When Si is heated with CH_3Cl at high temperature in the presence of Cu as a catalyst, a mixture of mono-, di- and trimethylchlorosilanes along with a small amount of tetramethylsilane is formed.

$$\underset{\text{methyl chloride}}{CH_3Cl} + Si \xrightarrow[570\text{ K}]{\text{Cu powder}} CH_3SiCl_3 + (CH_3)_2SiCl_2 + (CH_3)_3SiCl + (CH_3)_4Si$$

75. Hydrolysis of alkyltrichlorosilanes followed by condensation polymerisation gives cross-linked silicones.



$$Cl-\overset{R}{\underset{Cl}{Si}}-Cl + 3H_2O \xrightarrow[-3HCl]{} HO-\overset{R}{\underset{OH}{Si}}-OH$$

$$nHO-\overset{R}{\underset{OH}{Si}}-OH \xrightarrow[-(n-1)\,H_2O]{\text{polymerisation}}$$

cross-linked silicone

77. Al_2Cl_6, In_2Cl_6, Ca_2Cl_6

78. B_4C is the hardest substance along with diamond.

79. Aluminium metal burns in air at high temperature. This reaction is highly exothermic.

$$4Al + 3O_2 \longrightarrow 2Al_2O_3$$

Round II

1. Borax is a salt of strong base (NaOH) and weak acid (H_3BO_3), therefore, its aqueous solution is basic in nature.

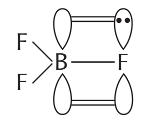
2. In B_2H_6, each boron atom is sp^3-hybridised.

3. (i) $$\underset{\text{borax }(A)}{Na_2B_4O_7} + 2HCl + 5H_2O \longrightarrow 2NaCl + \underset{\substack{\text{orthoboric acid}\\(X)}}{4H_3BO_3}$$

(ii) $$\underset{(X)}{H_3BO_3} \xrightarrow{\Delta,\,370\text{ K}} \underset{\text{metaboric acid}}{HBO_2} + H_2O$$

$$4HBO_2 \xrightarrow[-H_2O]{\Delta,\,>370\text{ K}} \underset{\text{tetraboric acid}}{[H_2B_4O_7]} \xrightarrow{\text{Red heat}} \underset{\substack{\text{boron trioxide}\\(Z)}}{2B_2O_3} + H_2O$$

4. In BF_3, boron is sp^2 hybridised. It has a vacant 2*p*-orbital. Each fluorine in BF_3 has completely filled unutilized 2*p*-orbitals. Since, both of these orbitals belong to same energy level so $p\pi$-$p\pi$ back bonding occurs in which a lone pair of electrons is transferred from unutilized completely filled 2*p*-orbital of F to vacant 2*p*-orbital of B. This type of bond formation is known as back bonding. Therefore, B—F bond has some double bond character. That's why all the three boron-fluorine bonds are shorter than the usual single boron-fluorine bond.



Back bonding in BF_3 molecule

In $[BF_4]^-$ ion, boron is sp^3 hybridised. It does not have empty 2*p*-orbital, so there is no back bonding. In $[BF_4]^-$ ion all the four B—F bonds are purely single bonds. Double bonds are shorter than single bonds. Therefore, B—F bond length in BF_3 is shorter (130 pm) than B—F bond length (143 pm) in $[BF_4]^-$.

5. When an aqueous solution of borax is acidified with HCl, boric acid is formed.

$$\underset{\text{borax}}{Na_2B_4O_7} + 2HCl + 5H_2O \longrightarrow 2NaCl + \underset{\text{boric acid}}{4H_3BO_3}$$

Boric acid is a white crystalline solid. It is soapy to touch because of its planar layered structure. Boric acid is a weak monobasic acid. It is not a protonic acid but acts as a Lewis acid by accepting electrons from a hydroxyl ion.

$$B(OH)_3 + 2HOH \longrightarrow [B(OH)_4]^- + H_3O^+$$

6. Boron trihalides are Lewis acid. The order of their acidic strength is as:

$$BF_3 < BCl_3 < BBr_3 < BI_3$$

7. Boric acid is used in carom boards for smooth gliding of pawns because H-bonding in H_3BO_3 gives it a layered structure.

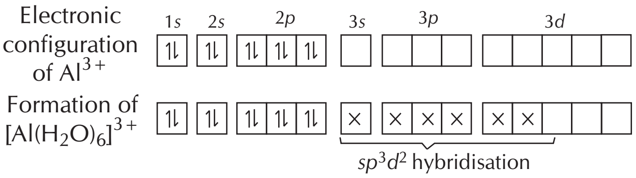
8. BCl_3 on hydrolysis in water forms tetrahedral $[M(OH)_4]^-$ species; in which the hybridisation state of B is sp^3.

$$BCl_3 + 3H_2O \longrightarrow B(OH)_3 + 3HCl$$

$$B(OH)_3 + H_2O \longrightarrow [B(OH)_4]^- + H^+$$

$AlCl_3$ in acidified aqueous solution forms octahedral $[Al(H_2O)_6]^{3+}$ ion. In this complex, the 3d orbitals of Al are involved and the hybridisation state of Al is sp^3d^2.

$$AlCl_3 + \text{water} \xrightarrow{HCl} [Al(H_2O)_6]^{3+} + 3Cl^-(aq)$$



9. NaOH reacts with Al to evolve dihydrogen gas. The pressure of the hydrogen gas can be used to open drains.

$$2Al(s) + 2NaOH(aq) + 2\,H_2O(l) \longrightarrow 2NaAlO_2(aq) + 3H_2(g)$$

10. Graphite has layered structure. Layers are held together by weak van der Waals' forces and hence, can be made to slip over one another. Therefore, graphite acts as a dry lubricant.

11. CO is a strong reducing agent but it cannot reduce ZnO as for $CO \rightarrow CO_2\ \Delta_rG°$ is always higher than that of ZnO. Thus, no reaction takes place.

12. CO_2 is a green house gas. About 75% of the solar energy reaching the earth is absorbed by the earth's surface. The rest of the heat (IR rays) radiates back to the atmosphere. But the heat radiated by the heated surface cannot pass freely into the space because excessive CO_2 in the atmosphere absorb higher wavelength IR rays. This results in increase in the average temperature of the atmosphere. This is known as green house effect.

13. In SiF_6^{2-} and $SiCl_6^{2-}$, SiF_6^{2-} is known due to the small size of F atoms. The small six F atoms can be easily accommodated around Si atom to form SiF_6^{2-} while in $SiCl_6^{2-}$, six large Cl atoms cannot be accommodated around Si atom.

14. Aluminium oxide is highly stable therefore, it is not reduced by chemical reactions.

15. Anodising of Al results in the formation of a protective oxide layer over Al surface.

16. Solid CO_2 is known as dry ice because it evaporates at −78°C without changing in the liquid state.

17. Zeolite have SiO_4 and AlO_4 tetrahedrons linked together in a three dimensional open structure in which four or six membered ring predominate. Due to open chain structure they have cavities and can take up water and other small molecules.

18. Alzeimer disease causes senility and loss of memory.

19. Carbon suboxide has linear structure with C—C bond length equal to 130 Å and C—O bond length equal to 120 Å.

$$O{=}C{=}C{=}C{=}O \longleftrightarrow {}^-O{-}C{\equiv}C{-}C{\equiv}O^+$$

20. CO_2 get is absorbed by $Ca(OH)_2$ to form insoluble $CaCO_3$.

21. $$CO + NaOH \xrightarrow{200°C} \underset{\text{sodium formate}}{HCOONa}$$

22. Iron oxide impurity — Baeyer's process

Silica impurity — Serpeck's process

23. The stability of hydrides of carbon family decreases down the group, hence order is

$$CH_4 > SiH_4 > GeH_4 > SnH_4 > PbH_4$$

24. Lead react with water to form lead hydroxide $Pb(OH)_2$ hence, lead pipes are not suitable for drinking purpose.

25. Since, metal X on treatment with sodium hydroxide gives white precipitate which dissolves in excess of NaOH to give soluble complex (B), therefore, the metal X is Al.

$$\underset{(X)}{Al} + 3NaOH \longrightarrow \underset{\substack{\text{white ppt.}\\(A)}}{Al(OH)_3\downarrow} + 3Na^+$$

$$\underset{(A)}{Al(OH)_3} + \underset{\text{(excess)}}{NaOH} \longrightarrow \underset{\substack{\text{sodium tetrahydroxoaluminate (III)}\\(B)}}{2Na^+[Al(OH)_4]^-}$$

$$\underset{(A)}{Al(OH)_3} + 3HCl(aq) \longrightarrow \underset{(C)}{AlCl_3} + 3H_2O$$

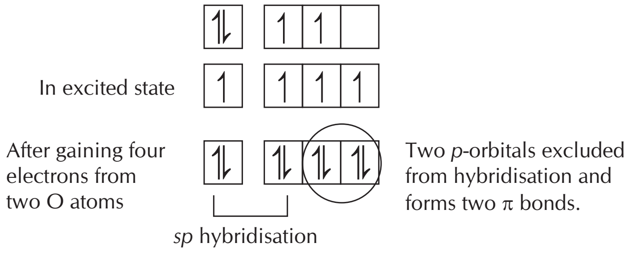
$$\underset{(A)}{2Al(OH)_3} \xrightarrow{\Delta} \underset{(D)}{Al_2O_3} + 3H_2O$$

26. $_{13}Al = 1s^2, 2s^2, 2p^6, 3s^2, 3p^1$

$_{31}Ga = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^1$

From the electronic configuration it is clear that Ga have extra 10d electrons. Because of the poor screening effect of these electrons, nuclear charge increases and hence, the nucleus holds the outer electrons more tightly and results in reduced radii.

27. $C_6 = 1s^2, 2s^2, 2p^2$



28. Because of the presence of only one —OH group in the hydrolysis product of Me_3SiCl, it blocks the terminal of silicon polymer thus, controls the chain length.

29. Fullerenes are cage-like molecules and graphite is the thermodynamically most stable allotrope of carbon. It is slippery and soft and hence, used as a dry lubricant in machines.

30. The given structure reveals that four terminal H-atoms and two B atoms lie in one plane and two bridged H-atoms lie in a plane perpendicular to the rest of the molecules. Out of the six B—H bonds, two are $3c\text{-}2e^-$ bonds and four are $2c\text{-}2e^-$ bonds.

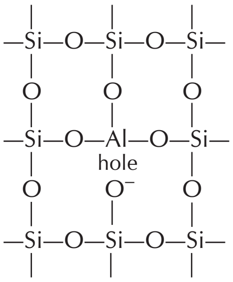
31. $BF_3 + H_2O \longrightarrow H[BF_3OH]$

$BF_3 + 3H_2O \longrightarrow H_3BO_3 + 3HF$

Since B has 6 electrons in the outer shell in BF_3 molecules, it can readily accept a lone pair of electrons from a donor atoms. Thus, acts as a catalyst. Other given is also correct.

32. Calcium carbide on hydrolysis gives acetylene. Calcium carbide contains C_2^{2-} anion.

33. Aluminium is a trivalent metal when it replaces a few Si atoms (tetravalent) from 3D structure of SiO_2, the structure takes the following form.



34. Increased stability of lower valent states on descending a group is illustrated by the facts that Ge^{2+} and Sn^{2+} are strong reducing agent.

35. Si—Si bonds are weaker than Si—O bonds and Si has no tendency to form double bonds with itself.

36. Silicones are organosilicon polymers which have $—R_2SiO—$ as repeating unit. These are water repellant in nature because of the presence of cross-linking in their structure in the presence of moisture.

37. Boric acid is a Lewis acid, in it boron possesses sp^2 hybridisation and their molecules are held together by hydrogen bonding.

38. The more representative formula of $NaBO_3$ is $Na_2[B_2CO_2(OH)_4]\cdot 6H_2O$ with O_2 signifying peroxide linkage and with a +3 oxidation number.

39. Boric acid is slippery due to hydrogen bonding.

40. Only one electron pair of pyridine can be accommodated, not two electron pairs.

41. $AlCl_3$ exists as Al_2Cl_6, It is covalent and gets easily hydrolysed. It is a Lewis acid and due to covalent bonding it has lower melting point.

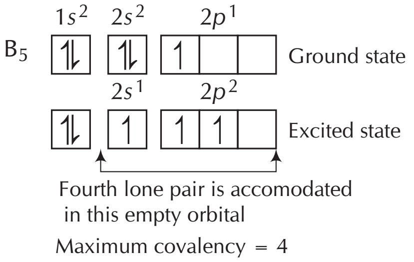
42. Due to high heat of hydration in water, it dedimerises and forms complex of type R_3NAlCl_3 with R_3N.

43. In case of Sn, +4 oxidation state is more stable due to absence of inert pair effect.

44. For Pb the more stable oxidation state is +2 but in PbO_2, it is in +4 oxidation state thus PbO_2 has great tendency to get reduced into PbO (+2 OS). Therefore, it acts as an oxidising agent.

45. Lighter elements of a group like B does not exhibit inert pair effect.

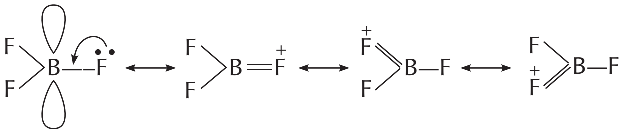
46.



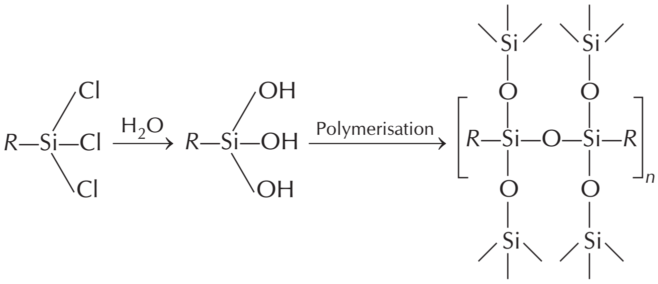
Due to absence of 2*d*-orbital, maximum covalency is four. Thus, BF_6^{3-} is not formed,

Thus (a) is not formed. BH_4^- $(BH_3 + H^-)$, $B(OH)_4^-$ $(B(OH)_3 + OH^-)$ and BO_2^- are formed.

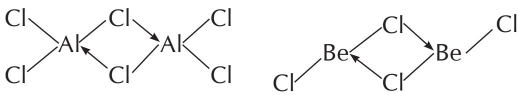
47. In BF_3 there is significant $p\pi$-$p\pi$ interaction between unshared *p*-orbital (having no electron) over boron and the lone pair of electron over fluorine in 2*p*-orbital.



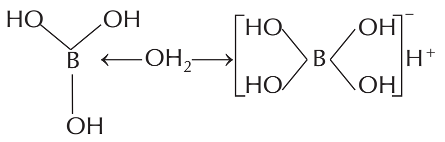
48. $RSiCl_3$ gives cross linked silicone polymer on hydrolysis.



49. Chlorides of both beryllium and aluminium have bridged structures in solid phase



Boric acid is not a protonic acid.



Borazole, inorganic benzene is $B_3N_3H_6$

50. Due to inert pair effect, the stability of +2 oxidation state increases as we move down this group.

$$\therefore \quad SiX_2 < GeX_2 < SnX_2 < PbX_2$$

51. In MCl_2, oxidation state of $M = +2$

In MCl_4, oxidation state of $M = +4$

Higher the oxidation state, smaller the size.

Greater the polarising power, greater the covalent characteristic.

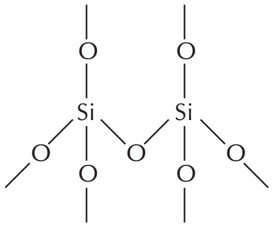
Hence, MCl_4 is more covalent and MCl_2 is more ionic.

52. A species is amphoteric if it is soluble in acid (behaves as a base) as well as in base (behaves as an acid).

$$\underset{\text{basic}}{SnO_2} + \underset{\text{acid}}{4HCl} \longrightarrow SnCl_4 + 2H_2O$$

$$\underset{\text{acid}}{SnO_2} + \underset{\text{base}}{2NaOH} \longrightarrow Na_2SnO_3 + H_2O$$

53.



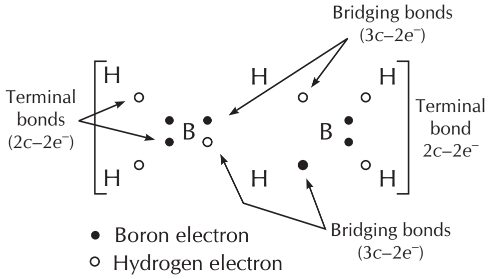
54. Aqueous solution of $AlCl_3$ is acidic due to hydrolysis.

$$AlCl_3 + 3H_2O \rightleftharpoons Al(OH)_3 + 3HCl$$

On strongly heating $Al(OH)_3$ is converted into Al_2O_3.

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$$

55. B_2H_6 has structure



56. $AlCl_3$ is covalent but in water, it becomes ionic due to large hydration energy of Al^{3+}.

$$AlCl_3 + 6H_2O \rightleftharpoons [Al(H_2O)_6]^{3+} + 3Cl^-$$

57. As temperature decreases, white tin (β-form) changes to grey tin (α-form).

$$\alpha\text{-Sn} \xrightleftharpoons{13.2^\circ C} \beta\text{-Sn}$$

α-Sn has a much lower density.

58. C-atoms form covalently bonded plates (layers). Layers are bonded weakly together, that's why one layer can slide over other and cause lubricacy. It cannot be melted easily as large number of atoms being bonded strongly in the layer form big entity.

59. Mud is colloidal charged solution which on treatment with alum (Al^{3+}) gets neutralised or coagulated.

12

Purification and Characterisation of Organic Compounds

JEE Main MILESTONE

- Methods of Purification
- Detection of Carbon, Hydrogen and Oxygen
- Soda Lime Test for Nitrogen
- Lassaigne's Test
- Test for Halogens
- Test for Phosphorus
- Estimation of Carbon and Hydrogen
- Estimation of Nitrogen
- Estimation of Halogens
- Estimation of Sulphur
- Estimation of Phosphorus
- Estimation of Oxygen
- Calculation of Molecular Weight

12.1 Methods of Purification

The methods which are generally employed for the purification of organic compounds are

1. Filtration
2. Crystallisation
3. Fractional crystallisation
4. Sublimation
5. Distillation, [Fractional distillation, Distillation under reduced pressure, Steam distillation, Azeotropic distillation],
6. Differential extraction
7. Chromatography.

Organic compounds either obtained from natural sources or synthesised in the laboratory have some impurities associated with them, i.e., these are not pure. Hence, it is essential to remove these impurities from the organic compound. The process of removal of impurities is called purification.

The pure compound is then tested quantitatively and qualitatively.

1. Filtration

(i) **Principle** It is based on the difference in filterability of different component of a solution.

(ii) **Process** Filtration is used to separate the insoluble solid component of the mixture from the soluble components in a given solvent. Sometime we use the filtrate of hot solution for separation. If the process of filtration is slow then it is carried out under reduced pressure using a Buchner funnel and a filter pump.

(iii) **Applications** Separation of sand from salt by dissolving in water, separation of tea leaves from tea is done by this method.

2. Crystallisation

(i) **Principle** It is based on the difference in the solubilities of the compound and the impurities in a suitable solvent.

(ii) **Process** This method is used to purify organic solids which dissolve in a particular solvent either as such or on heating while the impurities does not dissolve. A hot concentrated solution of the compound is prepared and this upon filtration and cooling gives the crystals of the pure compound.

The solvents commonly used for dissolving organic solids are water, alcohol, ether, chloroform, benzene, petroleum ether, etc.

Table 12.1 **Solvents to be Used for Crystallisation of Different Substances**

S.N.	Substances	Solvents	Polarity of solvents
1.	Hydrocarbons	Pentane, hexane, benzene, petroleum ether	Hydrophobic (non-polar)
2.	Ethers	Diethyl ether; methylene chloride (CH_2Cl_2)	
3.	Halohydrocarbons	Chloroform	
4.	Tertiary amines	Acetone	
5.	Ketones, aldehydes, esters	Ethyl acetate/methyl acetate	
6.	Phenols, alcohols	Ethanol	
7.	Carboxylic acids	Methanol	
8.	Sulphonic acid	Water	
9.	Organic salts	Water	Hydrophilic (polar)

(iii) **Applications** Sugar having common salt as impurity, can be crystallised through hot ethanol as it is soluble in hot ethanol but, common salt does not. Similarly, hot water is used to separate a mixture of benzoic acid and naphthalene.

3. Fractional Crystallisation

(i) **Principle** It is based on the slight difference in solubilities of different components of a mixture in the same solvent.

(ii) **Process** In this method, a hot concentrated solution of mixture is prepared and is allowed to cool. The less soluble component crystallises out earlier as compared to more soluble one. The various fractions are separated from time to time. Now these fractions are subjected to crystallisation.

(iii) **Applications** The mixture of glucose and fructose; sodium sulphate and sodium dichromate, $KClO_3$ + KCl are separated by this method.

4. Sublimation

(i) **Principle** This process is employed for those solids which convert directly into vapours on heating without converting into liquid phase and the vapours upon cooling give back the solid.

$$\text{Solid} \underset{\text{Cool}}{\overset{\text{Heat}}{\rightleftharpoons}} \text{Vapour}$$

(ii) **Process** In this process, the impure solid is taken into China dish and is covered with a perforated filter paper. An inverted funnel is placed over the dish and its stem is plugged with cotton. The dish is heated gently and the substance volatilises as the result. The substance now called **sublimate** is collected over the inner cold surface of the funnel. The non-volatile impurities are left behind in the China dish. The perforated filter paper allows only the vapours to go upwards and check the sublimate from falling back down into the dish.

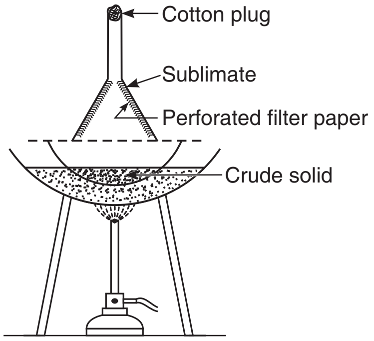


Fig. 12.1 Sublimation

(iii) **Applications** Impure samples of naphthalene, anthracene, camphor, benzoic acid, NH_4Cl, $HgCl_2$, dry ice, salicylic acid, iodine etc., can be purified by this method provided the impurities are non-volatile.

Caution Point *A mixture of two or more sublimates cannot be separated by sublimation. Such mixtures are separated by chemical methods.*

5. Distillation

(i) **Principle** It is based upon the difference in the boiling points of two liquids or two components and is generally used if an organic liquid contains a non-volatile impurity.

(ii) **Process** When a given liquid is heated to its boiling point, it is converted into vapours and the vapours on cooling condense to give back the original liquid in its pure form. The liquid so obtained is called **distillate** and the process is distillation.

Several distillation methods employed to separate mixtures are as follows

(a) **Simple distillation** It is used only for the purification of liquids which boil without decomposition at atmospheric pressure and contain non-volatile impurity. Generally, the impurity and liquid which differ in their boiling points by 30-50K are separated by this process.

A mixture of ether and toluene, hexane and toluene; benzene and aniline etc., is separated by this method.

(b) **Fractional distillation** For the separation of two liquids which have nearly equal boiling points *i.e.,* their boiling points are within the limit of 10 to 15 K (For example, acetone 329 K and methyl alcohol 338 K), the process of simple distillation cannot be used as vapours of both the liquids will be formed simultaneously and thus, the distillate will also contain both of them. In such case, the distillation is done with the help of **specially designed fractionating columns.** Such a distillation is called **fractional distillation.**

A mixture of acetone and methyl alcohol is separated by this process.

(c) **Distillation under reduced pressure** It is used for those liquids which have a tendency to decompose at a temperature below their boiling point. As we know at boiling point,

vapour pressure of liquid = its atmospheric pressure

Hence, under reduced pressure the liquid will boil at low temperature. Thus, temperature for decomposition is not reached. For example, boiling point of glycerol is 563 K but it decomposes much before its boiling temperature. However at 12 mm of Hg pressure, glycerol boils at 453 K without decomposition. Other examples include H_2O_2, concentration of sugar cane juice in sugar industry etc.

(d) **Steam distillation** It is used to purify the substances which

1. are volatile in steam but are immiscible with water.
2. possess sufficiently high vapour pressure at the boiling point of water.
3. contain non-volatile impurities.

The compound to be purified is distilled with steam under reduced pressure at a temperature below its boiling point. The pure compound comes out with steam (as it is volatile with steam) and separates on cooling down (as it is immiscible with water). The impurities being non-volatile remains in mother liquor.

In steam distillation, the liquid boils when the sum of vapour pressure due to the organic liquid (p_1) and that due to water vapour (p_2) becomes equal to the atmospheric pressure.

$$p = p_1 + p_2$$

Since, $p_1 < p_2$, the compound vaporizes at lower temperature than its boiling point.

The process of steam distillation can also be used to separate a mixture of two organic compounds one of which is steam volatile while the other is not. For example, *ortho* and *para* nitrophenols (the latter is non-volatile) compounds like aniline, nitrobenzene, sandal wood oil, terpentine oil, bromobenzene, *o*-hydroxy acetophenone etc., are purified or obtained by this process.

Azeotropic Distillation

The liquid mixtures which have constant boiling point and distill with unchanged composition are called **azeotropes.** These mixtures behave as pure liquids and cannot be separated with simple distillation. The method designed to separate **azeotropes** is called **azeotropic distillation.**

(a) Principle

It is based on the more solubility of a component of azeotrope in another solvent as compared to the other component of the azeotrope.

(b) Process

In this process a suitable solvent is added to form a new azeotrope resulting to the removal of one of the components of older azeotrope with the solvent.

(c) Applications

Dehydration of 96% ethanol (azeotrope with 96% C_2H_5OH + 4% water) to absolute alcohol with the help of benzene, as ethanol is more soluble in benzene as compared to water.

6. Differential Extraction

(i) **Principle** It is based on the more solubility of solute in a suitable organic compound as compared to water.

(ii) **Process** The process of **differential extraction** is used to separate a given organic compound present in an aqueous solution from water present in it. The process involves shaking of solution with a suitable organic solvent in which compound is more soluble as compared to water such as ether, chloroform or benzene, in a separating funnel. While performing such an act one point should be kept in mind that solvent and water must not be miscible with each other. In order to get the more amount of organic solvent, the process is repeated again and again with same sample.

(iii) **Application** Benzoic acid is separated from water by using benzene.

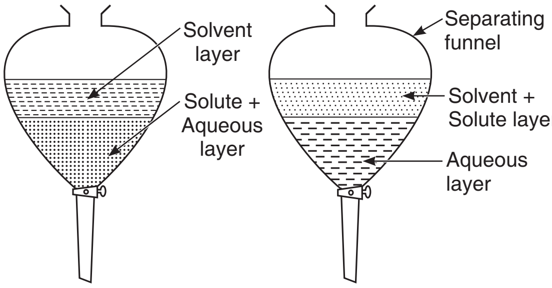


Fig. 12.2 Process of differential extraction

7. Chromatography

It is the modern technique used for separation, isolation, identification and purification of organic compounds (available in small amounts). The method was discovered by **Tswett** (a Russian botanist) in 1906. He used the technique for the separation of coloured pigments from a plant.

(i) **Principle** The process is based upon the principle of distribution of components of a given organic mixture between two phases *i.e.,* the **stationary phase** and the **mobile phase** or in other words, it is based upon the difference in the rates at which the components of a mixture move through a porous medium (stationary phase) under the influence of some solvent or gas (mobile phase).

(ii) **Process and Application** In this technique, the stationary phase can either be solid or liquid supported over a solid and the mobile phase may be a liquid or gas. Over the years the number of techniques has been developed under chromatography which are used in the separation of different compounds according to the need. For example, column or adsorption chromatography, paper chromatography, thin layer chromatography, gas-liquid chromatography etc. A brief outline review of these has been given in the following table.

Table 12.2 **Types of Chromatography**

S.N.	Types of chromatography	Mobile/ Stationary phase	Uses
1.	Adsorption or column chromatography	Liquid/solid	Large scale separations
2.	Thin layer chromatography (TLC)	Liquid/solid	Qualitative analysis
3.	High performance liquid chromatography (HPLC)	Liquid/solid	Qualitative and quantitative analysis
4.	Gas liquid chromatography (GLC)	Gas/liquid	Qualitative and quantitative analysis
5.	Paper or partition chromatography	Liquid/liquid	Qualitative and quantitative analysis

Some Important Facts Related to Chromatography are

1. In chromatography stationary phase is of solid Al_2O_3; SiO_2, starch and charcoal mainly, while mobile phase is of pure solvent.

2. The relative adsorption of each constituent of the mixture is expressed in terms of its **retardation factor,** *i.e.,* R_f value

$$R_f = \frac{\text{Distance moved by the substance from base line } (x)}{\text{Distance moved by the solvent from base line } (y)}$$

$$R_f = \frac{x}{y}$$

3. The R_f value of a substance depends on the
(i) nature of the substance,
(ii) nature of the solvent,
(iii) nature of the filter paper used, and
(iv) temperature. The spots of the coloured compounds are visible on the TLC plate.

4. The spots of colourless compounds are seen under U.V. (ultra violet) light. Another detection method is to place the TLC plate in a covered jar containing crystals of I_2 (iodine). The compound which absorbs I_2 will be seen as brown spots.

5. Sugars are separated by using the solvent BAW (*n*-butanol acetic acid-H_2O in the volume ratio of 4 : 1 : 3) and detected by spraying the plate with aniline hydrogen phthalate solution.

6. If the solvent is placed at the top and the upper end of the filter paper dips in it, the solvent moves downwards. This is called **descending paper chromatography.** If the condition is revers, it is called **ascending paper chromatography.**

Caution Point *In the purification of petroleum and coal tar products for their acidic, basic and neutral components, sulphuric acid is used to separate the basic component and caustic soda solution to separate the acid component.*

Sample **Problem 1** *The fragrance of flowers is due to the presence of some steam volatile organic compounds, called the essential oils. These are generally insoluble in water at room temperature but are miscible with water vapour in vapour phase. A suitable method for the extraction of these oils from the flowers is* **[NCERT Exemplar]**

(*a*) *distillation*
(*b*) *crystallisation*
(*c*) *distillation under reduced pressure*
(*d*) *steam distillation*

Interpret (*d*) Since, essential oils are steam volatile, these are extracted from the flowers by steam distillation.

Sample **Problem 2** *The principle involved in paper chromatography is* **[NCERT Exemplar]**

(*a*) *adsorption* (*b*) *partition*
(*c*) *solubility* (*d*) *volatility*

Interpret (*b*) Paper chromatography is based on the principle of partition.

Sample **Problem 3** *During hearing of court case, the judge suspected that some changes in the documents had been carried out. He asked the forensic department to check the ink used at two different places. According to you which technique can give the best results?* **[NCERT Exemplar]**

(a) *Column chromatography*
(*b*) *Solvent extraction*
(c) *Distillation*
(*d*) *Thin layer chromatography*

Interpret (*d*) Thin layer chromatography is based on different rates of adsorption of different substances, thus found useful for identification and separation of two different dyes.

Check Point 1

1. Under what conditions can the process of steam distillation be used?
2. Why impure glycerol is purified by distillation under reduced pressure?
3. Why sublimation method can't be used for the purification of liquids?
4. In steam distillation, a compound vaporise below its boiling point, why?

Qualitative Analysis

The qualitative analysis of an organic compound implies the detection of all the major elements which can be present in it with the help of suitable chemical tests.

12.2 Detection of Carbon, Hydrogen and Oxygen

The detection of **carbon and hydrogen** is done with the help of copper oxide test. In this test the compound is mixed with double the amount of pure and dry copper oxide. The mixture is heated in a hard glass test tube which is fitted with a bulb containing delivery tube as shown in the figure below

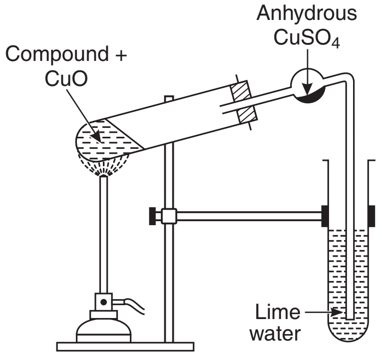


Fig. 12.3 Detection of carbon and hydrogen inorganic compounds

The other end of the delivery tube is dipped in a tube containing lime water. The bulb of delivery tube contains anhydrous $CuSO_4$ in it. The organic compound undergoes combustion as

$$\text{C of organic compound} + 2\,CuO \xrightarrow{\Delta} CO_2 + 2Cu$$

$$\text{H of organic compound} + CuO \xrightarrow{\Delta} H_2O + Cu$$

H_2O vapours turn anhydrous $CuSO_4$ blue and CO_2 evolved turns lime water milky.

$$CuSO_4 + 5H_2O \longrightarrow \underset{\text{hydrated copper sulphate (blue)}}{CuSO_4 \cdot 5H_2O}$$

$$Ca(OH)_2 + CO_2 \longrightarrow \underset{\text{milky}}{CaCO_3} + H_2O$$

Since, oxygen is present almost everywhere, no direct method is available for its detection.

Caution Point *While testing for hydrogen, it is necessary that the apparatus, copper oxide and the substance are absolutely dry. Cupric oxide being hygroscopic in nature, is strongly heated just before use.*

12.3 Sodalime Test for Nitrogen

Sodalime test involves strong heating of compound with sodalime (NaOH / CaO). The evolution of NH_3 gives the indication of nitrogen.

$$CH_3CONH_2 + NaOH / CaO \longrightarrow CH_3COO^-Na^+ + NH_3 \uparrow$$

12.4 Lassaigne's Test

This test is used to detect the presence of elements like N, S, F, Cl, Br, I, etc., and involves two steps

(i) Preparation of Lassaigne's extract
(ii) Detection of elements using Lassaigne extract

To prepare Lassaigne extract the organic substance is fused with small quantity of Na pieces in a fusion tube. The red hot tube is, then, plunged into distilled water contained in a China dish. The contents of dish are boiled for couple of minutes, then cooled and filtered. The filtered liquid is called **sodium extract** or **Lassaigne's extract.** The Lassaigne's extract is usually alkaline. If not, it is made alkaline by adding a few drops of NaOH.

During fusion, the elements like N, S, C, F, Cl, Br, I, etc., present in the organic compound, get fused with Na and convert into their ionic form as

$$Na + C + N \xrightarrow{\text{Fusion}} \underset{\text{sodium cyanide}}{Na^+C^-{\equiv}N}$$

$$2Na + S \xrightarrow{\text{Fusion}} \underset{\text{sodium sulphide}}{Na_2S}$$

$$Na + C + N + S \longrightarrow \underset{\text{sodium sulphocyanide}}{NaSCN}$$

(when N and S both are present)

$$Na + \underset{\text{halogen}}{X} \longrightarrow \underset{\text{sodium halide}}{NaX}$$

Caution Point Li *and* K *both cannot be used in Lassaigne's test in place of* Na *as the former reacts very slowly and forms covalent compounds while later reacts vigorously and thus, cannot be handled properly.*

1. Detection of Nitrogen

To a part of soda extract $FeSO_4$ solution is added and the contents are warmed. A few drops of $FeCl_3$ solution are then added and resulting solution is acidified with conc. HCl. The appearance of **bluish green** or **Prussian blue** colouration confirms the presence of nitrogen. *The reactions that occur during this test are as*

1. On heating the extract with $FeSO_4$, sodium ferrocyanide is formed.

$$2NaCN + FeSO_4 \longrightarrow Na_2SO_4 + Fe(CN)_2$$

$$Fe(CN)_2 + 4NaCN \longrightarrow \underset{\text{sodium ferrocyanide}}{Na_4[Fe(CN)_6]}$$

2. The treatment with $FeCl_3$ yield ferric ferrocyanide which has bluish green or Prussian blue colouration.

$$3Na_4[Fe(CN)_6] + 4FeCl_3 \longrightarrow \underset{\substack{\text{ferric ferro}\\ \text{cyanide}\\ \text{(Prussian blue)}}}{Fe_4[Fe(CN)_6]_3} + 12NaCl$$

3. The function of conc. HCl is destruction of $Fe(OH)_2$ which might have been formed by the action of $FeSO_4$ with NaOH.

$$FeSO_4 + 2NaOH \longrightarrow \underset{\text{green}}{Fe(OH)_2} + Na_2SO_4$$

$$Fe(OH)_2 + 2HCl \longrightarrow FeCl_2 + 2H_2O$$

If this is not done, the green colour of $Fe(OH)_2$ will interfere with the detection of nitrogen.

Caution Point *In the above test, if* Fe^{3+} *ions are in excess, green colour appears instead of blue.*

4. If the compound contains sulphur and nitrogen both sodium sulphocyanide is formed in Lassaigne's extract, which gives blood red colouration of $Fe(SCN)_3$ with $FeCl_3$.

$$Na + C + N + S \longrightarrow \underset{\text{sodium sulphocyanide.}}{NaSCN}$$

$$\xrightarrow{\text{With } FeCl_3} \underset{\substack{\text{ferric sulphocyanide}\\ \text{(blood red)}}}{Fe(SCN)_3} + 3NaCl$$

Sample Problem 4 *Lassaigne's test for the detection of nitrogen fails in*

(*a*) $NH_2CONHNH_2 \cdot HCl$ (*b*) $NH_2NH_2 \cdot HCl$
(*c*) NH_2CONH_2 (*d*) $C_6H_5NHNH_2 \cdot HCl$

Interpret (*b*) Lassaigne's test is positive for nitrogen only when the compound contains carbon alongwith nitrogen. $NH_2NH_2 \cdot HCl$ contains nitrogen but does not contain carbon, thus, NaCN is not formed and hence, test of N is negative.

2. Detection of Sulphur

Following two tests are used to detect the presence of sulphur in organic compounds :

(i) A part of Lassaigne extract is acidified with CH_3COOH and then $(CH_3COO)_2Pb$ solution is added. Formation of black precipitate confirms the presence of sulphur in the compound.

$$Na_2S + (CH_3COO)_2Pb \longrightarrow \underset{\text{black ppt.}}{PbS\downarrow} + 2CH_3COO^-Na^+$$

Caution Point *In this test* H_2SO_4 *cannot be used for dilution because lead acetate itself will react with* H_2SO_4 *to form white ppt. of lead sulphate.*

$$\underset{\text{lead acetate}}{Pb(OCOCH_3)_2} + H_2SO_4 \longrightarrow \underset{\text{white ppt.}}{PbSO_4\downarrow} + 2CH_3COOH$$

Hence, white precipitate of $PbSO_4$ *will interfere with the following test of sulphur.*

$$Pb(CH_3COO)_2 + Na_2S \longrightarrow \underset{\text{black ppt.}}{PbS\downarrow} + 2CH_3COONa$$

However, if acetic acid is used, it does not react with lead acetate, so does not interfere in the test.

(ii) A few drops of sodium nitroprusside solution are added to a part of soda extract. The appearance of purple colouration confirms the presence of sulphur.

$$Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow \underset{\text{purple colour}}{Na_4[Fe(CN)_5NOS]}$$

12.5 Test for Halogens

The soda extract of organic compound is boiled with conc. HNO_3 to expel the gases. Here, the HNO_3 decomposes NaCN and Na_2S (if present) in the soda extract as

$$NaCN + HNO_3 \longrightarrow NaNO_3 + HCN\uparrow$$

$$Na_2S + 2HNO_3 \longrightarrow 2NaNO_3 + H_2S\uparrow$$

$$Na + X \longrightarrow \underset{\text{soda extract}}{NaX} \quad (X = Cl, Br, I)$$

It is then cooled and treated with $AgNO_3$ solution. Formation of

(i) A white ppt. soluble in NH_4OH solution indicates the presence of chlorine in organic compound.

$$NaCl + AgNO_3 \longrightarrow \underset{\text{white ppt.}}{AgCl\downarrow} + NaNO_3$$

(ii) A dull yellow ppt. partially soluble in NH_4OH solution indicates the presence of bromine in the organic compound.

$$NaBr + AgNO_3 \longrightarrow \underset{\text{dull yellow ppt.}}{AgBr\downarrow} + NaNO_3$$

(iii) A yellow ppt insoluble in NH_4OH indicates the presence of iodine in the organic compound.

$$AgNO_3 + NaI \longrightarrow \underset{\text{yellow ppt.}}{AgI} + NaNO_3$$

Caution Points

(*i*) *In the detection of halogens if cyanide and sulphide are not removed before adding silver nitrate solution, these radicals will combine with silver nitrate and produce white and black precipitate of* AgCN *and* Ag_2S *respectively.*

(*ii*) H_2SO_4 *cannot be used instead of* HNO_3 *as it gives white ppt. of* Ag_2SO_4 *with* $AgNO_3$ *which interfere with the test of chlorine.*

Beilstein Test for Halogens

If organic compound gives blue or green colour at the tip of red hot copper wire, this indicates the presence of halogens in the organic compound. Several halogen free compounds such as pyridine, purines, urea, thiourea, etc., also give green colour to the flame, thus this test is not very reliable. However, if no green or blue colour appears, it confirms the absence of halogen. Thus, the test is confirmatory one to show the absence of halogens, rather than to show their presence.

Caution Point *Since* CuF_2 *is non-volatile, fluorine does not give this test.*

Layer Test for Bromine and Iodine

The presence of nitrogen and sulphur does not interfere in this test. In this test acidify a little sodium extract with dil. HNO_3 or dil. H_2SO_4 and add $CHCl_3$ or CCl_4 and excess of chlorine water. If organic layer becomes yellow or brown, bromine is present and if violet, iodine is present.

$$2NaBr + Cl_2 \longrightarrow 2NaCl + Br_2$$

$$CHCl_3 + Br_2 \longrightarrow \text{Yellow brown layer}$$

$$2NaI + Cl_2 \longrightarrow 2NaCl + I_2$$

$$CHCl_3 + I_2 \longrightarrow \text{Violet layer}$$

12.6 Test for Phosphorus

For the detection of phosphorus, organic compound is fused with sodium peroxide, hence phosphorus is converted into sodium phosphate.

$$5Na_2O_2 + \underset{\text{compound}}{2P} \xrightarrow{\text{Fuse}} \underset{\text{sodium phosphate}}{2Na_3PO_4} + 2Na_2O$$

The fused mass is extracted with water and the water extract is boiled with conc HNO_3. Upon cooling a few drops of ammonium molybdate solution are added, a yellow ppt. confirms the presence of phosphorus in the organic compound.

$$Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$$

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow \underset{\text{yellow ppt.}}{(NH_4)_3PO_4\cdot 12MoO_3} + 21NH_4NO_3 + 12H_2O$$

Check Point 2

1. Which halogen gives negative Beilstein test and why?
2. Why does hydrazine give negative Lassaigne's test however, it contains nitrogen?
3. While testing for halogens, the extract is boiled with conc. HNO_3. Explain why?
4. Why is it necessary to use acetic acid and not sulphuric acid for acidification of sodium extract for testing sulphur by lead acetate test? **[NCERT]**
5. For testing halogens in an organic compound with $AgNO_3$ solution, sodium extract (Lassaigne's test) is acidified with dilute HNO_3. What will happen if a student acidifies the extract with dilute H_2SO_4 in place of dilute HNO_3? **[NCERT Exemplar]**

Quantitative Analysis

The next step after the identification of elements is their estimation *i.e.,* to know the percentage of various elements present in an organic compound.

12.7 Estimation of Carbon and Hydrogen

The C and H in an organic compound are estimated by **Liebig method.** In this method, the organic compound is heated with dry cupric oxide in an atmosphere of dry oxygen (or air) free from CO_2. Thus, the C and H present in the organic compound are oxidised to CO_2 and water vapours respectively.

$$C + 2CuO \longrightarrow CO_2 + 2Cu$$

$$2H + 2CuO \longrightarrow H_2O + 2Cu$$

1. CO_2 vapours are passed through weighed potash bulb which absorbs CO_2 completely. The increase in the weight of potash bulb corresponds to the weight of CO_2 produced.

$$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$

2. Water vapours are passed through weighed calcium chloride tube (U-shaped). Increase in the weight of $CaCl_2$ corresponds to the weight of H_2O formed.

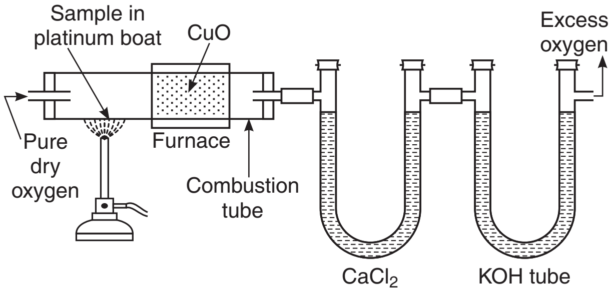


Fig. 12.4 Apparatus for the estimation of carbon and hydrogen

From the respective weights the percentage of C and H can be determined as

(i) $\% \text{ of carbon} = \dfrac{12 \times \text{mass of } CO_2 \times 100}{44 \times \text{mass of organic compound}}$

(ii) $\% \text{ of hydrogen} = \dfrac{2 \times \text{mass of } H_2O \times 100}{18 \times \text{mass of organic compound}}$

Caution Point *In this method, near the exit, a silver foil and a bright copper spiral is placed in order to remove halogen and oxides of nitrogen respectively as* Ag *foil converts halogens into* Ag*X while copper reduces oxides of nitrogen into* N_2.

Sample **Problem 6** *An organic compound contains* 69% *carbon and* 4.8% *hydrogen, the remainder being oxygen. Calculate the masses of carbon dioxide and water produced when* 0.20 *g of this substance is subjected to complete combustion.*

(*a*) 0.69 *g and* 0.048 *g* (*b*) 0.506 *g and* 0.086 *g*
(*c*) 0.345 *g and* 0.024 *g* (*d*) *None of these*

Interpret (*b*) $\%C = \dfrac{12}{44} \times \dfrac{\text{mass of } CO_2 \text{ formed}}{\text{mass of substance taken}} \times 100$

$$69 = \frac{12}{44} \times \frac{\text{Mass of } CO_2 \text{ formed}}{0.2} \times 100$$

$$\therefore \text{ Mass of } CO_2 \text{ formed} = \frac{69 \times 44 \times 0.2}{12 \times 100} = 0.506 \text{ g}$$

$$\%H = \frac{2}{18} \times \frac{\text{mass of } H_2O \text{ formed}}{\text{mass of substance taken}} \times 100$$

$$4.8 = \frac{2}{18} \times \frac{x}{0.2} \times 100$$

$$x = \frac{4.8 \times 18 \times 0.1}{100} = 0.086 \text{ g}$$

12.8 Estimation of Nitrogen

Estimation of nitrogen can be done by two ways

1. Duma's Method

In this method, organic compound is heated with dry cupric oxide in a combustion tube in the atmosphere of CO_2, which is created by heating $NaHCO_3$ and removing its moisture by passing it in conc H_2SO_4. Upon heating C and H present, are oxidised to CO_2 and water vapours respectively, while N_2 is set free. A roll of oxidised copper gauze is placed in combustion tube which prevents the backward diffusion of gases evolved. A small amount of N_2 might be oxidised to its oxides but they are reduced back to N_2 with the help of Cu placed at the end of the combustion tube.

$$2C + 2CuO \xrightarrow{\Delta} 2Cu + 2CO_2 \uparrow$$

$$2H + CuO \xrightarrow{\Delta} Cu + H_2O \uparrow$$

$$N + CuO \longrightarrow N_2 + \text{oxides of N}$$

$\text{Oxides of nitrogen} + Cu \longrightarrow CuO + N_2$

The volume of N_2 evolved is recorded with the help of **Schiff's nitrometer tube** which contains 40% KOH solution and is provided with Hg seal at the bottom to check the backward flow of the liquid. This volume is then reduced to STP by applying the gas equation, $\dfrac{p_1V_1}{T_1} = \dfrac{p_2V_2}{T_2}$

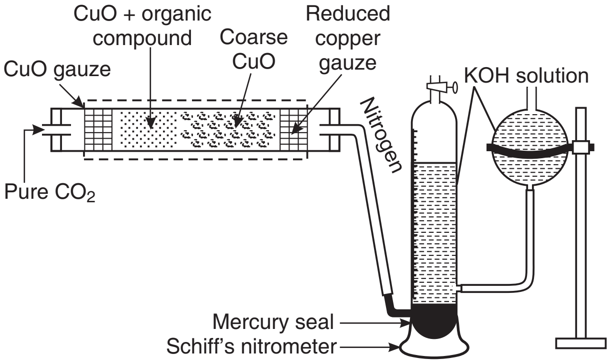


Fig. 12.5 Apparatus for the estimation of nitrogen by Duma's method

From the volume of N_2 at STP, the percentage of nitrogen is calculated as

$$\% \text{ of nitrogen} = \frac{28\,V \times 100}{22400 \times w}$$

Here, V = volume of N_2 evolved at STP

w = weight of organic compound taken

Sample Problem 7 *In Duma's method for the estimation of nitrogen, 0.30 g of an organic compound gave 50 cm^3 of nitrogen collected at 300 K and 715 mm pressure. Calculate the percentage of nitrogen in the compound. (Vapour pressure of water or aqueous tension of water at 300 K is 15 mm.)*

(*a*) 17.46
(*b*) 20.56
(*c*) 28
(*d*) 15.68

Interpret (*a*) Here, mass of the substance taken = 0.30 g

Volume of nitrogen collected = 50 cm^3

Atmospheric pressure = 715 mmHg

Room temperature = 300 K

Vapour pressure of water at 300 K = 15 mm

$\therefore$ Actual pressure of the gas (dry gas) = 715 − 15 = 700 mm Hg

Step I The volume at experimental conditions is converted to volume at STP as

$$p_1 = 700 \text{ mm}, p_2 = 760 \text{ mm}$$
$$V_1 = 50 \text{ cm}^3, V_2 = ?$$
$$T_1 = 300 \text{ K}, T_2 = 273 \text{ K}$$

Experimental STP

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

$$\Rightarrow \quad \frac{700 \text{ mm} \times 50 \text{ cm}^3}{300 \text{ K}} = \frac{760 \text{ mm} \times V_2 \text{ cm}^3}{273 \text{ K}}$$

or $$V_2 = \frac{273 \times 700 \times 50}{300 \times 760} = 41.9 \text{ cm}^3$$

Step II The volume at STP is converted into mass.

According to the definition of gram molar volume,

22400 cm^3 of nitrogen at STP weigh = 28 g

$\therefore$ 41.9 cm^3 of nitrogen at STP will weigh $= \frac{28 \times 41.9}{22400}$ g

Step III The percentage of nitrogen is calculated as

Percentage of nitrogen,

$$= \frac{\text{mass of } N_2 \text{ at STP}}{\text{mass of the substance taken}} \times 100$$

$$= \frac{28 \times 41.9 \times 100}{22400 \times 0.3} = 17.46$$

2. Kjeldahl's Method

This method is based on the principle that when the nitrogenous compound is heated with conc H_2SO_4 in the presence of potassium sulphate, (which raises the boiling point of H_2SO_4) and $CuSO_4$ (catalyst), the nitrogen present in the compound is converted to ammonium sulphate. The ammonium sulphate, so formed, is decomposed with excess of alkali and NH_3 evolved is estimated volumetrically, *i.e.*, by the titration of an acid and NH_3. The percentage of N_2 is then calculated from the amount of NH_3.

The % of nitrogen in a compound $= \frac{1.4 \times N \times V}{w}$

where, N = normality of acid used for the estimation of NH_3 volumetrically

V = volume of acid used

w = weight of organic compound taken

or $$\% \text{ N} = \frac{1.4 \times M \times 2\left(V - \frac{V_1}{2}\right)}{\text{mass of organic compound}}$$

where, V = volume of H_2SO_4 in mL

V_1 = volume of NaOH

M = molarity of H_2SO_4

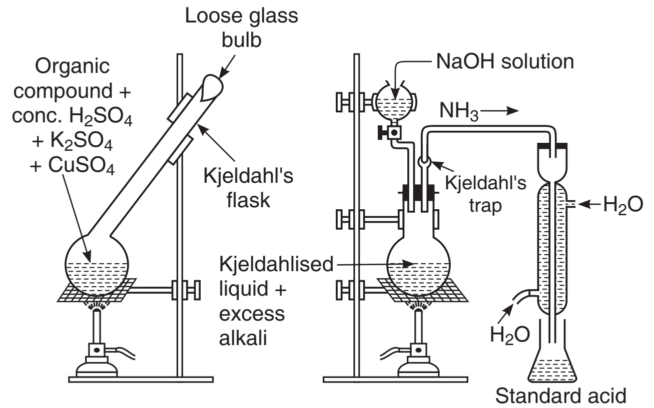


Fig. 12.6 Estimation of nitrogen by Kjeldahl's method

Cauton Point *Kjeldahl's method is not applicable to compounds containing nitrogen in nitro and azo groups and nitrogen present in the ring, as nitrogen of these compounds is not quantitatively converted into ammonium sulphate.*

Sample **Problem 8** *A sample of 0.50 g of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50 mL of 0.50 M* H_2SO_4. *The residual acid required 60 mL of 0.5 M solution of* NaOH *for neutralisation. Find the percentage composition of nitrogen in the compound.* **[NCERT]**

(*a*) 46%
(*b*) 53%
(*c*) 56%
(*d*) 87%

Interpret (*c*) Volume of the acid taken

$$= 50 \text{ mL of } 0.5 \text{ M } H_2SO_4$$
$$= 25 \text{ mL of } 1.0 \text{ M } H_2SO_4$$

Volume of alkali used for neutralisation of excess acid

$$= 60 \text{ mL of } 0.5 \text{ M NaOH}$$
$$= 30 \text{ mL of } 1.0 \text{ M NaOH}$$

$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$$

$$1 \text{ mole of } H_2SO_4 = 2 \text{ moles of NaOH}$$

Hence, 30 mL of 1.0 M NaOH = 15 mL of 1.0 M H_2SO_4

$\therefore$ Volume of acid used by ammonia = 25 − 15 = 10 mL

$$\% \text{ of nitrogen} = \frac{1.4 \times N_1 \times \text{vol. of acid used}}{w}$$

(where, N_1 = normality of acid and w = mass of the organic compound taken)

$$\% \text{ of nitrogen} = \frac{1.4 \times 2 \times 10}{0.5} = 56.0$$

12.9 Estimation of Halogens

In the case of halogens, estimation is done with **Carius method.** Here, the weighed amount of organic compound is heated in a sealed tube with fuming HNO_3 in the presence of $AgNO_3$. As a result, halogen present in the organic compound is converted into AgX which is weighed. The percentage of halogens can be calculated with the help of direct formulae as

$$\% \text{ of chlorine} = \frac{35.5}{143.5} \times \frac{\text{wt. of AgCl} \times 100}{\text{wt. of compound}}$$

$$\% \text{ of bromine} = \frac{80}{188} \times \frac{\text{wt. of AgBr} \times 100}{\text{wt. of compound}}$$

$$\% \text{ of iodine} = \frac{127}{235} = \frac{\text{wt. of AgI} \times 100}{\text{wt. of compound}}$$

Sample **Problem 9** 0.3780 *g of an organic chloro compound gave* 0.5740 *g of silver chloride in Carius estimation. Calculate the percentage of chlorine present in the compound.* **[NCERT]**

(*a*) 40% (*b*) 37% (*c*) 25% (*d*) 85%

Interpret (*b*) The mass of the organic compound taken = 0.3780 g

Mass of AgCl formed = 0.5740 g

$$\text{Percentage of chlorine} = \frac{35.5}{143.5} \times \frac{\text{mass of AgCl formed}}{\text{mass of substance taken}} \times 100$$
$$= \frac{35.5}{143.5} \times \frac{0.5740}{0.3780} \times 100$$
$$= 37.566\%$$

12.10 Estimation of Sulphur

It is also estimated by **Carius method.** In this case, the compound is heated with conc HNO_3, resulting to oxidation of its sulphur to H_2SO_4 which is collected as $BaSO_4$ by using barium chloride solution. The percentage of sulphur is calculated by the formula

$$\% \text{ of sulphur} = \frac{32}{233} \times \frac{\text{wt. of } BaSO_4 \times 100}{\text{wt. of organic compound}}$$

Sample **Problem 10** *In the estimation of sulphur by Carius method,* 0.468 *g of an organic sulphur compound afforeded* 0.668 *g of barium sulphate. Find the percentage of sulphur in the given compound.* **[NCERT]**

(*a*) 15%
(*b*) 20%
(*c*) 45%
(*d*) 50%

Interpret (*b*) The mass of organic compound taken = 0.468 g

Mass of $BaSO_4$ formed = 0.668 g

$$\text{Percentage of sulphur} = \frac{32}{233} \times \frac{\text{mass of } BaSO_4 \text{ formed}}{\text{mass of substance taken}} \times 100$$
$$= \frac{32}{233} \times \frac{0.668}{0.468} \times 100$$
$$= 19.60\%$$

12.11 Estimation of Phosphorus

For the estimation of phosphorus weighed amount of organic compound is heated with conc HNO_3 in a **Carius tube.** Phosphorus present in the compound is converted into phosphoric acid. Contents of the tube are heated with $MgCl_2$ solution in the presence of NH_4Cl and NH_4OH

(magnesia mixture), the $MgNH_4PO_4$ so formed is collected washed, dried and ignited to get magnesium pyrophosphate ($Mg_2P_2O_7$) which is weighed and the percentage of P is calculated with the help of formula

$$\text{Percentage of P} = 62 \times \frac{\text{wt. of } Mg_2P_2O_7 \text{ formed}}{222 \times \text{wt. of the compound}} \times 100$$

12.12 Estimation of Oxygen

The amount of oxygen cannot be calculated by any method. In case, the sum of percentage of all other elements present is less than 100 then,

$$\% \text{ of oxygen} = 100 - \text{sum of } \% \text{ of all other elements}$$

Hot Spot 1

CALCULATION of Empirical Formula

Although this chapter is not very important but the question, if asked, generally based on this topic. It is a very easy topic and with a small practice you can solve out the problems based on this topic easily.

The **empirical formula** of a compound is the simplest formula which expresses the relative number of atoms present in the molecule. It is calculated from the percentage composition of the compound by the following steps.

Step I **Calculation of percentage** Calculate the percentage of elements present from the given data, if percentage is not given. If in the question problem, percentage is given, left this step and start from step II.

Step II **Determination of relative number of atoms** For this divide the percentage composition of each element by its atomic weight. The different numbers so obtained are the relative number of different atoms present in the molecule.

Step III **Determination of simplest ratio** For this divide the relative number of different atoms obtained in the above step by the lowest one among them.

Step IV **Whole number** The numbers expressing the simplest atomic ratio may or may not be whole number. In case any of the number is not whole number *i.e.*, it is fractional, then multiply all the numbers by a common suitable integer to get the smallest possible whole number. Minor fractions are neglected.

Step V **Empirical formula** Write down all the constituent elements of the compound in a line and then put the above whole numbers as subscripts to the lower right corner of each respective element. This gives the empirical or simplest formula.

Sample **Problem 11** *An organic compound is found to contain* C = 40.0%, H = 6.66%. *The empirical formula is*

(*a*) CH_2O (*b*) CHO_2 (*c*) CHO (*d*) C_2H_6O

Interpret (*a*)

Element	Percentage	Atomic weight	Molar ratio	Simplest ratio
C	40	12	3.33	$\frac{3.33}{3.33} = 1$
H	6.66	1	6.66	$\frac{6.66}{3.33} = 2$
O	53.34	16	3.33	$\frac{3.33}{3.33} = 1$

Thus, the empirical formula of the compound is CH_2O.

12.13 Calculation of Molecular Weight

Following methods can be employed to calculate the molecular weight of a compound.

Molecular Weight (*m*) of Volatile Substances

Victor Meyer's Method (applicable only to volatile substances).

$$m = 2 \times \text{V.D.}$$

$$\text{or} \quad m = \frac{\text{wt. of compound} \times 22400}{\text{volume of vapour given by substance at NTP}}$$

Molecular Weight of Non-volatile Substances

(a) **Silver Salt Method** (For organic acids only)

A known mass of an organic acid is converted into its silver salt by using ammoniacal silver nitrate solution. On ignition, the silver salt of the acid leaves a residue of metallic silver.

$$RCOOH \xrightarrow[AgNO_3]{NH_4OH} RCOOAg \xrightarrow{\text{Ignition}} Ag$$

$$m = \text{equivalent wt.} \times \text{basicity}$$

$$\text{Eq. wt.} = \left(\frac{\text{wt. of silver salt} \times 108}{\text{wt. of silver}}\right) - 107$$

Sample Problem 12 *0.759 g of a silver salt of a dibasic organic acid on ignition left 0.463 g metallic silver. The equivalent weight of acid is*

(a) 50 (b) 65 (c) 70 (d) 85

Interpret (c) Eq. weight of silver salt = Eq. weight of Ag

$$\frac{0.759}{E} = \frac{0.463}{108}$$

$\therefore$ Eq. weight of silver salt $= 177$

$\therefore$ Eq. weight of acid $= 177 - 108 + 1 = 70$

(b) **Chloroplatinate Method**

(For organic bases only)

Amines and most organic bases react with chloroplatinic acid (H_2PtCl_6) to form salts, chloroplatinates of general formula $B_2H_2\ PtCl_6$ where, B is a monoacidic base. On heating, the salt decomposes to yield platinum metal.

$$2RNH_3 + H_2PtCl_6 \longrightarrow (RNH_3)_2PtCl_6 \xrightarrow{\text{Ignition}} Pt$$

$$m = \text{Eq. wt.} \times \text{acidity}$$

$$\frac{\text{wt. of chloroplatinate } (W)}{\text{wt. of platinium } (w)} = \frac{2B + 410}{195}$$

or
$$2B = \left(\frac{W}{w} \times 195\right) - 410$$

or
$$B = \left(\frac{W}{w} \times \frac{195}{2}\right) - 205$$

where, B is the equivalent weight of base.

Hot Spot 2

DETERMINATION of Molecular Formula

It is also an important topic for JEE Main alongwith calculation of empirical formula. Generally combined questions based on these two topics are asked.

The formula which expresses the actual number of atoms of various elements present in the molecule of a compound is called its **molecular formula.**

In general, molecular and empirical formula of an organic compound are related as

$$\text{Molecular formula} = (\text{Empirical formula})_n$$

where, n is a whole number. Thus, when the value of $n = 1$, the compound in question has the same empirical and molecular formula.

Further, n is the ratio between the molecular weight and the empirical formula weight of the substance, *i.e.,*

$$n = \frac{\text{molecular weight}}{\text{empirical formula weight}}$$

Thus, for determining the molecular formula of a compound, its empirical formula weight and molecular weight must be known.

Note For problems based on organic qualitative analysis see chapter experimental chemistry.

Check Point 3

1. Some potassium sulphate is added during the estimation of nitrogen by Kjeldahl's method. Why?
2. Why can Kjeldahl's method not used to estimate the percentage of nitrogen in azoxy compounds or in pyridine ?
3. Why is a copper spiral placed near the exit in Leibig method of estimation of carbon and hydrogen ?
4. Why are the results obtained for iodine by Carius method not satisfactory?
5. How a molecular formula is different from the empirical formula?

WORKED **OUT**
Examples

Example 1 *Simple distillation can be used to separate*

- (*a*) *a mixture of ethanol (bp* 78°C*) and water (bp* 100°C*)*
- (*b*) *a mixture of benzene (bp* 80°C*) and toluene (bp* 110°C*)*
- (*c*) *a mixture of ether (bp* 35°C*) and toluene (bp* 110°C*)*
- (*d*) *None of the above*

Solution (*c*) Simple distillation is used when the boiling point of two components differ widely.

Example 2 *An organic compound is heated with* CuO *in a test tube. The evolved gases are allowed to pass into lime water which turns milky. The milkiness of lime is due to*

- (*a*) $CaSO_4$ *and confirms the presence of* S
- (*b*) $CaCO_3$ *and confirms the presence of* C
- (*c*) $CaSO_3$ *and confirms the presence of* C
- (*d*) $CaCO_3$ *and confirms the presence of* S

Solution (*b*)

$$Ca(OH)_2 + SO_2 \longrightarrow \underset{\text{milky}}{CaSO_3} + H_2O$$

$$Ca(OH)_2 + CO_2 \longrightarrow \underset{\text{milky}}{CaCO_3} + H_2O$$

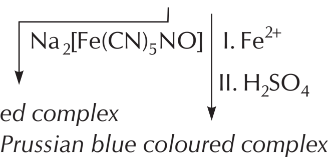
Example 3 *Which of the following compounds will give blood red colour in the Lassaigne's test for* N *?*

- (*a*) $(NH_2)_2C{=}O$
- (*b*) $H_2N(C_6H_4)SO_3H$
- (*c*) $C_6H_5SO_3H$
- (*d*) $CHCl_3$

Solution (*b*) Compounds containing both N and S give blood red colour in Lassaigne's test due to the formation of $Fe(SCN)_3$.

Thus, $H_2N(C_6H_4)SO_3H$ gives blood red colour in Lassaigne's test of nitrogen.

Example 4 *Organic compound '* A*'* $\longrightarrow$ *Lassaigne's extract*



The above Lassaigne's extract on treatment with Fe^{2+} *does not give blood red colour because of the*

- (*a*) *absence of* S *in the organic compound*
- (*b*) *presence of halogen in the organic compound*
- (*c*) *dissociation of* NaSCN *into* Na_2S *and* NaCN
- (*d*) *conversion of* NaSCN *into* HSCN

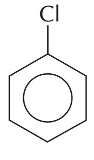
Solution (*c*) Lassaigne's extract gives violet colour complex, it clearly confirms the presence of sulphur. The formation of Prussian blue coloured complex confirms the presence of nitrogen. If that Lassaigne's extract doesn't give red colour complex it means excess of Na metal caused dissociation of NaSCN into Na_2S and NaCN.

$$2Na + NaSCN \xrightarrow{\Delta} Na_2S + NaCN$$

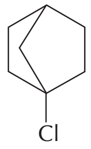
Example 5 *Which of the following compounds produce a white precipitate of* AgCl *on warming with ethanolic silver nitrate solution?*

- (*a*) $CH_2{=}CHCl$
- (*b*) $O_2N{-}CH{=}CH{-}Cl$

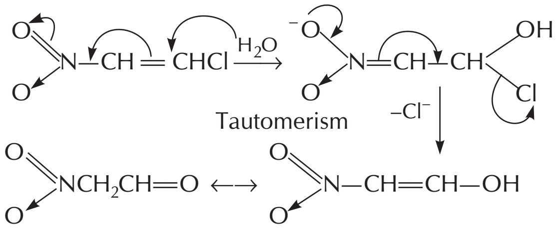
(*c*)



(*d*)



Solution (*b*)



Example 6 *An organic compound of formula* C_3H_7N *was analysed for nitrogen by Duma's method. Calculate the volume of* N_2 *gas evolved at NTP from 2 g of substance.*

- (*a*) 405 *mL*
- (*b*) 342 *mL*
- (*c*) 392 *mL*
- (*d*) 100 *mL*

Solution (*c*) % of N in $C_3H_7N = \frac{14}{57} \times 100$

Further $\quad \% \text{ of N} = \frac{1}{8} \times \frac{\text{volume of } N_2 \text{ at NTP}}{\text{weight of substance}}$

$$\Rightarrow \quad \frac{14}{57} \times 100 = \frac{1}{8} \times \frac{V}{2}$$

$$V = 392 \text{ mL}$$

Example 7 *A gaseous hydrocarbon has 85% carbon and vapour density of 28. The possible formula of the hydrocarbon will be*

(*a*) C_3H_6 (*b*) C_2H_4
(*c*) C_2H_2 (*d*) C_4H_8

Solution (*d*)

Symbol	Percent age	At. mass	Relative no. of atoms	Simplest ratio
C	85	12	$\frac{85}{12}=7.08$	$\frac{7.08}{7.08}=1$
H	15	1	$\frac{15}{1}=15$	$\frac{15}{7.08}=2.11=2$

Empirical formula is CH_2

$$\text{Mol. mass} = 2\times \text{VD} = 2\times 28 = 56$$

$$n = \frac{\text{mol. formula mass}}{\text{emp. formula mass}} = \frac{56}{14} = 4$$

Hence, molecular formula $= (CH_2)_n = (CH_2)_4 = C_4H_8$

Example 8 *60 g of an organic compound on analysis gave following results :* C = 24 g; H = 4 g *and* O = 32 g. *The compound can be*

(*a*) CH_2O_2 (*b*) C_2H_2O
(*c*) $C_2H_2O_4$ (*d*) CH_2O

Solution (*d*) 60 g of the compound contains C = 24 g

$$100 \text{ g of the compound contains C} = \frac{24\times 100}{60} = 40$$

60 g of the compound contains H = 4 g

$$100 \text{ g of the compound contains H} = \frac{4\times 100}{60} = 6.66$$

$\therefore$ Percentage age of oxygen $= 100 - (40 + 6.66) = 53.34$

Element	Percentage	Atomic mass	Relative no. of atoms	Ratio
C	40.0%	12	$\frac{40}{12}=3.33$	$\frac{3.33}{3.33}=1$
H	6.66%	1	$\frac{6.66}{1}=6.66$	$\frac{6.66}{3.33}=2$
O	53.34%	16	$\frac{53.34}{16}=3.33$	$\frac{3.33}{3.33}=1$

So, empirical formula is CH_2O.

Example 9 *In a compound* C, H *and* N *are present in* 9 : 1 : 3.5 *by weight. Molecular weight of the compound is* 108. *Molecular formula of compound is*

(*a*) $C_6H_8N_2$
(*b*) C_3H_4N
(*c*) $C_9H_{12}N_3$
(*d*) $C_2H_6N_2$

Solution (*a*) The mole ratio of C, H and N is

$$\frac{9}{12} : \frac{1}{1} : \frac{3.5}{14}$$

$$0.75 : 1 : 0.25$$

$$3 : 4 : 1$$

Empirical formula $= C_3H_4N$

Empirical formula weight = 54

Molecular weight = 108

$$n = \frac{108}{54} = 2$$

The molecular formula $= C_6H_8N_2$

Example 10 *500 mL of a hydrocarbon gas burnt in excess of oxygen yielded 2500 mL of* CO_2 *and 3.0 L of water vapour. The formula of the hydrocarbon is*

(*a*) C_5H_{12}
(*b*) CH_4
(*c*) C_2H_4
(*d*) C_3H_6

Solution (*a*)

$$\begin{array}{ccccc} C_xH_y & + \left[x+\frac{y}{4}\right]O_2 & \longrightarrow & x\,CO_2 & + \frac{y}{2}H_2O(v) \\ 500 & & & 0 & 0 \\ 0 & & & 500x & \frac{y}{2}\times 500 \end{array}$$

Now, $500x = 2500$

$\therefore$ $x = 5$

$$\frac{500y}{2} = 3000$$

$\therefore$ $y = 12$

$\therefore$ Alkane is C_5H_{12}.

Start Practice for JEE Main

Round I (Topically Divided Problems)

Purification of Organic Compounds

1. In a solution, solvent can be separated from solute by one of the following process

(a) decantation (b) filtration
(c) distillation (d) sedimentation

2. Which of the following is useful for making pure water from a solution of salt in water?

(a) Filtration (b) Distillation
(c) Chromatography (d) Steam distillation

3. A mixture of oil and water is separated by

(a) filtration
(b) fractional distillation
(c) sublimation
(d) separating funnel

4. Fractional crystallisation is carried out to separate a mixture of

(a) organic solids mixed with inorganic solids
(b) organic solids slightly soluble in water
(c) organic solids having small difference in their solubilities in suitable solvent
(d) organic solids having great difference in their solubilities in suitable solvent

5. A mixture of iodine and sodium chloride can be easily separated by

(a) fractional distillation (b) steam distillation
(c) chromatography (d) sublimation

6. Anthracene is purified by

(a) filtration (b) distillation
(c) crystallisation (d) sublimation

7. A mixture of camphor and benzoic acid can be easily separated by

(a) sublimation
(b) extraction with solvent
(c) fractional crystallisation
(d) chemical method

8. A mixture of acetone and methanol can be separated by

(a) steam distillation (b) vacuum distillation
(c) fractional distillation (d) None of these

9. Fractional distillation is useful to obtain

(a) petroleum (b) coal tar
(c) crude alcohol (d) All of these

10. Sublimation is a process in which a solid

(a) changes into vapour form
(b) changes into another allotropic form
(c) changes into liquid form
(d) None of the above

11. Impure glycerine can be purified by

(a) steam distillation (b) simple distillation
(c) vacuum distillation (d) extraction with a solvent

12. The best and latest technique for isolation, purification and separation of organic compounds is **[NCERT]**

(a) crystallisation (b) distillation
(c) sublimation (d) chromatography

13. Absolute alcohol cannot be obtained by simple fractional distillation because

(a) pure C_2H_5OH is unstable
(b) C_2H_5OH forms hydrogen bonds with water
(c) boiling point of C_2H_5OH is very close to that of water
(d) constant boiling azeotropic mixture is formed with water

14. A mixture of iron fillings and sulphur cannot be separated by

(a) heating
(b) magnet
(c) shaking with CS_2
(d) washing in a current of water

15. Chromatography was discovered by

(a) Kekule (b) Pauling
(c) Rutherford (d) Tswett

16. Chromatography technique is used for the separation of
(a) small samples of mixture
(b) plant pigments
(c) dyestuff
(d) All of the above

17. Adsorbent is made of … in TLC.
(a) silica gel (b) alumina
(c) Both (a) and (b) (d) None of these

18. In paper chromatography
(a) mobile phase is liquid and stationary phase is solid
(b) mobile phase is solid and stationary phase is liquid
(c) Both phases are liquids
(d) Both phases are solids

19. Steam distillation is based on the fact that vaporisation of organic liquid takes place at
(a) lower temperature than its boiling point
(b) higher temperature than its boiling point
(c) its boiling point
(d) water and organic liquid both undergo distillation

20. Essential oils can be isolated by
(a) crystallization (b) steam distillation
(c) sublimation (d) distillation

21. Sublimation can't be used for the purification of
(a) benzoic acid (b) camphor
(c) urea (d) naphthalene

22. Which of the substance is purified by sublimation?
(a) Naphthalene (b) Benzoic acid
(c) Camphor (d) All of these

Qualitative Analysis of Organic Compounds

23. The sodium extract of an organic compound on acidification with acetic acid and addition of lead acetate solution gives a black precipitate. The organic compound contains
(a) nitrogen (b) halogen
(c) sulphur (d) phosphorus

24. Which of the following sodium compound/compounds are formed when an organic compound containing both nitrogen and sulphur is fused with sodium?
(a) Cyanide and sulphide
(b) Thiocyanate
(c) Sulphite and cyanide
(d) Nitrate and sulphide

25. The sodium extract of an organic compound on treatment with $FeSO_4$ solution, $FeCl_3$ and HCl gives a red solution. The organic compound contains
(a) both nitrogen and sulphur
(b) nitrogen only
(c) sulphur only
(d) halogen

26. Nitrogen containing organic compound when fused with sodium forms
(a) sodium azide (b) sodium cyanide
(c) sodamide (d) sodium cyanate

27. Lassaigne's test is used for the detection of
(a) carbon only
(b) hydrogen only
(c) oxygen only
(d) nitrogen, sulphur and halogens

28. In Lassaigne's test, the organic compound is fused with a piece of sodium metal in order to
(a) increase the ionisation of the compound
(b) decrease the melting point of the compound
(c) increase the reactivity of the compound
(d) convert the covalent compound into a mixture of ionic compounds

29. Copper wire test of halogens is known as
(a) Liebig's test (b) Lassaigne's test
(c) Fusion test (d) Beilstein's test

30. Which of the following statements is not applicable to Beilstein test?
(a) Green or bluish green flame is due to the formation of volatile cupric halides
(b) It does not tell us to which halogen is present in the organic compound
(c) It is a very sensitive test that can be easily performed
(d) It is a sure test for the presence of halogen

31. Detection of phosphorus in the compound can be done by its conversion into phosphate. Reagent to identify phosphate ion is
(a) sodium nitroprusside
(b) ammonium molybdate
(c) potassium ferrocyanide
(d) potassium ferricyanide

32. The presence of carbon in an organic compound is detected by heating it with
(a) sodium metal to convert it into NaCN
(b) CaO to convert it into CO which burns with a blue flame
(c) CuO to convert it into CO_2 which turns lime water milky
(d) Cu wire to give a bluish green flame

33. The sodium extract of an organic compound on boiling with HNO_3 and then adding of ammonium molybdate solution gives a yellow precipitate. The compound contains
(a) nitrogen (b) phosphorus
(c) sulphur (d) chlorine

34. In Lassaigne's solution, pink/violet colouration is produced when sodium nitroprusside solution is added. It indicates the presence of

(a) sulphur (b) nitrogen
(c) chlorine (d) None of these

35. Select the correct statement about the detection of element in the organic compounds.

(a) Sulphur present in the organic compound on fusion with sodium converts into $Na_2S_2O_3$
(b) $FeCl_3$ gives purple colour when added to the sodium fusion extract
(c) Sodium nitroprusside is used to detect the presence of sulphur
(d) All of the above

36. The function of boiling sodium extract with conc. HNO_3 before testing for halogen is

(a) to make the solution acidic
(b) to make the solution clear
(c) to convert Fe^{2+} to Fe^{3+}
(d) to destroy CN^- and S^{2-} ions

37. In the Lassaigne's test for nitrogen in an organic compound, the Prussian blue colour is obtained due to the formation of **[NCERT]**

(a) $Na_4[Fe(CN)_6]$ (b) $Fe_4[Fe(CN)_6]_3$
(c) $Fe_2[Fe(CN)_6]$ (d) $Fe_3[Fe(CN)_6]_4$

Quantitative Analysis of Organic Compounds

38. Carbon and hydrogen are estimated in organic compounds by

(a) Kjeldahl's method
(b) Duma's method
(c) Liebig's method
(d) Carius method

39. Percentage of hydrogen is maximum in

(a) C_2H_4 (b) CH_4
(c) C_2H_2 (d) C_6H_6

40. Duma's method involves the determination of nitrogen content in the organic compound in the form of

(a) NH_3 (b) N_2
(c) NaCN (d) $(NH_4)_2SO_4$

41. In the estimation of nitrogen by Duma's method, 1.18 g of an organic compound gave 224 mL of N_2 at NTP. The percentage of nitrogen in the compound is

(a) 20.0 (b) 11.8
(c) 47.7 (d) 23.7

42. In Kjeldahl's method for the estimation of nitrogen, the formula used to

(a) $\%\text{ of N} = \frac{1.4\,Vw}{N}$ (b) $\%\text{ of N} = \frac{1.4\,VN}{w}$
(c) $\%\text{ of N} = \frac{VNw}{1.8}$ (d) $\%\text{ of N} = \frac{1.4\,wN}{V}$

43. Mark the incorrect statement for Kjeldahl's method of estimation of nitrogen.

(a) Nitrogen gas is collected over caustic potash solution
(b) Potassium sulphate is used as boiling point elevator of H_2SO_4
(c) Copper sulphate or mercury acts as a catalyst
(d) Nitrogen is quantitatively decomposed to give ammonium sulphate

44. The simplest formula of a compound containing 50% of element X (at. wt. 10) and 50% of element Y (at. wt. 20) is

(a) XY (b) XY_2
(c) X_2Y (d) X_2Y_2

45. A compound containing 80% C and 20% H is likely to be

(a) C_6H_6 (b) C_2H_6
(c) C_2H_4 (d) C_2H_2

46. The empirical formula of an acid is CH_2O_2, the probable molecular formula of the acid may be

(a) $C_2H_4O_2$ (b) $C_3H_6O_4$
(c) $C_2H_2O_4$ (d) CH_2O_2

47. In the estimation of sulphur in an organic compound, fuming nitric acid is used to convert sulphur into

(a) SO_2 (b) H_2S
(c) H_2SO_3 (d) H_2SO_4

48. Phosphorus is estimated as

(a) Na_3PO_4 (b) P_2O_5
(c) P_2O_3 (d) $Mg_2P_2O_7$

49. 0.4 g of a silver salt of a monobasic organic acid gave 0.26 g pure silver on ignition. The molecular weight of the acid is (atomic weight of silver = 108)

(a) 58 (b) 37
(c) 89 (d) 105

50. An organic compound contains 29.27% carbon, 5.69% hydrogen and 65.04% bromine. Its empirical formula is

(a) C_3H_5Br (b) C_3H_3Br
(c) $C_2H_4Br_2$ (d) C_3H_7Br

51. The silver salt of a monobasic acid on ignition gave 60% of Ag. The molecular weight of the acid is

(a) 37 (b) 57
(c) 73 (d) 88

52. How much of sulphur is present in an organic compound, if 0.53 g of the compound gave 1.158 g of $BaSO_4$ on analysis ?

(a) 10% (b) 15%
(c) 20% (d) 30%

Miscellaneous

53. Molecular mass of a volatile substance may be obtained by

(a) Beilstein method
(b) Lassaigne method
(c) Victor Meyer's method
(d) Liebig's method

54. The most satisfactory method to separate sugars is to use

(a) fractional crystallisation
(b) chromatography
(c) Benedict's reagent
(d) Carius method

55. Incorrect statement is

(a) Aniline can be purified by steam distillation
(b) Beilstein test is not given by fluorine
(c) Kjeldahl's method is used for the estimation of sulphur
(d) Lassaigne's test is used in the qualitative detection of elements in organic compounds

Round II (Mixed Bag)

Only One Correct Option

1. During $AgNO_3$ test for detection of halogens, sodium extract is boiled with few drops of conc. HNO_3 to decompose

(a) NaCN (b) Na_2S
(c) Both (a) and (b) (d) None of these

2. In Carius method, 0.099 g organic compound gave 0.287 g AgCl. The percentage of chlorine in the compound will be

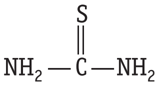
(a) 28.6 (b) 71.7
(c) 35.4 (d) 64.2

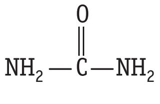
3. Red colour complex ion formed on adding $FeCl_3$ to sodium extract when N and S both are present in organic compound is

(a) $[Fe(CN)_6]^{4-}$ (b) $[Fe(CNS)]^{2+}$
(c) $[Fe(CNS)_2]^{+}$ (d) $[Fe(CN)_6]^{3-}$

4. Which of the organic compounds will give red colour in Lassaigne's test?

(a) NaCN

(b) 
$NH_2-\overset{\overset{S}{\|}}{C}-NH_2$

(c) 
$NH_2-\overset{\overset{O}{\|}}{C}-NH_2$

(d) None of these

5. In kjeldahl's method of estimation of nitrogen, $CuSO_4$ acts as

(a) oxidising agent
(b) reducing agent
(c) catalytic agent
(d) hydrolysis agent

6. 4 g of hydrocarbon on complete combustion gave 12.571 g of CO_2 and 5.143 g of water. What is the empirical formula of the hydrocarbon?

(a) CH (b) C_2H_3
(c) CH_2 (d) CH_3

7. Glycerol can be separated from spent-lye in soap industry by

(a) steam distillation
(b) fractional distillation
(c) distillation under reduced pressure
(d) ordinary distillation

8. The relative adsorption of each component of the mixture is expressed in terms of

(a) adsorption factor (b) retention factor
(c) co-factor (d) sorption factor

9. Which of the following elements can't be detected by direct tests?

(a) N (b) O (c) S (d) Br

10. Mixture of sugar and common salt is separated by crystallisation by dissolving in

(a) H_2O (b) C_2H_5OH
(c) C_6H_6 (d) None of these

11. A hydrocarbon contains 10.5 g carbon and 1 g hydrogen. Its 2.4 g has 1 L volume at 1 atm and 127°C. Hydrocarbon is

(a) C_6H_7 (b) C_6H_8 (c) C_5H_6 (d) C_6H_6

12. 0.5 g of hydrocarbon gave 0.9 g water on combustion. The percentage of carbon in the hydrocarbon is

(a) 60.6 (b) 28.8
(c) 80.0 (d) 68.6

13. An organic compound having carbon, hydrogen and sulphur contains 4% of sulphur. The minimum molecular weight of the compound is

(a) 500 (b) 800 (c) 400 (d) 100

14. When thiourea is heated with metallic sodium, the compound which can't be formed is

(a) NaCNS (b) NaCN

(c) Na_2SO_4 (b) Na_2S

15. If a compound on analysis was found to contain C = 18.5%, H = 1.55%, Cl = 55.04% and O = 24.81%, then its empirical formula is

(a) CH_2OCl (b) CH_2ClO_2 (c) $ClCH_2O$ (d) CHClO

16. An organic compound has carbon and hydrogen percentage in the ratio 6 : 1 and carbon and oxygen percentage in the ratio 3 : 4. The compound has the empirical formula

(a) C_2H_6O (b) CHO_2 (c) CH_4O (d) CH_2O

17. Percentage composition of an organic compound is as follows

$$C = 10.06, H = 0.84, Cl = 89.10$$

Which of the following corresponds to its molecular formula if the vapour density is 60.0?

(a) CH_3Cl (b) $CHCl_3$

(c) CH_2Cl_2 (d) None of these

18. The ammonia evolved from the treatment of 0.30 g of an organic compound for the estimation of nitrogen was passed in 100 mL of 0.1 M sulphuric acid. The excess of acid required 20 mL of 0.5 M sodium hydroxide solution for complete neutralization. The organic compound is

(a) acetamide (b) benzamide

(c) urea (d) thiourea

More than One Correct Option

19. Which of the following statement is correct?

(a) Impure glycerine can be purified by ordinary distillation

(b) Ethanol and water can't be separated from each other completely by simple distillation method as they form azeotropic mixture

(c) Two solid organic substances are said to be different if their mixed melting point is depressed below the melting points of both of these

(d) Naphthalene can be separated from benzoic acid by sublimation

20. Which of the following compounds can be purified by steam distillation?

(a) Nitrobenzene (b) Bromobenzene

(c) Salicylaldehyde (d) *p*-hydroxybenzaldehyde

21. Which of the following statements is/are correct?

(a) Liebig's method is used for the quantitative estimation of both C and H.

(b) Duma's method is used for the quantitative estimation of N in all nitrogen containing organic compounds.

(c) In Liebig's combustion method, ordinary CuO is used.

(d) Silver salt method is a chemical method for the determination of equivalent mass of organic acids.

22. Which of the following statements is/are correct?

(a) When a Lassaigne's solution is heated with HNO_3, cooled, and $AgNO_3$ solution is added, a yellow precipitate, partially soluble in NH_3 or NH_4OH, indicates the presence of iodine in organic compound.

(b) When $(CH_3COO)_2Pb$ solution is added to the acidified Lassaigne's extract of an organic compound having S, a black precipitate of PbS is formed.

(c) An organic compound containing N, on heating with conc. H_2SO_4 gives $(NH_4)_2SO_4$ which liberates NH_3 on treatment with excess of NaOH.

(d) The molecular mass of a non-volatile organic compound is determined either by Duma's method or by Victor Meyer's method.

23. Kjeldahl's method can't be used for the estimation of nitrogen in

(a) pyridine (b) $C_6H_5NO_2$

(c) $C_6H_5NHCOCH_3$ (d) $C_6H_5—N{=}N—C_6H_5$

Assertion and Reason

Directions (Q. No. 24 to 29) *Each of these questions contains two statements : Statement* I (*Assertion*) *and Statement* II (*Reason*). *Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes* (*a*), (*b*), (*c*), (*d*) *given below :*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I.

(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.

(c) Statement I is true; Statement II is false.

(d) Statement I is false; Statement II is true.

24. **Statement I** Benzoic acid is purified by sublimation process.

Statement II Sublimation process is very useful in separating a volatile solid from a non-volatile solid.

25. **Statement I** Essential oils are volatile and are insoluble in H_2O.

Statement II Essential oils are purified by steam distillation.

26. **Statement I** Hydroxylamine (NH_4OH) contains N, and hence gives Prussian blue colour in Lassaigne's test.

Statement II Hydroxylamine does not contain C, so with Na metal, $CN^{\ominus}$ ion is not formed.

27. **Statement I** Duma's method is more applicable to nitrogen containing organic compounds than Kjeldahl's method.

Statement II Kjeldahl's method does not give satisfactory results for compounds in which N is linked to O atom.

28. **Statement I** In Messenger's method, the colourless solution, the liquid is transferred to beaker and barium chloride is added to estimate sulphuric acid as $BaSO_4$ in the usual way.

Statement II If in an experiment 0.36 g of an organic compound gave 0.35 of $BaSO_4$, the percentage of sulphur in the compound is 13.35%.

29. **Statement I** The empirical formula of glucose is CH_2O which represents the relative number of atoms of each element present in the molecule.

Statement II In glucose, the elements C, H, O have combined in the ratio 1 : 2 : 1.

Comprehension Based Questions

Directions (Q. Nos. 30 to 32) In Carius method, a known mass of the organic compound is heated with excess of fuming HNO_3 and a few crystals of $AgNO_3$ in a sealed tube, called the Carius tube. C and H are oxidised to CO_2 and H_2O respectively and the halogens are converted into silver halides. The ppt. of silver halide is filtered, washed, dried and weighed. The percentage of halogen can be calculated from the mass of silver halide formed.

Percentage of

$$\text{Cl} = \frac{35.5}{143.5} \times \frac{\text{mass of AgCl formed}}{\text{mass of substance taken}} \times 100$$

Percentage of

$$\text{Br} = \frac{80}{188} \times \frac{\text{mass of AgBr formed}}{\text{mass of substance taken}} \times 100$$

Percentage of

$$\text{I} = \frac{127}{235} \times \frac{\text{mass of AgI formed}}{\text{mass of substance taken}} \times 100$$

30. When 0.35 g of an organic compound is heated with HNO_3 and $AgNO_3$ in a Carius tube, it gives 0.70 g of silver chloride. The percentage of chlorine in the compound is

(a) 54.8% (b) 49.47%
(c) 34.6% (d) 25.85%

31. Which of the following methods is used to estimate iodine in the laboratory?

(a) Duma's method (b) Liebig's method
(c) Kjeldahl's method (d) Carius method

32. 0.197 g of an organic substance when heated with excess of strong nitric acid and silver nitrate gave 0.3525g of silver iodide. The percentage of iodine in the compound is

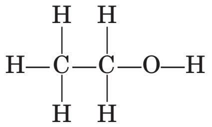
(a) 84.6% (b) 38.6%
(c) 96.68% (d) 53.86%

Directions (Q. Nos. 33 to 35) The molecular formula of a compound gives the actual number of atoms of each element present in a molecule of the compound. It is either the same as the empirical formula or a simple multiple of it.

$$\text{Molecular formula} = (\text{Empirical formula})_n$$

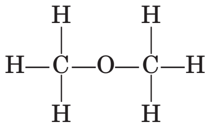
Where, n is a whole number and its value is obtained by dividing the molecular mass of the compound by its empirical formula mass.

Structural formula is that formula which shows in what way different kinds of atoms in a molecule are united or linked together.



$\mathrm{H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-O-H}$

ethyl alcohol



$\mathrm{H-\underset{H}{\overset{H}{C}}-O-\underset{H}{\overset{H}{C}}-H}$

dimethyl ether

33. What is the molecular formula of a compound, its empirical formula is CH_2O and its molecular weight is 90?

(a) $C_3H_6O_3$ (b) $C_6H_6O_3$
(c) $C_4H_8O_4$ (d) $C_2H_6O_2$

34. An organic compound contains C = 40%, H = 13.33% and N = 46.67%. Its empirical formula would be

(a) CHN (b) C_2H_2N
(c) C_3H_7N (d) CH_4N

35. The empirical formula of a compound is CH_2. One mole of this compound has a mass of 42 g. Its molecular formula is

(a) C_2H_2
(b) C_3H_6
(c) C_3H_8
(d) CH_4

Previous Years' Questions

36. 29.5 mg of an organic compound containing nitrogen was digested according ot Kjeldahl's method and the evolved ammonia was absorbed in 20 mL of 0.1 M HCl solution. The excess of the acid required 15 mL of 0.1 M NaOH solution for complete neutralisation. The percentage of nitrogen in the compound is [AIEEE 2010]

(a) 59.0 (b) 47.4
(c) 23.7 (d) 29.5

37. An organic compound having molecular mass 60 is found to contain C = 20%, H = 6.67% and N = 46.67% while rest is oxygen. On heating it gives NH_3 along with a solid residue. The solid residue gives violet colour with alkaline copper sulphate solution. The compound is [AIEEE 2005]

(a) $CH_3CH_2CONH_2$ (b) $(NH_2)_2CO$
(c) CH_3CONH_2 (d) CH_3NCO

38. The compound formed in the positive test for nitrogen with the Lassaigne's solution of an organic compound is [AIEEE 2004]

(a) $Fe_4[Fe(CN)_6]_3$ (b) $Na_3[Fe(CN)_6]$
(c) $Fe(CN)_3$ (d) $Na_4[Fe(CN)_5NOS]$

Answers

Round I

1. (c)	**2.** (b)	**3.** (d)	**4.** (c)	**5.** (d)	**6.** (d)	**7.** (d)	**8.** (c)	**9.** (d)	**10.** (a)
11. (c)	**12.** (d)	**13.** (d)	**14.** (a)	**15.** (d)	**16.** (d)	**17.** (c)	**18.** (c)	**19.** (a)	**20.** (b)
21. (c)	**22.** (d)	**23.** (c)	**24.** (b)	**25.** (a)	**26.** (b)	**27.** (d)	**28.** (d)	**29.** (d)	**30.** (d)
31. (b)	**32.** (c)	**33.** (b)	**34.** (a)	**35.** (c)	**36.** (d)	**37.** (b)	**38.** (c)	**39.** (b)	**40.** (b)
41. (d)	**42.** (b)	**43.** (a)	**44.** (c)	**45.** (b)	**46.** (d)	**47.** (d)	**48.** (d)	**49.** (a)	**50.** (d)
51. (c)	**52.** (d)	**53.** (c)	**54.** (a)	**55.** (c)					

Round II

1. (c)	**2.** (b)	**3.** (b)	**4.** (b)	**5.** (c)	**6.** (c)	**7.** (c)	**8.** (b)	**9.** (b)	**10.** (b)
11. (a)	**12.** (c)	**13.** (b)	**14.** (c)	**15.** (d)	**16.** (d)	**17.** (b)	**18.** (c)	**19.** (b,c)	**20.** (a,b,c)
21. (a,b,d)	**22.** (b,c)	**23.** (a,b,d)	**24.** (c)	**25.** (a)	**26.** (d)	**27.** (b)	**28.** (b)	**29.** (a)	**30.** (b)
31. (d)	**32.** (c)	**33.** (a)	**34.** (d)	**35.** (b)	**36.** (c)	**37.** (b)	**38.** (a)		

the Guidance

Round I

1. Distillation is applied to separate a solute from the solvent if organic liquid is stable at its boiling point and contains a non-volatile impurity.

3. Oil and water are immiscible liquids, thus, are separated by using separating funnel.

4. Fractional crystallisation is used to purify organic solids which dissolve in a particular solvent, but their rate of solubility is slightly different.

5. Sublimation is the process employed for those solids which convert directly into vapours on heating without converting into liquid phase like I_2.

7. Camphor and benzoic acid both being sublimate cannot be separated by sublimation. Chemical reagents are used to separate such mixtures.

8. Acetone and methanol have nearly equal boiling point. Thus, they are separated by fractional distillation.

9. Fractional distillation is used for the separation of crude petroleum into various fractions like coal tar, crude alcohol and petroleum.

11. If a liquid decomposes at or below its boiling point like glycerine, it is purified by vacuum distillation.

12. Chromatography is the best and latest technique for the isolation, purification and separation of organic compounds.

13. The components of an azeotropic mixture are separated by special method, *i.e.,* azeotropic distillation. The simple fraction which distils at 337.8 K is a ternary azeotrope consisting of water, some alcohol and benzene.

14. On heating iron reacts with sulphur to give iron sulphide.

19. Organic compounds which are volatile in steam can be purified by steam distillation. It is based on the fact that vaporisation of organic liquid takes place at lower temperature than its boiling point.

21. Only urea does not sublime while naphthalene, camphor and benzoic acid do so.

23. The sulphur containing organic compounds when fused with sodium metal give Na_2S which react with lead acetate and forms black ppt. of PbS.

$$Na_2S + (CH_3COO)_2Pb \longrightarrow \underset{\text{black ppt}}{PbS} + 2CH_3COONa$$

24. When organic compound containing both nitrogen and sulphur is fused with sodium, sodium thiocyanate is formed.

$$Na + S + C + N \longrightarrow NaSCN$$

26. Organic compound containing nitrogen is fused with a small piece of sodium metal to form NaCN.

$$Na + \underbrace{C + N}_{\text{from organic compound}} \longrightarrow NaCN$$

30. If organic compound gives blue or green colour at the tip of red hot copper wire, this indicates the presence of halogens in the compound. However, compounds like urea, thiourea etc also give blue or green colour in this test even in the absence of halogens, thus, it is not a sure test for halogens.

31. Detection of phosphorus in the organic compound can be done by its conversion into phosphate. The ammonium molybdate is used to identify phosphate ion.

$$Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$$

$$H_3PO_4 + \underset{\text{ammonium molybdate}}{12(NH_4)_2MoO_4} + 21HNO_3 \xrightarrow{\Delta}$$

$$\underset{\text{yellow ppt.}}{(NH_4)_3PO_4 \cdot 12MoO_3} + 21NH_4NO_3 + 12\,H_2O$$

33. Phosphorus gives canary yellow precipitate with HNO_3 and ammonium molybdate.

$$\underset{\text{sod. extract}}{Na_3PO_4} + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$$

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow$$

$$\underset{\text{yellow ppt.}}{(NH_4)_3PO_4 \cdot 12MoO_3} + 21NH_4NO_3 + 12H_2O$$

34. $$\underset{\text{sod. extract}}{Na_2S} + \underset{\text{sodium nitroprusside}}{Na_2[Fe(CN)_5NO]} \longrightarrow \underset{\text{pink/violet colour}}{Na_4[Fe(CN)_5NOS]}$$

Thus, organic compound contains sulphur.

35. Sulphur is present in the sodium extract in the form of sodium sulphide (Na_2S).

$FeCl_3$ gives blood red colour with sodium extract having N and S both.

38. Carbon and hydrogen are estimated in organic compounds by Liebig's method.

$$C + 2CuO \xrightarrow{\Delta} 2Cu + CO_2$$

$$2H + CuO \xrightarrow{\Delta} Cu + H_2O$$

Percentage of carbon and hydrogen is calculated from the weights of CO_2 and H_2O produced.

39. CH_4 has highest ratio of H to C.

40. Duma's method involves the determination of nitrogen content in the organic compound in the form of N_2.

$$N_2O + Cu \longrightarrow N_2 + CuO$$

$$\%\text{ of N} = \frac{28}{22400} \times \frac{\text{volume of } N_2 \text{ at NTP}}{\text{weight of compound}} \times 100$$

41. $$\%\text{ of N} = \frac{28}{22400} \times \frac{\text{volume of } N_2 \text{ at NTP}}{\text{weight of compound}} \times 100$$

$$= \frac{28}{22400} \times \frac{224}{1.18} \times 100$$

$$= \frac{28}{1.18} = 23.72\%$$

43. In case of Kjeldahl's method the percentage of N_2 is then calculated from the amount of NH_3.

44.

Atom	At. mass (*a*)	% (*b*)	$\frac{b}{a}$	Simplest ratio
X	10	50	$\frac{50}{10} = 5$	2
Y	20	50	$\frac{50}{20} = 2.5$	1

Hence, empirical formula = X_2Y

46. Empirical formula of acid $= CH_2O_2$

We know that molecular formula $= n$ (empirical formula)

If $n = 1$, molecular formula $= (CH_2O_2)_1 = CH_2O_2$

If $n = 2$, molecular formula $= (CH_2O_2)_2 = C_2H_4O_4$

If $n = 3$, molecular formula $= (CH_2O_2)_3 = C_3H_6O_6$

Thus, the probable molecular formula $= CH_2O_2$

48. Phosphorus is estimated as $Mg_2P_2O_7$.

$$P \xrightarrow[\Delta]{HNO_3} H_3PO_4$$

$$H_3PO_4 + Mg^{2+} + NH_4OH \longrightarrow MgNH_4PO_4$$

$$2MgNH_4PO_4 \longrightarrow Mg_2P_2O_7 + H_2O + 2NH_3$$

$$\%\text{ of P} = \frac{62 \times \text{wt. of } Mg_2P_2O_7 \times 100}{222 \times w}$$

49. Mass of silver salt $= 0.4$ g

Mass of silver $= 0.26$ g

$$\frac{\text{Eq. mass of silver salt}}{\text{Eq. mass of Ag}} = \frac{\text{wt. of silver salt}}{\text{wt. of silver}}$$

$$\text{Eq. mass of silver salt} = \frac{108 \times 0.4}{0.26} = 166$$

$$\text{Eq. mass of acid} = 166 - 108 = 58$$

50. $C : H : Br = \frac{29.27}{12} : \frac{5.69}{1} : \frac{65.04}{80}$

$= 2.43 : 5.69 : 0.813$

$= 3 : 7 : 1$

or empirical formula $= C_3H_7Br$

51. $\frac{E}{108} = \frac{100}{60}$

Eq. wt. of the silver salt, $E = 108 \times \frac{100}{60} = 180$

$\therefore$ Eq. wt. of the acid $= E - 108 + 1 = 73$

52. $\% \text{ of S} = \frac{32}{233} \times \frac{\text{wt. of } BaSO_4}{\text{wt. of organic compound}} \times 100$

$$= \frac{32}{233} \times \frac{1.158}{0.53} \times 100 = 30\%$$

53. Victor Meyer's method is applicable only for the determination of molecular mass of volatile substances.

55. The correct statement is "Kjeldahl's method is used for estimation of nitrogen".

Round II

1. $NaCN + HNO_3 \xrightarrow{\Delta} HCN\uparrow + NaNO_3$

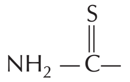
$Na_2S + 2HNO_3 \xrightarrow{\Delta} H_2S\uparrow + 2NaNO_3$

2. $\% \text{ of chlorine} = \frac{35.5}{143.5} \times \frac{\text{mass of AgCl}}{\text{mass of the compound}} \times 100$

$$= \frac{35.5}{143.5} \times \frac{0.287}{0.099} \times 100 = 71.71\%$$

3. When N and S both are present in the organic compound, a red colour complex ion $[Fe(CNS)]^{2+}$ is formed on adding $FeCl_3$ to sodium extract.

$$NaCNS + FeCl_3 \longrightarrow \underset{\text{blood red colour}}{[Fe(SCN)]Cl_2} + NaCl$$

4. In the Lassaigne's test, if organic compound consists of both N and S then a red colour is obtained on adding aqueous $FeCl_3$ to sodium extract.  $NH_2-\overset{\overset{\displaystyle S}{\|}}{C}-NH_2$ contains both N and S hence, it will give red colour in Lassaigne test.

$$NaCNS + FeCl_3 \longrightarrow \underset{\text{blood red colour}}{[Fe(SCN)]Cl_2} + NaCl$$

5. Kjeldahl's method is used for the estimation of nitrogen. The organic compound is heated with conc. H_2SO_4 in the presence of K_2SO_4 (used to raise boiling point of H_2SO_4) and $CuSO_4$ (used as catalyst) to convert all the nitrogen into $(NH_4)_2SO_4$.

6. $\% \text{ C} = \frac{12}{44} \times \frac{12.571}{4.0} \times 100 = 85.7$

$$\% \text{ H} = \frac{2}{18} \times \frac{5.143}{4.0} \times 100 = 14.3$$

The mole ratio of C to H is $\frac{85.7}{12} : \frac{14.3}{1}$

$$= 7.14 : 14.3 = 1 : 2 = CH_2$$

7. Glycerol can be separated from spent lye in soap industry by the distillation under reduced pressure because it decomposes near its boiling point.

8. In thin layer chromatography, the relative adsorption of each component of the mixture is expressed in terms of retention factor (R_f).

$$R_f = \frac{\text{distance moved by the spot centre from base line}}{\text{distance moved by the solvent from the base line}}$$

9. Oxygen cannot be detected by direct test because oxygen is present in atmosphere and all tests are carried in atmosphere of oxygen.

10. Common salt is not soluble in alcohol but sugar is.

11. $C = 10.5 \text{ g} = \frac{10.5}{12} \text{ mol} = 0.87 \text{ mol}$

$$H = 1 \text{ g} = \frac{1}{1} \text{ mol} = 1 \text{ mol}$$

$$\therefore \quad (C_{0.87}H_1)_7 = C_{6.09}H_7 \approx C_6H_7$$

$$pV = nRT = \frac{w}{m}RT$$

$$1 \times 1 = \frac{2.4}{m} \times 0.082 \times 400$$

$$m = 79$$

Hence, the hydrocarbon is C_6H_7.

12. $\% \text{ of H} = \frac{2}{18} \times \frac{\text{weight of } H_2O}{\text{weight of organic compound}} \times 100$

$$= \frac{2}{18} \times \frac{0.9}{0.5} \times 100 = 20\%$$

$\therefore$ The percentage of carbon $= 100 - 20 = 80\%$

13. As the minimum molecular weight must have at least one S atom, so

$$S\% = \frac{\text{wt. of one S atom}}{\text{min. mol. wt.}} \times 100$$

$$4 = \frac{32}{\text{min mol wt}} \times 100$$

$$\text{min. mol. wt.} = \frac{32 \times 100}{4} = 800$$

14. The chemical formula of thiourea is NH_2CSNH_2 so here Na_2S, NaCN and NaCNS will be formed but not Na_2SO_4.

15. $C : H : Cl : O = \frac{18.5}{12} : \frac{1.55}{1} : \frac{55.04}{35.5} : \frac{24.81}{16} = 1:1:1:1$

16. $C : H : O = 6 : 1 : 8$

$$= \frac{6}{15} \times 100 : \frac{1}{15} \times 100 : \frac{8}{15} \times 100$$

$$= 40 : 6.67 : 53.3$$

$$= \frac{40}{12} : \frac{6.67}{1} : \frac{53.3}{16}$$

$$= 1 : 2 : 1 \quad \textit{i.e.,} \quad CH_2O$$

17.

Atom	Atomic mass (*a*)	Percentage (*b*)	$\frac{b}{a} = x$	Ratio
C	12	10.06	$\frac{10.06}{12} = 0.83$	1
H	1	0.84	$\frac{0.84}{1} = 0.84$	1
Cl	35.5	89.10	$\frac{89.10}{35.5} = 2.50$	3

Empirical formula $= CHCl_3$

Empirical formula mass $= 12 + 1 + 106.5 = 119.5 \approx 120$

Molecular mass $= 2 \times VD = 2 \times 60 = 120$

$$n = \frac{\text{molar mass}}{\text{empirical formula mass}} = \frac{120}{120} = 1$$

Molecular formula $= (CHCl_3)_1 = CHCl_3$

18. Let unreacted 0.1 M (= 0.2 N) $H_2SO_4 = V$ mL

20 mL of 0.5 M NaOH $= V$ mL of 0.2 N H_2SO_4

$$20 \times 0.5 = V \times 0.2$$

$$V = \frac{20 \times 0.5}{0.2} = 50 \text{ mL}$$

Used $\quad H_2SO_4 = 100 - 50 = 50$ mL

$$\% \text{ of N} = \frac{1.4\,NV}{w} = \frac{1.4 \times 0.2 \times 50}{0.30}$$

$$= 46.67\%$$

% of nitrogen in

(a) $CH_3CONH_2 = \frac{14 \times 100}{59} = 23.73\%$

(b) $C_6H_5CONH_2 = \frac{14 \times 100}{121} = 11.57\%$

(c) $NH_2CONH_2 = \frac{28 \times 100}{60} = 46.67\%$

(d) $NH_2CSNH_2 = \frac{28 \times 100}{76} = 36.84\%$

19. Glycerine is purified by vacuum distillation. It boils with decomposition at 563 K but if pressure is lowered to 12 mm, it boils at 453 K without decomposition.

Naphthalene and benzoic acid both sublime thus cannot be separated by sublimation.

Other given statements are true.

20. The process of steam distillation is used for the separation and purification of liquids which are volatile in steam like nitrobenzene, bromobenzene, salicylaldehyde etc.

21. For this method dry CuO is used.

22. Test given in (a) indicates the presence of Br.

(d) Victor Meyer's method is used to determine the molecular mass of volatile organic compound. Duma's method is used to calculate the percentage of nitrogen.

23. Kjeldahl's method can't be used for the estimation of nitrogen in azo compounds and compounds containing nitrogen in the ring since these compounds are not completely converted into $(NH_4)_2SO_4$ during digestion.

24. In sublimation, certain substances like benzoic acid when heated, first directly convert from the solid to the vapour state without melting leaving behind the non-sublimates. The vapour when cooled, give back the pure solid substance.

25. Essential oils being steam volatile, are purified by steam distillation.

26. Hydroxylamine does not give positive test for N since it does not contain carbon. Thus, CN^- ion is not obtain which is essential condition for the test of nitrogen.

27. Both the given statements are correct.

28. Percentage of sulphur

$$= \frac{32}{233} \times \frac{0.35}{0.36} \times 100 = 13.35\%$$

29. The empirical formula of a compound is the simplest formula deduced from its percentage composition showing its composition by mass.

30. $\% \text{ of chlorine} = \frac{35.5}{143.5} \times \frac{\text{wt. of AgCl}}{\text{wt of organic compound}} \times 100$

$$= \frac{35.5}{143.5} \times \frac{0.70}{0.35} \times 100 = 49.47\%$$

31. Carius method is used to estimate iodine.

32. $\underset{(108\,+\,127)}{\text{AgI}} = \underset{127}{\text{I}}$

Thus, percentage of iodine $= \frac{127}{235} \times \frac{0.3525}{0.197} \times 100 = 96.68\%$

33. Empirical formula $= CH_2O$

Molecular weight $= 90$

Empirical formula weight of CH_2O

$$= 12 + (1 \times 2) + 16 = 30$$

$$n = \frac{\text{molecular weight}}{\text{empirical formula weight}} = \frac{90}{30} = 3$$

Molecular formula $= (CH_2O)_3 = C_3H_6O_3$

34. $C : H : N = \frac{40}{12} : \frac{13.33}{1} : \frac{46.67}{14} = 1 : 4 : 1$

So, empirical formula = CH_4N.

35. $CH_2 = 12 + 2 = 14$

$$n = \frac{42}{14} = 3 \text{ mol}$$

Formula $= (CH_2)_3 = C_3H_6$.

36. Weight of organic compound = 29.5 mg

$$NH_3 + HCl \longrightarrow NH_4Cl$$

$$\underset{\text{(remaining)}}{HCl} + \underset{\substack{15 \times 0.1\,M \\ = 1.5\text{ mmol}}}{NaOH} \longrightarrow NaCl + H_2O$$

Total millimole of HCl = 2

Millimole used by $NH_3 = 2 - 1.5 = 0.5$

$$\text{Weight of } NH_3 = 0.5 \times 17 \text{ mg} = 8.5 \text{ mg}$$

$$\text{Weight of nitrogen} = \frac{14}{17} \times 8.5 \text{ mg} = 7 \text{ mg}$$

$$\% \text{ of nitrogen} = \frac{7}{29.5} \times 100 = 23.7\%$$

37.

Element	Percentage	Percentage/at wt	Simple ratio
C	20.0	20.0/12 = 1.66	1.66/1.66 = 1
H	6.67	6.67/1 = 6.67	6.67/1.66 = 4
N	46.67	46.67/14 = 3.33	3.33/1.66 = 2
O	26.66	26.66/16 = 1.66	1.66/1.66 = 1

Empirical formula $= CH_4N_2O$

Empirical formula weight $= 12 + (4 \times 1) + (2 \times 14) + 16 = 60$

$$\therefore \quad n = \frac{\text{mol. formula weight}}{\text{emp. formula weight}} = \frac{60}{60} = 1$$

$\therefore$ Molecular formula $= CH_4N_2O$

Given compound gives biuret test. Thus, given compound is urea, $(NH_2)_2CO$.

38. If organic compound contains nitrogen, NaCN will be present in the sodium extract.

$$Na + C + N \xrightarrow{\text{Fuse}} NaCN$$

$$FeSO_4 + 6NaCN \longrightarrow \underset{\text{'}A\text{'}}{Na_4[Fe(CN)_6]} + Na_2SO_4$$

A changes to Prussian blue $Fe_4[Fe(CN)_6]_3$ on reaction with $FeCl_3$.

$$4FeCl_3 + 3Na_4[Fe(CN)_6] \longrightarrow Fe_4[Fe(CN)_6]_3 + 12NaCl$$

13

Some Basic Principles of Organic Chemistry

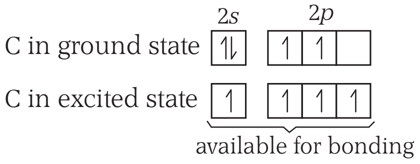
JEE Main MILESTONE

- Tetravalency of Carbon
- Organic Compounds
- Classification of Organic Compounds
- Homologous Series
- Structural Representation of Organic Compounds
- Systems of Nomenclature of Organic Compounds
- IUPAC System of Nomenclature
- Functional Groupwise Nomenclature
- Nomenclature of Cyclic Compounds
- Conversions Used in IUPAC System of Nomenclature
- Covalent Bond Fission
- Reaction Intermediates
- Attacking Reagent or Species
- Electronic Displacement in a Covalent Bond
- Common Types of Organic Reactions

13.1 Tetravalency of Carbon

We are familiar with the fact that carbon is the essential element of all the organic molecules and its electronic configuration is 2,4, or $1s^2, 2s^2, 2p^2$. Two p-orbitals are half-filled, and hence, carbon is expected to exhibit a valency of two. But in all of its compounds, it exhibits tetravalency.

The tetravalency of carbon can be explained by the excited state concept *i.e.*, by moving one of the paired $2s$ electron to empty $2p$ orbital by gaining energy from the system (according to classical concept of bonding) however 4 equivalent C—H bonds in CH_4 is explained on the basis of concept of **hybridisation** (according to modern concept of bonding).



Being tetravalent carbon requires four electrons to complete its octet *i.e.*, to achieve a state of high stability. But it is not possible for carbon to accept or donate four electrons to achieve inert gas configuration (to achieve stability), due to energy conceptions. Thus, carbon always combines with other atoms by mutual sharing of electrons and thus, forms covalent bonds.

Compounds of carbon other than its oxides and carbonates are ***called organic compounds*** *and studied under separate branch of chemistry, called the* ***organic chemistry.***

Organic compounds are vital for sustaining life on the earth and include complex molecules like genetic information bearing DNA (deoxyribonucleic acid) and proteins.

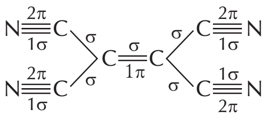
σ and π-Bonding in Organic Compounds

Carbon has a unique property that it can form both the types of covalent bonds, *i.e.,* the σ (called sigma, the bond formed by the linear or axial or end to end overlapping of orbitals) and the π (pi, the bond formed by the parallel or sidewise overlapping of orbitals) bonds. *A single bonds contains only one σ bond. Whereas there are one σ and one π bonds in case of a double bond and one σ and two π bonds in case of a triple bond.*

Sample Problem 1 *The number of σ and π bonds in tetracyanoethylene are respectively*

(a) 5, 1 (b) 9, 1 (c) 9, 9 (d) 9, 3

Interpret (c) The structure of tetracyanoethylene is as



(∵ Single bond contains only σ bond, double bond contains 1σ and 1π bond and triple bond contains 1σ and 2π bonds).

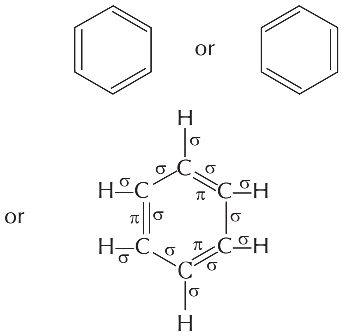
Therefore, there are 9σ and 9π bonds in tetracyanoethylene molecule.

Sample Problem 2 *The ratio of σ and π bonds in benzene is*

(a) 5 : 1 (b) 3 : 12

(c) 1 : 4 (d) 4 : 1

Interpret (d) The structure of benzene is as



In benzene,

number of sigma bonds = 12

number of pi bonds = 3

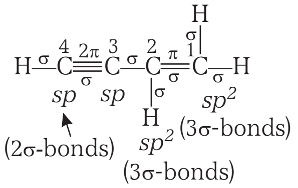
$$\therefore \quad \frac{\text{number of } \sigma \text{ bonds}}{\text{number of } \pi \text{ bonds}} = \frac{12}{3} = 4:1$$

Shapes of Simple Molecules : Hybridisation

The shapes of organic molecules can be decided by the number of σ bonds or concept of hybridisation. We know that organic compounds being covalent are the result of overlapping of orbitals of different elements.

Before overlapping with the orbitals of other element, the orbitals of an element intermix and give the orbitals of almost equal energy. This phenomenon is called hybridisation. Thus, *hybridisation can be defined as "Intermixing of orbitals of almost similar energy to form the same number of orbitals of exactly similar energy".* Because of the absence of *d*-orbitals, the carbon atoms show only three types of hybridisations depending upon the number of σ bonds formed in its compounds. *If there are four σ bonds, the hybridisation is sp^3, if three σ bonds, the hybridisation is sp^2 and if only two σ bonds, the hybridisation is sp.*

Usually saturated hydrocarbons are sp^3 hybridised while unsaturated hydrocarbons may be sp^2 or *sp* hybridised. This can be best understood by the following example. The complete structure of but-1-ene-3-yne is as



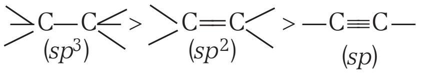
(π bonds give no contribution to hybridisation).

A sp^3 hybridised molecule is generally tetrahedral (if lone pairs are not present), a sp^2 hybridised molecule is generally trigonal planar and a *sp* hybridised molecule is planar.

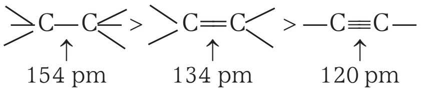
Bond parameters like bond length, bond angle etc, are affected by hybridisation. The effect of hybridisation on different bond parameters is discussed below.

(a) Bond Length

The size of *p*-orbitals is much larger as compared to the size of *s*-orbitals and a larger orbital forms a longer bond, therefore C—C sigma bond length increases as the number of *p*-orbitals (hybridised *p*-orbitals) increases. The carbon bonded through triple bond are *sp* hybridised (50% *p* character), and that bonded through double bond are sp^2 hybridised (66.7% *p*-character) whereas that bonded through single bond are sp^3 hybridised (75% *p*-character). The order of percentage of *p*-character is



Therefore, the order of bond length is also as



Similarly, a C—H bond in alkanes, alkenes and alkynes, may be formed by the overlap of a sp^3, sp^2 or sp-orbital of carbon atoms of alkanes, alkenes and alkynes respectively with an s-orbital of hydrogen, hence, as the size of the hybrid orbital decreases, the C—H bond lengths decrease accordingly.

$$\underset{111\text{ pm}}{C(sp^3)\text{—}H} > \underset{110\text{ pm}}{C(sp^2)\text{—}H} > \underset{108\text{ pm}}{C(sp)\text{—}H}$$

(b) Bond Strengths

Shorter the bond length, greater is the bond strength. Thus, the σ-bond formed by sp-hybridised carbon is the strongest (sp-orbital has highest electron density) while that formed by sp^3 hybridized carbon is the weakest (sp^3-orbital has lowest electron density). The bond energies of different C—H and C—C bonds follow the following order :

(i) $\underset{507\text{ kJ mol}^{-1}}{C(sp)\text{—}H} > \underset{443\text{ kJ mol}^{-1}}{C(sp^2)\text{—}H} > \underset{435\text{ kJ mol}^{-1}}{C(sp^3)\text{—}H}$

(ii) $\underset{433\text{ kJ mol}^{-1}}{C(sp)\text{—}C(sp)} > \underset{383\text{ kJ mol}^{-1}}{C(sp^2)\text{—}C(sp^2)} > \underset{347\text{ kJ mol}^{-1}}{C(sp^3)\text{—}C(sp^3)}$

(The above order is true only for C—C σ bonds.)

A carbon-carbon double bond because of the presence of a strong σ bond and a weak π bond is, however, stronger (598 kJ mol^{-1}) as compared to a carbon-carbon single bond which contains only a σ bond. Similarly, a carbon-carbon triple bond is still stronger (803 kJ mol^{-1}) as compared to a carbon-carbon double bond.

(c) Electronegativity

It varies directly with s-character but inversely with p-character, *i.e.*, greater the s-character of the hybrid orbitals, more is the electronegativity of the atom. Thus, the order of the electronegativity is as

Hybridisation	sp >	sp^2 >	sp^3
Electronegativity	3.3	2.75	2.5

(d) Bond Angles

As the s-character in hybridised orbital decreases, the bond angle also decreases. The bond angle is 180° in sp hybridisation; 120° in case of sp^2 hybridisation and, 109°28′ in case of sp^3 hybridisation.

Sample Problem 3 In *the organic compound* $CH_2{=}CH\text{—}CH_2\text{—}CH_2\text{—}C{\equiv}CH$, *the pair of hybridised orbitals involved in the formation of* $C_2\text{—}C_3$ *bond is* **[NCERT]**

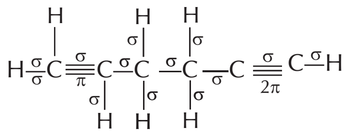
(a) $sp - sp^2$

(b) $sp - sp^3$

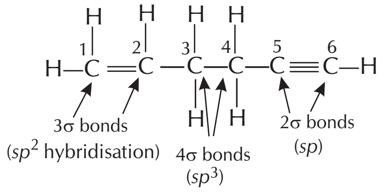
(c) $sp^2 - sp^3$

(d) $sp^3 - sp^3$

Interpret (c) To solve such problems first assign σ and π-bonds as



As we know π-bond does not contribute in hybridisation, count only the number of σ-bond and decide the hybridisation.



Thus, C_2 — C_3 bond involves sp^2-sp^3 hybridised orbitals.

Note : While numbering is done, $=$ bond is preferred over $\equiv$ bond. For details see rules of nomenclature.

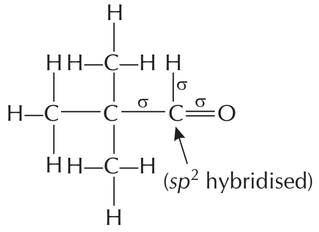
Sample Problem 4 *The compound in which carbon uses only* sp^3*-hybrid orbitals for bond formation is*

(a) $(CH_3)_3C\text{—}CHO$ (b) $(CH_3)_3C\text{—}OH$

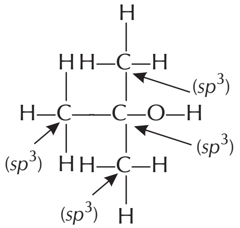
(c) NH_2CONH_2 (d) HCOOH

Interpret (b) The complete structures of the given compounds are as

(a)

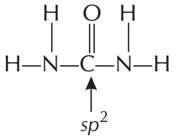


(b)

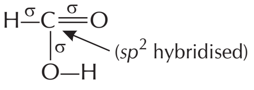


(All carbons are sp^3 hybridised)

(c)



(d)



Thus, $(CH_3)_3C\text{—}OH$ uses only its sp^3-hybrid orbitals for bond formation.

(**Remember** ! if no double or triple bonds are present in a molecule, the carbons of the molecules are usually sp^3 hybridised.)

Sample Problem 5 *A sp^3 hybrid orbital contains*

(a) $\frac{1}{4}$ *s-character* (b) $\frac{1}{3}$ *s-character*

(c) $\frac{1}{2}$ *s-character* (d) $\frac{2}{3}$ *s-character*

Interpret (a) $s\text{-character} = \frac{\text{part of } s\text{- character}}{\text{total character}} \times 100$

In sp^3 hybrid orbital,

$$s\text{-character} = \frac{1}{4} \times 100 = \frac{1}{4} \ s\text{-character}$$

Caution Point (*i*) *For p-character, use the formula,*

$$p\text{ - character} = \frac{\text{part of } p\text{-character}}{\text{total character}} \times 100$$

(*ii*) *Total means total number of orbitals and part means number of p-orbitals.*

Sample Problem 6 *Molecule having the longest bond distance between two adjacent carbon atoms is*

(a) *ethane* (b) *ethene*

(c) *ethyne* (d) *benzene*

Interpret (a) Higher the *p*-character, longer is the bond. In ethane ($CH_3—CH_3$) both the carbons are sp^3 hybridised, thus *p*-character is 75%. In ethene and benzene, the carbon atoms are sp^2 hybridised, thus percentage of *p*-character is 66.7. In ethyne, since carbons are *sp* hybridised, the *p*-character is 50%. Thus, due to the presence of highest *p*-character, C—C bond distance is longest in ethane.

13.2 Organic Compounds

More than a century ago all substances then known were classified on the basis of sources from which they were derived. The compounds which were of mineral origin were called **inorganic** and those of vegetable or animal origin were called **organic** (the word organic signifies life).

It was assumed that the organic compounds could be produced only by living matter inside their body. **Lavoisier** 'Father of Chemistry', in 1785, first of all showed that these organic compounds always contain C and H and frequently N and P. **Berzilius** assumed that some vital force (infact life force) was necessary to produce organic compounds and synthesis of these compounds in laboratory was impossible. (This concept was commonly named as **vital force theory).**

The vital force theory was suffered from death blow in 1828, when German chemist **Friedrich Wholer** heated ammonium cyanate (which was derived from inorganic substances) and obtained the organic compound **urea.** (The urea thus, formed was proved to be identical in all respects with urea isolated from urine).

$$\underset{\text{potassium cyanate}}{KOCN} + NH_4Cl \xrightarrow{\text{Heat}} KCl + \underset{\text{ammonium cyanate}}{NH_4OCN}$$

$$\xrightarrow{\text{Heat}} \underset{\text{urea}}{NH_2CONH_2}$$

This synthesis did not immediately break down the old concept of vital force. A further blow to vital force theory was given by **Kolbe** in 1845, when he synthesised acetic acid (CH_3COOH) (the first organic compound synthesised in laboratory from its elements) and afterwards by **Berthelot** (1865) who synthesised **methane.** Since, then a large number of organic compounds have been synthesised with their formation governed by simple laws of formation.

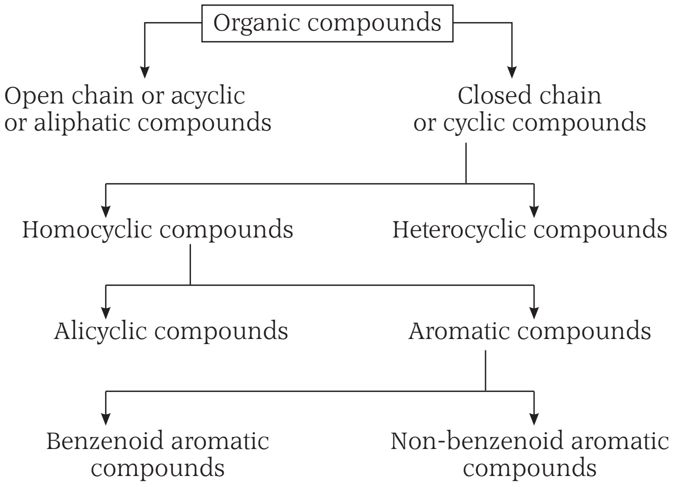
Although the original meaning of the term organic chemistry is no longer applicable, but this word has been retained because so many substances involved in organic chemistry do come directly or indirectly from living matter. In modern terms, **the organic compounds are defined as the hydrides of carbon** (hydrocarbons) **and their derivatives.**

13.3 Classification of Organic Compounds

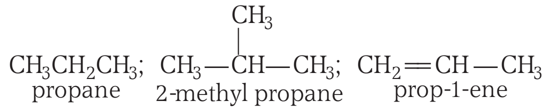
Due to the unique power of catenation in C-atom, organic compounds number in millions. In order to facilitate the study of such a large number of compounds, it is necessary to classify them. The organic compounds have been classified on the basis of **carbon skeleton** (structure) or **functional groups with the concept of homology.**

Classification Based on Structure

Depending on the structure, the organic compounds can be classified as :

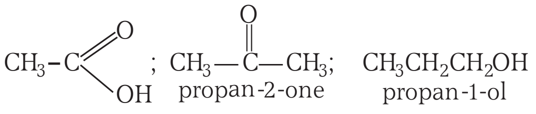


Some examples of aliphatic compounds are



$CH_3CH_2CH_3$; $CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_3$; $CH_2=CH-CH_3$

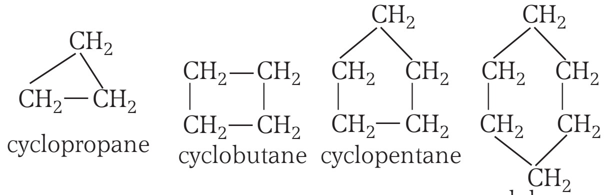
propane; 2-methyl propane; prop-1-ene



$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$; $CH_3CH_2CH_2OH$

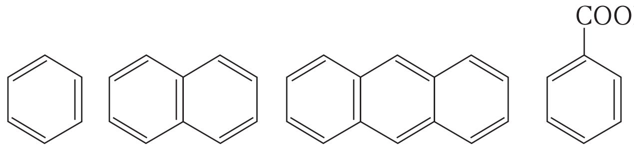
ethanoic acid; propan-2-one; propan-1-ol

Some examples of alicyclic compounds are



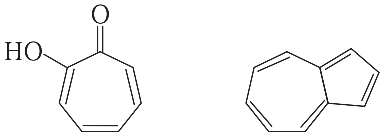
cyclopropane; cyclobutane; cyclopentane; cyclohexane

Some examples of benzenoid aromatic compounds are



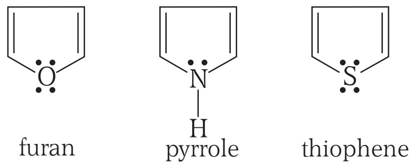
benzene (monocyclic); naphthalene (bicyclic); anthracene (tricyclic); benzoic acid

Some examples of non-benzenoid aromatic compounds are

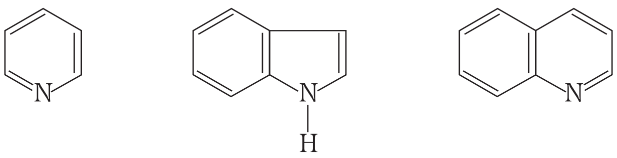


tropolone; azulene

Some examples of heterocyclic compounds are



furan; pyrrole; thiophene

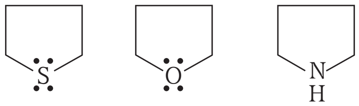


pyridine; indole; quinoline

Sample Problem 7 *Which of the following is alicyclic heterocyclic compound?*

(a) *Tetrahydrothiophene* (b) *Tetrahydrofuran*
(c) *Tetrahydropyrrole* (d) *All of these*

Interpret (d) All those compounds which contain a foreign atom like N, O, S (an atom other than carbon) are called alicyclic heterocyclic compounds. The structures of the given compounds are as



Hence, all these are alicyclic heterocyclic compounds.

Classification Based on Functional Group

The compounds of carbon and hydrogen, *i.e.*, hydrocarbon are considered as the parents of all the organic compounds because all other compounds are obtained from them by the replacement of one or more H-atoms with other atoms or groups.

$$\underset{\text{hydrocarbon}}{R-H}\xrightarrow[-X]{-H}\underset{\text{hydrocarbon derivative}}{R-Y}$$

Thus, all the organic compounds except hydrocarbons, carry two part; one hydrocarbon part (*R*) and other functional group (*Y*). The hydrocarbon part affects the properties whereas, functional group *Y* is responsible for chemical properties. Thus,

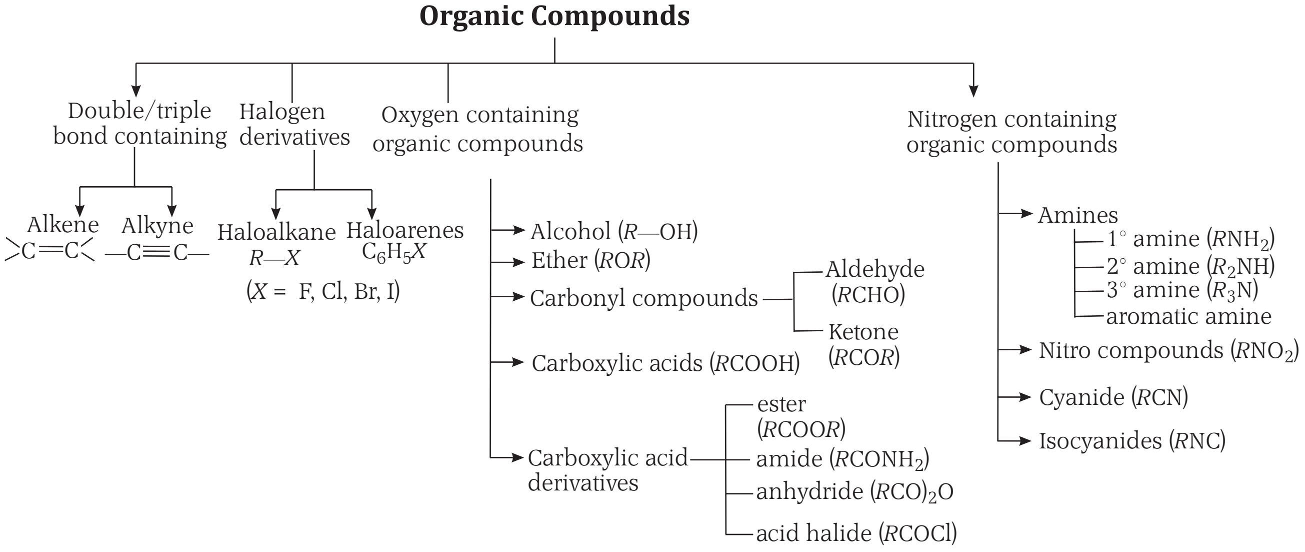
A functional group is an atom or group of atoms, in a molecule, which is responsible for the chemical properties of the molecule. e.g., Double and triple bonds are functional groups. Other examples include –Cl, –Br, –OH, $-NH_2$ etc., groups. In an organic molecule like

$$\boxed{R}-\boxed{F}\longrightarrow \text{functional group}$$

↙ hydrocarbon part

R— can be **alkyl** group (if hydrocarbon portion belongs to alkane *i.e.*, contains only single bond) or **alkenyl** group (if hydrocarbon portion belongs to alkene *i.e.*, contains at least one double bond) or **alkynyl** group (if hydrocarbon portion belongs to alkynes, *i.e.*, contains atleast one triple bond). Each functional group have its own characteristic reactions and by recognising the functional group in a molecule, it is possible to predict the reaction, which that molecule will undergo.

On the basis of functional groups, the organic compounds are classified as



An organic molecule can contain more than one functional group and then said to be **poly-functional.** In poly-functional compounds properties of each functional group may be modified by the presence of the other.

13.4 Homologous Series

Homologous series is a series of compounds in which adjacent members differ by a —CH_2 unit. The individual members are called **homologues,** *e.g.,* the homologous series of alcohols is as follows

CH_3OH	Methyl alcohol
CH_3CH_2OH	Ethyl alcohol
$CH_3CH_2CH_2OH$	Propyl alcohol
$CH_3CH_2CH_2CH_2OH$	Butyl alcohol
$CH_3CH_2CH_2CH_2CH_2OH$	Pentyl alcohol

The general characteristics of a homologous series are

1. All the members of a series contain same elements and the functional group.
2. All the members can be represented by a single general formula. *e.g.,* C_nH_{2n+2} is the general formula for alkanes.

   $C_nH_{2n+1}OH$ is the general formula for alcohols.
3. The molecular formula of each homologue differs from its previous and successive member by —CH_2 unit, *i.e.,* their molecular mass differs by 14 units.
4. All members of a series can be prepared by almost similar methods.
5. There is a gradual variation seen in physical properties of compounds with increasing molecular weight belonging to same homologus series.
6. All the members of a series show almost similar chemical properties.

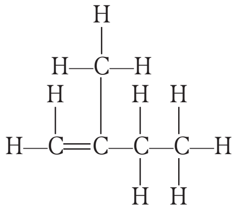
Note For isomerism see the next chapter, chapter 14.

13.5 Structural Representation of Organic Compounds

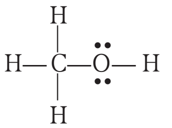
There are following three ways by which an organic compound can be represented. These are complete, condensed and bond line notations.

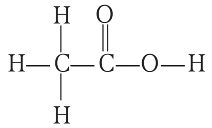
Complete Notation

Complete structure means all the bonds (either single or double or triple) present between any two atoms are shown clearly. *e.g.,* the complete structure of 2-methyl butene is as



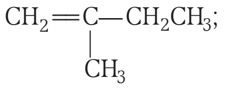
Similarly, the complete structures of methanol and acetic acid are as


(methanol)


(acetic acid)

Condensed Structure

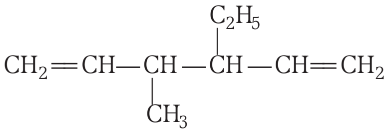
When all the bonds (except double and triple bonds between two carbon atoms) are omitted, the obtained structure is called condensed structure.

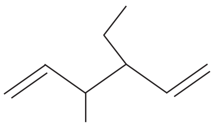
e.g., 
$CH_2{=}\underset{\underset{CH_3}{|}}{C}{-}CH_2CH_3$; CH_3OH ; CH_3COOH

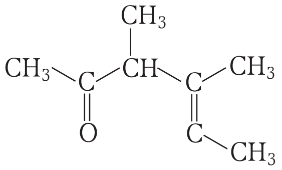
(methanol) (acetic acid)

Bond Line Notation

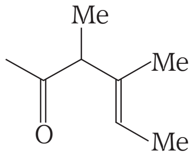
It is a simple and convenient method of representing structures. In this notation bonds are represented by lines and C-atoms by line ends and intersections. It is assumed that required number of H-atoms are present wherever, they are necessary (to satisfy tetravalency of carbon), *e.g.,*


$CH_2{=}CH{-}\underset{\underset{CH_3}{|}}{CH}{-}\overset{\overset{C_2H_5}{|}}{CH}{-}CH{=}CH_2$ can be represented as

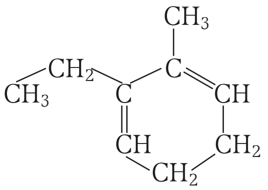




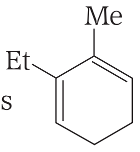
can be written as



Me = Methyl



can be written as



Et = ethyl

13.6 Systems of Nomenclature of Organic Compounds

Trivial System

It is the oldest system of naming organic compounds. These names have no part used in a systematic sense, whenever a new compound was discovered, it was given an individual name. Such a name was assigned at the wish of discoverer and had no system. These names are also called **common names** and are generally based on the source or some property or any other reason. Quite frequently these names had their Latin or Greek roots, *e.g.,*

(i) Acetic acid (*Acetum* = Vinegar). Vinegar is liquid which contain CH_3COOH as its chief constituent.
(ii) Oxalic acid (derived from *Oxalus*)
(iii) Malic acid (derived from *Pyrus malus*)
(iv) Citric acid (derived from *Citrus*)
(v) Formic acid (first obtained from red ants *Formicus*)
(vi) Urea and uric acid (from urine in which both are present)
(vii) Methyl alcohol (from methu hul means wine alcohol)
(viii) Butyric acid (from butyrum *i.e.*, butter)

Semisystematic or Semitrivial System

It is a name in which at least one part is used in a systematic sense, *e.g.,*

Glycer(ol), Acet(one), Styr(ene), 5-α-cholest(ane)

Here, words in brackets are used in systematic sense.

As these names are derived from two sources, hence these are also called **derived names.**

IUPAC System

In 1957, the International Union of Pure and Applied Chemistry evolved a scheme for giving systematic name to organic compounds on the basis of their structure. This is known as the **IUPAC system of nomenclature.** This system has set of rules for naming organic molecules from their structure. One organic compound can have only one IUPAC name and it is always superior to all common and derived names. After knowing the IUPAC names it is possible to draw the structures of organic compounds also. Remember IUPAC amends these rules from time to time and in this book we are following the 1993 (most recent) recommendations of IUPAC nomenclature.

13.7 IUPAC System of Nomenclature

Rules for Writing IUPAC Names

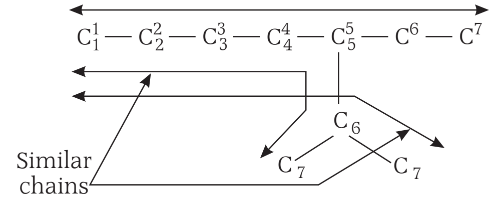
Following rules are followed while giving IUPAC *name to an organic compound.*

Longest Chain Rule

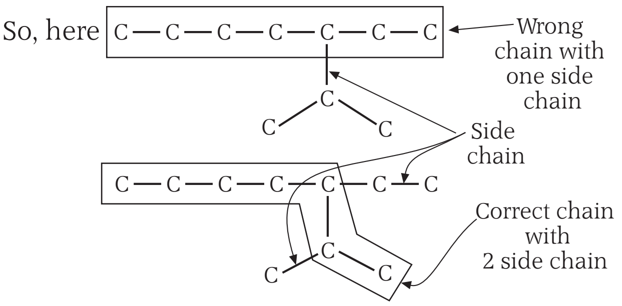
The longest possible chain can be selected in accordance with the following rules

1. Normally the chain with maximum number of C–atoms will be the longest possible chain.

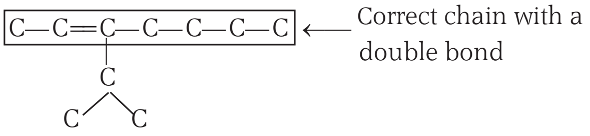
2. In case of two or more chains with same number of C–atoms, select the chain with maximum number of side chains as the longest possible chain. (IUPAC prefers such a situation to avoid complicated names), *e.g.,*



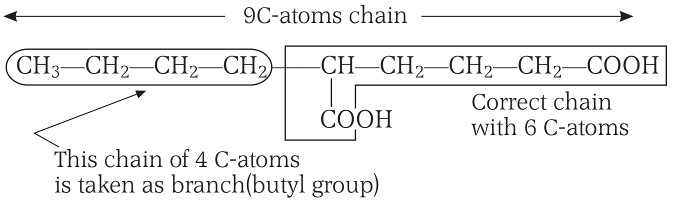
In this example, all the 3 chains possible contain 7 C-atoms in them. Out of these 3, two chains are similar as seen in diagram.



3. If a double bond/triple bond/functional group is present in the molecule, it must be included in the longest possible chain, *e.g.,*



4. Avoid the longest chain rule even if the chain containing multiple bonds or functional group falls smaller than other chains (the rule of exception), *e.g.,*



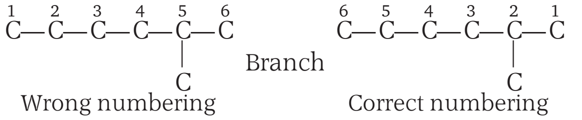
In this particular case although the longest chain is of 9 C-atoms (see figure) but the preference will be given to the chain of 6 C-atoms.

So, the longest possible chain can be defined as *"the chain containing the principal functional group + secondary functional group + multiple bonds as many as possible"*.

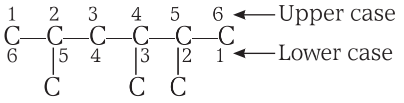
Rules of Numbering the Longest C-Chain

In numbering a chain following rules are considered

1. Numbering can be done from either of its ends for a symmetrical compound.
2. If single branch (side chain) is present in the compound then numbering must be done in such a manner so that the side chain acquires the least possible number, *e.g.,*



3. If more than one side chains are present in the compound and if
   (i) All the chains are of same length, then numbering must be done in accordance with **lowest sum rule** *i.e.,* numbering should be done in such a way that the sum of numbers of side chains will be the least, *e.g.,*



Sum

for upper case 2 + 4 + 5 = 11 (wrong numbering)

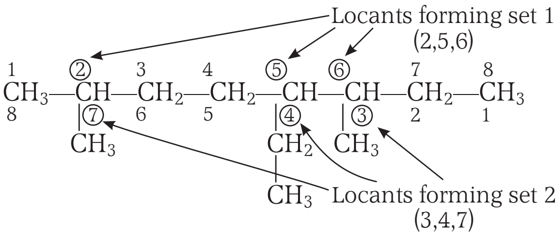
for lower case 2 + 3 + 5 = 10 (correct numbering)

Here, as the sum of lower case is lowest that is why, it is preferred.

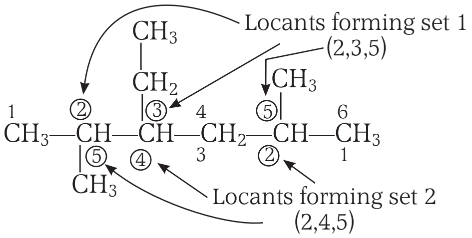
   (ii) In case of branches of different lengths, the numbering must be done in accordance with **"lowest set of locants rule".** (The word "locant" is used by IUPAC for those C-atoms in a chain which bear a branch or a multiple bond or a functional group).

According to this rule "while comparing two or more different sets of locants containing the same number of terms *then that set of locants is lowest which when compared term by term has the lowest term at the first point of difference, e.g.,*

***Case* 1** Suppose in a chain two sets of locants come as (2, 5, 6) and (3, 4, 7) then the first set will be preferred because the first term, *i.e.,* 2 in the first set is lower than the first term in the second set, *i.e.,* 3.

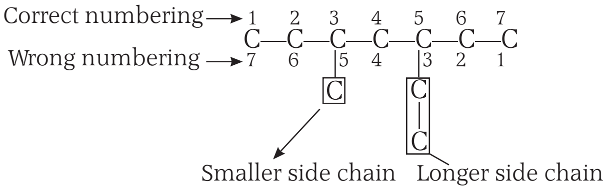


***Case* 2** Similarly, suppose, if 2 sets of locants come as (2, 3, 5) and (2, 4, 5) then here again first set is preferred because the second term (first term is being same in both the sets) in the first set is smaller.

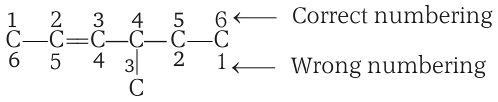


Now, from the above two examples it is clear that we are comparing the set of locants one by one and that set of locants is preferred which has a lower number at the first point of difference. That's why the rule is also called sometimes as **first point of difference rule.**

(iii) If the side chains of different lengths are present at the same distance from the ends, then the chain with lesser number of carbon atoms must get the least possible number, *e.g.,*

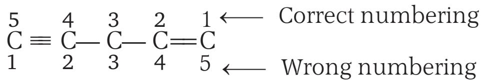


4. If multiple bond* is present alongwith the side chain then numbering must be done in such a manner that multiple bond will get the lowest possible number, *e.g.,*

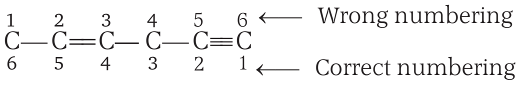


*multiple bond ⇒ double bond or triple bond

5. If double bond and triple bond both are present in the compound then double bond must be preferred.

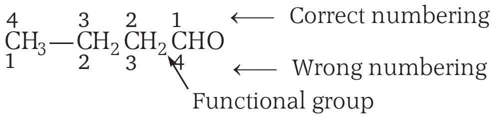


Remember here, the comparison can be made only if the bonds are present on the same footings i.e., situated at equal distance from the ends. e.g.,

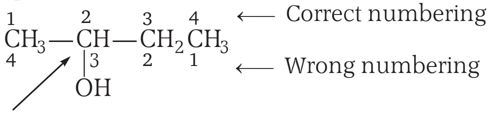


In the above example, triple bond and single bonds are not present at the same footings. Hence, out of these two, triple bond will be preferred *i.e.,* numbering must be done in such a manner that the triple bond will get least possible number.

6. If any other functional group is present in the compound (other than multiple bond) then numbering must be done in such a manner that the functional group will get the lowest possible number, *e.g.,*



The above example is for those functional groups which contain C-atom in them. For those functional groups which does not contain C-atom in them, the example is written below



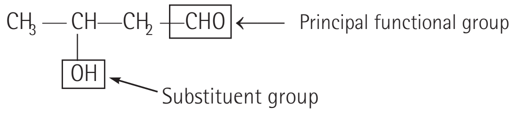
Here, this C-atom is considered as C-atom of functional group and this must get least possible number.

7. If more than one functional groups are present in the compound then the group which comes first in the following preferential order will be considered as **principal functional group** and rest of the functional groups are considered as **substituent groups or branch.**

The order of priority of various functional groups are as

1. Radicals
2. Anions
3. Cations
4. Zwitter ionic compounds
5. Acids (in the order COOH then their S and Se derivatives followed by sulphonic, sulphinic, selenonic, etc., phosphonic, arsonic, etc., acids)
6. Anhydrides
7. Esters
8. Acid halides
9. Amides
10. Hydrazides
11. Imides
12. Nitriles
13. Aldehydes followed by thioaldehydes, selenoaldehydes and telluroaldehydes.
14. Ketones followed by thioketones, selenoketones and telluroketones.
15. Alcohols and phenols followed by thiols, selenols and tellurols.
16. Hydroperoxides followed by thiohydroperoxides, selenohydroperoxides and tellurohydroperoxides.
17. Amines
18. Imines
19. Hydrazines, phosphanes, etc.,
20. Ethers followed by sulphides, selenides and tellurides
21. Peroxides followed by disulphides, diselenides and ditellurides.
22. Alkene
23. Alkyne
24. Halo, nitroso, nitro, alkoxy
25. Oxiranes (cyclic ethers)

The name of principal functional group must be written in suffix and that of substituent groups or branch is written in prefix. *e.g.,*



Hot Spot 1

WRITING the IUPAC Names

Naming an organic compound is an important topic for JEE Main examination point of view. The nature of question may vary from very simple to typical or confusing. A small practice can help you to solve the problem.

Following steps are used to write the IUPAC name of an organic compound :

Step I Locate the longest chain with as many possible secondary functional groups alongwith multiple bonds (*i.e.,* choose the longest possible chain).

Step II Select the word root corresponding to the length of longest possible chain. For one to four carbon atoms, special word roots are used whereas, for five or more carbon atoms, Greek numericals are used. The word roots alongwith the number of carbon atoms are tabulated below

Table 13.1 **Word Root Representing C-Atoms**

Chain length	Word root	Chain length	Word root
C_1	Meth–	C_7	Hept–
C_2	Eth–	C_8	Oct–
C_3	Prop–	C_9	Non–
C_4	But–	C_{10}	Dec–
C_5	Pent–	C_{11}	Undec–
C_6	Hex–	C_{12}	Dodec–

Step III Number the longest possible chain (according to the rules) to give an identification number to each C-atom of longest possible chain.

Step IV Add suitable prefixes and suffixes alongwith numerals to indicate the number and position of each side chain, substituent or functional group present in compound.

Prefix *It is used to indicate the substituents and is of the following two types*

(i) **Primary prefixes** are those prefixes which are usually used to distinguish between cyclic and acyclic compounds just like cyclo, bicyclo etc., or the prefixes used to tell us about the number of substituents present just like bi, di, tri, tetra, tris, tetrakis, ter, quater etc.

(ii) **Secondary prefixes** are infact the names of those groups to which IUPAC consider as substituents or branch either always (*e.g.,* halogens) or under certain conditions *i.e.,* whenever principal functional group is present alongwith the substituents in polyfunctional compounds. These prefixes are always written immediately before the root word. Some of these prefixes are given below

Table 13.2 **Prefixes for Substituents**

Substituent	Prefix	Substituent	Prefix
—F	Fluoro	—N═N—	diazo
—Cl	Chloro	—N ═O	nitroso
—Br	Bromo	$—NO_2$	nitro

Note The prefix used for functional group are given later alongwith their suffix.

Suffix It is used to indicate the functional group. The suffix also may be of two types

(i) **Primary suffixes** are those words which tells us about the saturation or unsaturation of longest possible chain. The three basic primary suffixes are

–ane for saturated chain,

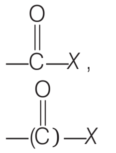
–ene for unsaturated chain with a double bond,

–yne for unsaturated chain with a triple bond.

(ii) **Secondary suffixes** are infact the names of principal functional groups either in monofunctional or in polyfunctional compounds. These are given in the following table.

Table 13.3 **Prefix and Suffix of Various Functional Groups** (in priority order)
(as given under the 1993 recommendations of IUPAC)

S. No.	Class	Formula	Prefix	Suffix
1.	Carboxylic acids	—COOH	carboxy-	–carboxylic acid
		—(C)OOH	—	–oic acid
2.	Sulphonic acids	$—SO_2—OH$	sulpho-	–sulphonic acid
3.	Esters (of carboxylic acids)	—COOR*	(R*)-oxy-carbonyl	(R*)… carboxylate
		—(C)OOR*	(R*)-oxycarbonyl	(R*)…oate

S. No.	Class	Formula	Prefix	Suffix
4.	Acid halides	 $-\overset{O}{\overset{\|}{C}}-X$, $-\overset{O}{\overset{\|}{(C)}}-X$ where, X = halogen	halocarbonyl – —	–carbonyl halide –oyl halide
5.	Amides	$-CO-NH_2$ $-(C)O-NH_2$	carbamoyl– —	–carboxamide –amide
6.	Nitriles	$-C\equiv N$ $-(C)\equiv N$	cyano– —	–carbonitrile –nitrile
7.	Aldehydes	$-CHO$ $-(C)HO$	formyl– —	–carbaldehyde –al
8.	Ketones	$(C)=O$	oxo	–one
9.	Alcohols, Phenols	$-OH$	hydroxy–	–ol
10.	Thiols	$-SH$	sulphanyl-	–thiol
11.	Amines	$-NH_2$	amino–	–amine
12.	Imines	$=NH$ $=NR^*$	imino– (R^*)-imino	–imine
13.	Ethers	$-OR^*$	(R^*)-oxy	–

***In the above table R designates any alkyl group and C-atom in ( ) means when it is included in the main chain while C-atom without ( ) means it is not included in the main chain.**

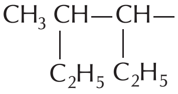
Hence, with the help of steps given above the IUPAC name of a compound can be written as

Prefixes	+	Root word	+	Suffixes
Tells us about the branches or substituents except in the case of multiple bonds		Tells us about the length of longest possible chain		Tells us about the principal functional groups mostly except in the case of halogens

OR

Primary prefix + Secondary prefix + Root word + Primary suffix + Secondary suffix

Sample Problem 8 *Correct IUPAC name for*



$$CH_3\,\underset{\large C_2H_5}{\underset{|}{CH}}-\underset{\large C_2H_5}{\underset{|}{CH}}-CH_3$$

is **[NCERT Exemplar]**

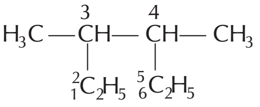
(a) 2-ethyl-3-methylpentane

(b) 3,4 -dimethyl hexane

(c) 2-sec-butyl butane

(d) 2,3- diethyl butane

Interpret (b) In the given compound first of all we choose the longest chain and choose the root word accordingly.



$$H_3C-\overset{3}{\underset{{}^{2}_{1}C_2H_5}{\underset{|}{CH}}}-\overset{4}{\underset{{}^{5}_{6}C_2H_5}{\underset{|}{CH}}}-CH_3$$

Six carbon : Root word = hex

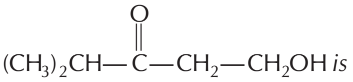
Only single bonds are present and no other functional group is present. So, suffix (ane) is added to the root word.

Moreover, this compound contains two substituents ($-CH_3$) at position 3 and 4, so their prefix with position number are used.

Hence, the name of the given compound is

$$\underbrace{3,4-\text{dimethyl}}_{\text{prefix}}\ \underbrace{\text{hexane}}_{\text{root word suffix}}$$

Sample Problem 9 *The IUPAC name of the compound*



$$(CH_3)_2CH-\overset{O}{\overset{\|}{C}}-CH_2-CH_2OH$$

is

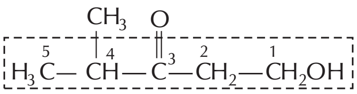
(a) *hexanol*-1-*one*-3

(b) 2-*methyl*-5-*hydroxy*-3-*pentane*

(c) 1-*hydroxy*-4-*methyl*-3-*pentanone*

(d) 4-*methyl*-3-*oxo*-1-*pentanol*

Interpret (d)



$$\overset{5}{H_3C}-\overset{CH_3}{\overset{|}{\underset{4}{CH}}}-\overset{O}{\overset{\|}{\underset{3}{C}}}-\overset{2}{CH_2}-\overset{1}{CH_2OH}$$

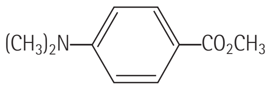
Number of C in longest chain = 5 so Root word pent. All bonds between C are single bond so suffix 'ane'. Although $C=O$ have priority but both sides its position is 3 so —OH is taken in main chain. For —OH suffix is –ol.

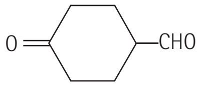
For $>C=O$ prefix is –oxo

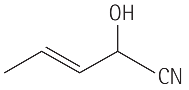
Thus, the name of the compound is 4-methyl-3-oxo-1-pentanol.

Check Point 1

1. Why carbon cannot exhibit dsp^3, sp^3d etc., hybridisations?
2. $CH\equiv CH$ is more electronegative as compared to $CH_2=CH_2$ Explain.
3. Circle the functional group with highest priority in each structure below.

(i)


(ii)


(iii)


4. Provide the systematic name of the following common names (i) propyl bromide, (ii) ethyl methyl ether, (iii) ethyl iodide
5. Between the 2, 5, 6-trimethyl heptane and 3, 4, 7-trimethyl heptane which one is correct? Explain why?

13.8 Functional Groupwise Nomenclature

After the study of rules and steps for writing IUPAC name, you can write the name of any class of compound but here with we are giving a detail of nomenclature of different classes step by step.

Hydrocarbons

Hydrocarbons are the compounds that contain carbon and hydrogen only.

These are of the following types

(a) Alkanes

Alkanes are the hydrocarbons that contain only single bonds (saturated). The first four members of the series are known by their common names *i.e.*, **methane, ethane, propane** and **butane.** The names of larger alkanes are derived from the Greek prefixes that indicate the number of C-atoms in the molecule, *e.g.*, pentane (with 5 C-atoms), hexane (with 6 C-atoms) and so on.

Infact the names of the alkanes are obtained by adding '–ane' to the root word.

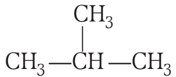
Root word + -ane = alkane

In the common system all isomeric alkanes have the same parent name, *e.g.*, two isomeric C_4H_{10} alkanes are known as butanes. The names of various isomers are distinguished by prefixes. The prefix indicates the type of branching present in the molecule.

1. **Prefix *n*** is used for those alkanes in which all carbons are in one continuous chain. The prefix *n*-stands for normal or straight chain of carbon atoms. *e.g.*,

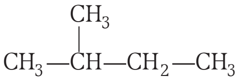
$CH_3CH_2CH_2CH_3$ *n*-butane $CH_3CH_2CH_2CH_2CH_2CH_3$ *n*-hexane

2. **Prefix *iso*** is used for those alkanes which have a methyl group $—CH_3$ attached to the second last carbon atom of the continuous chain. *e.g.*,



$$CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_3$$

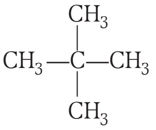
iso-butane



$$CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2-CH_3$$

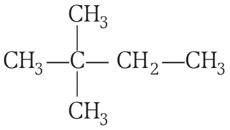
iso-pentane

3. **Prefix *neo*** is used for those alkanes which have two methyl groups attached to the second last carbon atom of the continuous chain. *e.g.*,



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

neo-pentane



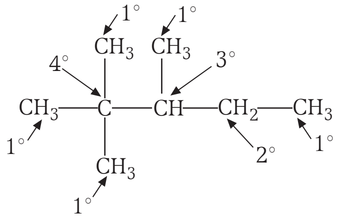
$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_3$$

neo-hexane

However, IUPAC does not recognise these prefixes.

The structural formula of alkanes contain four types of carbons

1. **Primary carbon** (or 1° carbon atom) is the carbon atom which is attached to one or no other carbon atom.
2. **Secondary carbon** (or 2° carbon atom) is the carbon atom that is attached to two other carbon atoms.
3. **Tertiary carbon** (or 3° carbon) atom is the carbon atom that is attached to three other carbon atoms.
4. **Quaternary carbon** (or 4° carbon) atom is the carbon atom which is attached to four other carbon atoms.



Hydrogen atoms attached to 1°, 2°, 3° carbon atoms are often referred to as primary, secondary and tertiary hydrogen atoms.

However, names of these carbon and hydrogen atoms are not recognised by IUPAC.

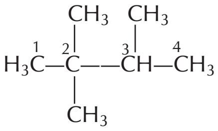
Caution Point *When a hydrogen atom is removed from an alkane, the remaining group is called alkyl group and represented by 'R' e.g.,* $—CH_3$ *(methyl group) is obtained by removing one H-atom from methane* (CH_4).

Sample Problem 10 *In the structure,*

$\overset{1}{H_3C}-\overset{2}{C}(CH_3)_2\overset{3}{C}H(CH_3)\overset{4}{C}H_3$, *which one is a quaternary carbon atom?*

(*a*) C-1 (*b*) C-2 (*c*) C-3 (*d*) C-4

Interpret (*b*) Quaternary carbon is the carbon atom which is attached with four other carbon atoms.



$$H_3\overset{1}{C}-\underset{CH_3}{\overset{CH_3}{\overset{2}{C}}}-\overset{CH_3}{\overset{3}{C}}H-\overset{4}{C}H_3$$

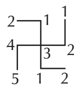
Structure shows that C-2 is attached with four other carbon atoms, so it is a quaternary carbon atom.

Sample Problem 11 *The correct IUPAC name for*

is

(*a*) *neo-nonane* (*b*) *tetraethylmethane*
(*c*) *3-ethylpentane* (*d*) *3,3-diethylpentane*

Interpret (*d*)



Hence, its IUPAC name is 3,3-diethylpentane.

(b) Alkenes

Alkenes are hydrocarbons that contain one or more carbon-carbon double bond. Their common names are obtained by changing the ending **–ane** to **–ene**. *i.e.,*

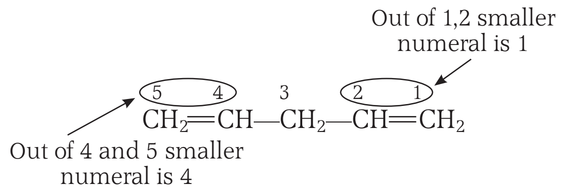
$$\boxed{\textbf{alkane –ane + ene = alkene}}$$

If parent chain contains 2, 3 or 4 double bonds than numerical prefixes like **di** (for two), **tri** (for three) or **tetra** (for four) are added to primary suffix. **Remember in all such cases –a of ane is retained,** *e.g.,* alkadiene, alkatriene etc., *e.g.,*

$$\overset{5}{C}H_2=\overset{4}{C}H-\overset{3}{C}H_2-\overset{2}{C}H=\overset{1}{C}H_2$$

penta-1,4-diene

While writing the position of double bond, always write the smaller numeral of the two atoms between which the bond is present. *e.g.,* in the above example



Hence, 1 and 4 are included in the name *e.g.,* penta-1,4-diene.

(c) Alkynes

Alkynes are the hydrocarbons that contain C—C triple bonds ($C\equiv C$). The IUPAC rules for naming alkynes are analogous to those for alkenes, *i.e.,*

$$\boxed{\textbf{alkane – ane + yne = alkyne}}$$

e.g., $$\underset{1}{C}H_3-\underset{2}{C}\equiv\underset{3}{C}-\underset{4}{C}H_2-\underset{5}{C}H_2-\underset{6}{C}H_3$$

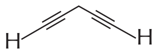
hex-2-yne

If both double and triple bonds are present in the compound, the endings like -en-yne, a (numeral) dien-(numeral)-yne etc., are used. Numbers as low as possible are given to double and triple bonds as a set, e.g.,

$$\underset{5}{C}H_3-\underset{4}{C}H=\underset{3}{C}H-\underset{2}{C}\equiv\underset{1}{C}H \qquad \overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H_2-\overset{4}{C}\equiv\overset{5}{C}H$$

pent-3-en-1-yne pent-1-en-4-yne

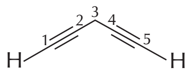
***Sample* Problem 12** *The compound*



has the IUPAC name

(*a*) *propane*-1,3-*diyne* (*b*) 1,4-*pentadiyne*
(*c*) 1,3-*pentadiyne* (*d*) *pentanone*-1,3-*diyne*

Interpret (*b*)



The condensed form of this bond line structure is

$$H\overset{1}{C}\equiv\overset{2}{C}-\overset{3}{C}H_2-\overset{4}{C}\equiv\overset{5}{C}H$$

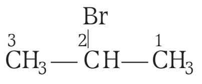
Hence, its IUPAC name is 1,4-pentadiyne,

AlKyl Halides

These are the compounds which contains carbon-halogen bonds. Their name is written by adding prefix 'halo' (chloro, bromo, iodo) with the position number to the name of parent alkane.

$$\boxed{n\text{-halo} + \text{Alkane} \longrightarrow n\text{-haloalkane}}$$

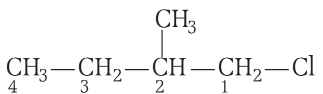
e.g.,



$$\overset{3}{C}H_3-\overset{Br}{\overset{2}{C}H}-\overset{1}{C}H_3$$

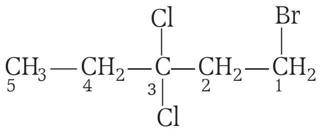
2-bromopropane

If there are two or more identical halogen substituents, the prefix, di, tri, tetra etc., are used *e.g.,*



$$\underset{4}{C}H_3-\underset{3}{C}H_2-\underset{2}{\overset{CH_3}{C}H}-\underset{1}{C}H_2-Cl$$

1-chloro-2-methylbutane



$$\underset{5}{C}H_3-\underset{4}{C}H_2-\underset{\underset{Cl}{3}}{\overset{Cl}{C}}-\underset{2}{C}H_2-\underset{1}{\overset{Br}{C}H_2}$$

1-bromo-3,3-dichloropentane

If the two different halo group occupy the same position from the opposite sides of the parent chain, the perference will be given to the halogen according to alphabetical order *e.g.,*

$$Br\underset{1}{C}H_2-\underset{2}{C}H_2-\underset{3}{C}H_2Cl$$

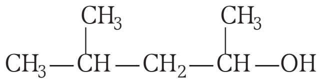
1-bromo-3-chloro propane

Alcohols

Alcohols are compounds in which a hydroxyl group (—OH) is bonded to a saturated carbon. They are classified as primary, secondary, or tertiary, depending upon whether the —OH group is attached to a primary, secondary, or tertiary carbon atom. Abbreviations for these terms are 1°, 2° and 3° respectively. *However, terms primary, secondary and tertiary are not recognised by IUPAC.*

Their name is obtained by dropping the final –e from the name of the alkane that contains the same number of carbon atoms and adding the ending '–ol'. *e.g.,*

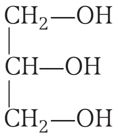
$$\boxed{\textbf{Alkane – e + ol} \longrightarrow \textbf{alkanol}}$$



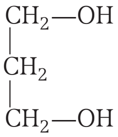
$CH_3—\underset{}{\overset{CH_3}{\overset{|}{C}H}}—CH_2—\overset{CH_3}{\overset{|}{C}H}—OH$

1,3-dimethylbutan-1-ol

Alcohols containing two or three —OH groups are named as alkanediols and alkanetriols respectively. *Note that -'e' of the corresponding alkane name is retained in such cases.*



propane-1,2,3-triol



propane-1,3-diol

Ethers

Ethers are the compounds in which an oxygen atom is bonded to two alkyl groups (*R*–O–*R*). In the common system, the two alkyl groups attached to the oxygen atom are named in alphabetic order and the word ether is added, *e.g.,*

$CH_3OC_2H_5$ methyl ethyl ether

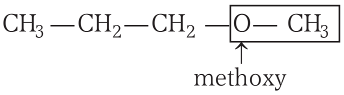
$C_2H_5OC_3H_7$ ethyl propyl ether

If the groups are same then prefix di is used as :

CH_3OCH_3 dimethyl ether

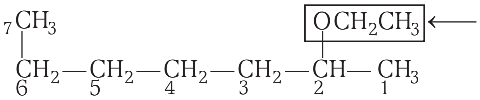
$C_2H_5OC_2H_5$ diethyl ether

In the IUPAC system, ethers are named as **alkoxyalkanes.** The smaller alkyl group plus the oxygen atom is called an **alkoxy substituent.**



$CH_3—CH_2—CH_2—\underset{\text{methoxy}}{\underset{\uparrow}{\boxed{O—CH_3}}}$

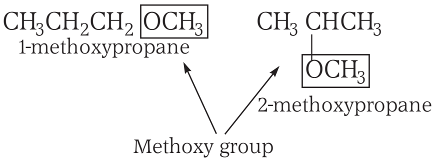
The name of the compound is 1 - methoxypropane



$\underset{6}{\overset{_7CH_3}{\overset{|}{C}H_2}}—\underset{5}{CH_2}—\underset{4}{CH_2}—\underset{3}{CH_2}—\underset{2}{\overset{\boxed{OCH_2CH_3}}{\overset{|}{C}H}}—\underset{1}{CH_3}$ ⟵ Ethoxy

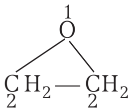
The name of the compound is 2-ethoxyheptane.

Remember always that terminal position cannot be assumed for alkoxy group, it can be placed with any C–atom of the chain, *e.g.,*



Oxiranes

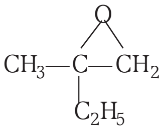
Oxiranes are infact cyclic ethers in which ethereal oxygen is a part of three membered oxirane ring. This ring seems as



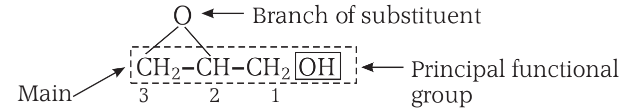
Oxirane ring

Here, oxygen of the ring is given number 1 and both the C–atoms as 2 by IUPAC.

These cyclic ethers are placed at the lowest preference in the preferential order and normally written as prefixes when any functional group present in the compound (except alkyl group). The prefix of this group is **epoxy,** *e.g.,*



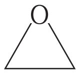
2-ethyl-2-methyl oxirane



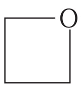
2,3-epoxypropan-1-ol

Oxiranes are also called **epoxides.** As they are readily prepared from alkenes, they are commonly called **alkene oxides.**

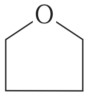
IUPAC name of the some of the oxiranes are as



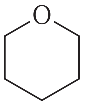
oxirane or 1,2-epoxyethane



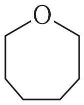
oxetane or 1,3-epoxypropane



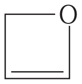
oxolane or 1,4-epoxybutane



oxane or 1,5-epoxypentane



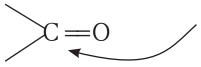
oxepane or 1,6-epoxyhexane



oxetene or 1,3-epoxyprop-1-ene

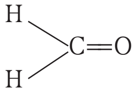
Aldehydes

These are the compounds in which carbonyl group [$>C{=}O$] is bonded to at least one hydrogen (alongwith one alkyl group).

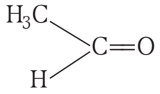


At least one hydrogen atom should be attached to either of these valencies.

Their common names are related to those of carboxylic acids, *e.g.,*



formaldehyde (Related to formic acid)



acetaldehyde (Related to acetic acid)

- Their IUPAC names are obtained by dropping final –e from the name of corresponding alkane and adding the ending -al,

i.e., $\boxed{\text{alkane} - \text{e} + \text{al} = \text{alkanal}}$

e.g., HCHO methanal; CH_3CHO ethanal; CH_3CH_2CHO propanal

Ketones

Ketones are the compounds in which carbonyl group [$>C{=}O$] is bonded to two alkyl groups.

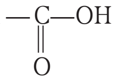
In the IUPAC system, ketones are named as alkanones *i.e.,*

$\boxed{\text{alkane} - \text{e} + \text{one} = \text{alkanone}}$

e.g., $\overset{1}{CH_3}\,\overset{2}{CO}\,\overset{3}{CH_3}$ propan-2-one; $\overset{1}{CH_3}\,\overset{2}{CO}\,\overset{3}{CH_2}\,\overset{4}{CH_3}$ butan-2-one

Carboxylic Acids

These are the compounds which contain



$-\underset{\underset{O}{\|}}{C}-OH$ group.

In IUPAC system these are named as alkanoic acid, *i.e.,*

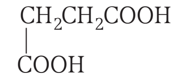
$\boxed{\text{alkane} - \text{e} + \text{oic acid} = \text{alkanoic acid}}$

e.g., HCOOH methanoic acid; CH_3COOH ethanoic acid; CH_3CH_2COOH propanoic acid

For all those functional groups which contain C-atom in them, following two conditions are also applicable

1. Two suffixes are given to these functional groups according to 1993 recommendations. (see table 13.3) *Out of these two, one - oic acid can be used normally while other one (carboxylic acid) is used when it is difficult to count the C-atom of functional group in the main chain, e.g,*

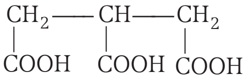
CH_3CH_2COOH propanoic acid



$\underset{|\atop COOH}{CH_2}CH_2COOH$

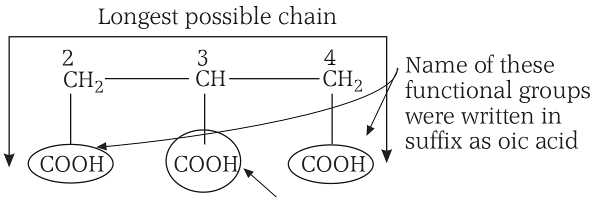
butane-1,4-dioic acid

But when another carboxylic group is attached to the main chain directly as,



$\underset{|\atop COOH}{CH_2}-\underset{|\atop COOH}{CH}-\underset{|\atop COOH}{CH_2}$

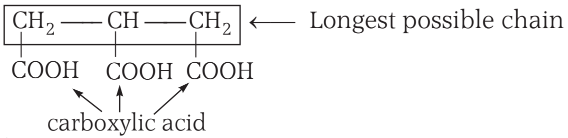
Here, *problem lies in the fact that all the functional groups cannot be taken in the main chain simultaneously.* This situation was not so clear in 1979 recommendations where the —COOH attached to centralised C-atom was written in prefix while rest two —COOH groups attached at terminals were written in suffix as:



The name of the compound according to 1979 recommendations was 3-carboxy pentane-1,5 dioic acid

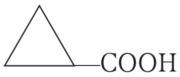
Name of this functional group was written in prefix as- carboxy

But in its recommendations of 1993, IUPAC cleared the situation for such cases and mentioned, *"If an unbranched chain is directly linked to more than two carboxy groups, these carboxy groups are named from the parent hydride by substitutive use of a suffix like carboxylic acid".* So, the name of the above written compound according to 1993 recommendations will be **propane–1, 2, 3 tricarboxylic acid.**

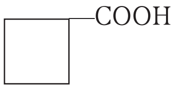


(C-atom of all the three is not included in the longest possible chain.)

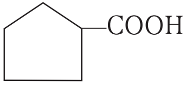
2. Such a situation is also applicable to the cases written below,



cyclopropane carboxylic acid



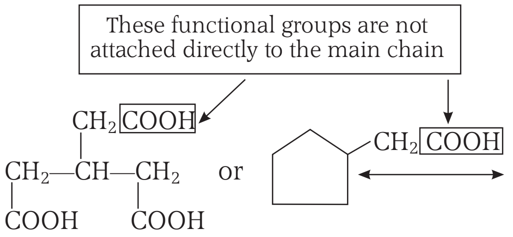
cyclobutane carboxylic acid



cyclopentane carboxylic acid

In all the above cases due to the presence of cyclic hydrocarbon difficulty lies in inclusion of C-atom of functional group within the longest possible chain. Hence, here also the suffix used is carboxylic acid and not the –oic acid which is normally used.

3. However, the suffix carboxylic acid cannot be used in situations like,



3-carboxymethyl, pentane-1,5-dioic acid

2-cyclopentyl ethanoic acid

Carboxylic Acid Derivatives

These are the compounds in which the —OH part of $-\underset{\underset{\text{O}}{\|}}{\text{C}}-\text{OH}$ group is replaced by various other groups. These various derivatives are

(a) Acid Chlorides

Here —OH group is replaced by —Cl group.

The group $-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{Cl}$ is commonly called as acyl chloride. Their IUPAC name can be written as,

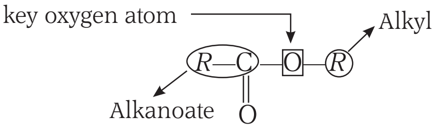
alkanoic acid – ic acid + yl chloride = alkanoyl chloride

e.g., CH_3COCl ethanoyl chloride; CH_3CH_2COCl propanoyl chloride

'Carbonyl chloride' is also assigned in case where this group is a substituent.

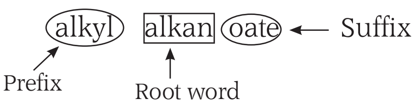
(b) Esters

Here, —OH group of acid is replaced by —O*R* group. Their IUPAC names are written as alkyl alkanoate.



Here, alkyl group present after key oxygen is written as alkyl and rest all the C-atoms before key oxygen are written as alkanoate.

Remember in alkyl alkanoate,



e.g., CH_3COOCH_3 methyl ethanoate; $CH_3COOC_2H_5$ ethyl ethanoate

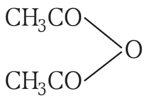
Suffix 'carboxylate' can also be assigned if this group is not present as principal group.

(c) Acid Anhydrides

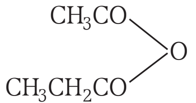
Here, —OH group of acid is replaced by — OC(*R*)═O. They are named as

alkanoic acid – acid + anhydride = alkanoic anhydride

e.g.,



ethanoic anhydride



ethanoic propanoic anhydride

(d) Amides

Here, —OH of carboxylic acid is replaced by $-NH_2$ group. They are named as

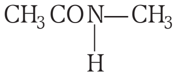
alkanoic acid – oic acid + amide = alkanamide

e.g., CH_3CONH_2 ethanamide; $HCONH_2$ methanamide

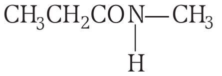
Suffix 'carboxamide' is used if $-CONH_2$ group is present as a substituent.

Alkyl group can also be attached to the nitrogen of $-NH_2$ group in place of hydrogen. In such cases the names of amides can be written as N—substituted amides.

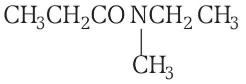
e.g.,


$CH_3CO\underset{\underset{\text{H}}{|}}{\text{N}}-CH_3$

N-methyl ethanamide


$CH_3CH_2CO\underset{\underset{\text{H}}{|}}{\text{N}}-CH_3$

N-methylpropanamide


$CH_3CH_2CO\underset{\underset{CH_3}{|}}{\text{N}}CH_2CH_3$

N-methyl-N-ethylpropanamide

Caution Point *Never treat the* $>C=O$ *and* $-NH_2$ *groups of an amide as separate entities.*

Sulphonic Acid

These compounds contain $-SO_3H$ group. Their IUPAC names are written as

alkane + sulphonic acid = alkane sulphonic acid

e.g., CH_3SO_3H methane sulphonic acid; $CH_3CH_2SO_3H$ ethane sulphonic acid

Nitro Compounds

These are the compounds which contain $-NO_2$ group in them. Their IUPAC names are obtained by adding the prefix 'nitro' to the name of alkane.

Nitro + alkane = Nitroalkane

e.g., CH_3NO_2 nitromethane, $CH_3CH_2NO_2$ nitroethane, $CH_3CH_2CH_2NO_2$ nitropropane

Cyanides or Nitriles

The compounds which contain —CN group are named as alkane nitriles in IUPAC system.

Alkane + nitrile ⟶ Alkane nitrile

e.g., $\overset{4}{CH_3}\,\overset{3}{CH_2}\,\overset{2}{CH_2}\,\overset{1}{CN}$ butane nitrile; CH_3CN ethane nitrile

CH_3CH_2CN propane nitrile; HCN methane nitrile

Like acids and others, for cyanides also two suffix, *i.e.,* carbonitrile and nitrile are assigned.

Amines

Amines are the derivatives of ammonia in which one or more hydrogen atoms have been replaced by alkyl/aryl groups. In the common system they are classified as primary (1°), secondary (2°) or tertiary (3°) depending upon the number of valencies of nitrogen atom satisfied by carbon atoms.

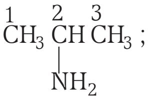
CH_3NH_2	$CH_3—NH—CH_3$	$CH_3—NCH_3—CH_3$
methyl amine	dimethyl amine	trimethyl amine
(primary)	(secondary)	(tertiary)

In the IUPAC system, primary amines are named by replacing the final –e of the parent alkane by amine, *i.e.,*

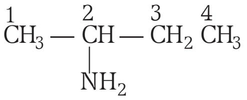
alkane –e + amine = alkanamine

The inclusion of number to indicate the position of $—NH_2$ group is also necessary (except the situation when $—NH_2$ group is attached at terminal position).

$CH_3CH_2NH_2$; ethanamine

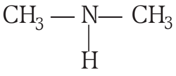

$\overset{1}{CH_3}\,\overset{2}{CH}(NH_2)\,\overset{3}{CH_3}$;

propan-2-amine

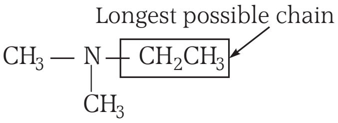

$\overset{1}{CH_3}—\overset{2}{CH}(NH_2)—\overset{3}{CH_2}\,\overset{4}{CH_3}$

butan-2-amine

The *secondary and tertiary amine are named as N-substituted and N,N-disubstituted amines*. The largest of the alkyl groups attached to nitrogen is chosen as the alkyl group of primary amine. (IUPAC does not considers secondary and tertiary amines as main compounds. According to IUPAC these are the substitution derivatives of primary amine). *e.g.,*

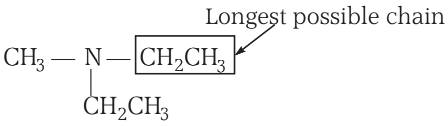

$CH_3—NH—CH_3$

N-methyl methanamine



$CH_3—N(CH_3)—\boxed{CH_2CH_3}$

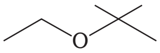
N,N-dimethyl ethanamine



$CH_3—N(CH_2CH_3)—\boxed{CH_2CH_3}$

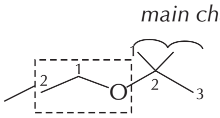
N-ethyl-N-methyl ethanamine

***Sample* Problem 13** *The systematic name for the given structure is*



(a) *2-ethoxy-2-methyl propane*
(b) *2-methoxy-2-ethoxypropane*
(c) *3-ethoxy-2-methoxypropane*
(d) *3-methoxy-2-ethyl propane*

Interpret (*a*)



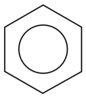
ethoxy group (substituent)

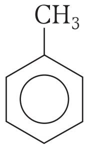
2-ethoxy-2-methyl propane

13.9 Nomenclature of Cyclic Compounds

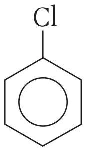
Naming the Aromatic Compounds

Common trivial names of aromatic compounds are accepted by IUPAC, they do not have separate IUPAC names. Thus,

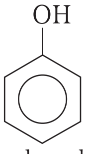

benzene



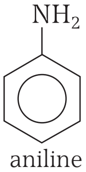
toluene



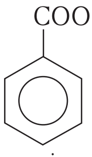
chlorobenzene



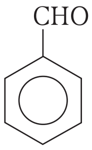
phenol



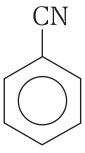
aniline



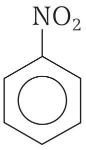
benzoic acid



benzaldehyde

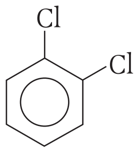


benzonitrile

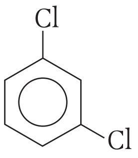


nitrobenzene

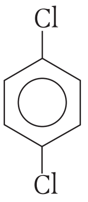
However, the use of *ortho* (*o*-), *meta* (*m*-), or *para* (*p*-) is avoided; instead, they are called 1,2; 1,3 and 1,4. Thus,



1,2-dichlorobenzene

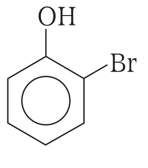


1,3-dichlorobenzene

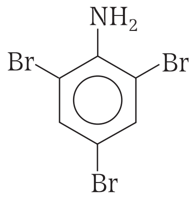


1,4-dichlorobenzene

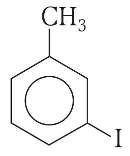
If the two groups attached to benzene ring are different then the main group is treated as the base compound. Thus,



2-bromophenol

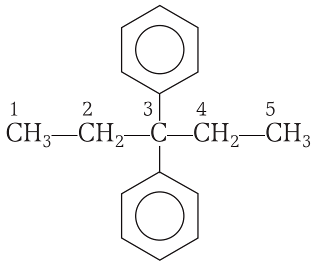


2,4,6-tribromoaniline

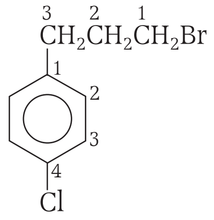


3-iodotoluene

If the aromatic compound has an open chain attached to benzene then this chain gets the main status; ring is treated as substituent. Thus,

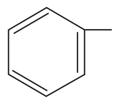


3,3-biphenyl pentane

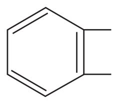


1-bromo-3-(4-chlorophenyl)propane

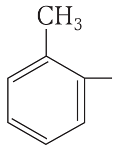
The following names are given to certain aromatic hydrocarbon residues formed by the loss of one or more hydrogen atoms from the parent hydrocarbon :



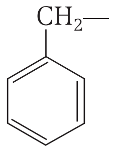
or C_6H_5—
phenyl



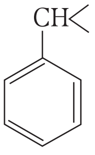
or $C_6H_4<$
o-phenylene



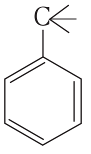
or $CH_3C_6H_4$—
o-tolyl



or $C_6H_5CH_2$—
benzyl or
phenyl methyl

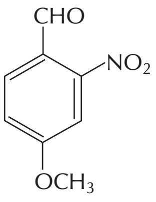


or $C_6H_5CH<$
benzal or
benzylidene



or $C_6H_5C\lessdot$
benzo or
benzylidyne

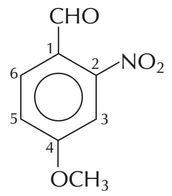
Sample **Problem 14** *What is the correct IUPAC name of*



(a) *4-formyl-3-nitro anisole*
(b) *4-methoxy-2-nitrobenzaldehyde*
(c) *4-methoxy-6-nitrobenzaldehyde*
(d) *2-formyl-5-methoxy nitrobenzene*

Interpret (*b*) The order of preference of given functional groups is

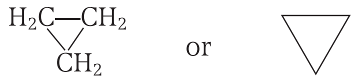
$$—CHO > —NO_2 > —OCH_3$$



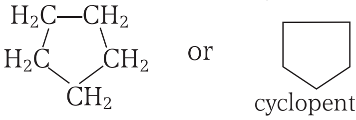
Thus, its IUPAC name is 4-methoxy-2-nitrobenzaldehyde.

Naming the Alicyclic (Monocyclic) Compounds

The alkanes in which carbon atoms are arranged in a ring are called **cycloalkanes.** They are named by attaching the prefix **'cyclo'** to the name of the alkane having the same number of carbons as in the ring.



cyclopropane



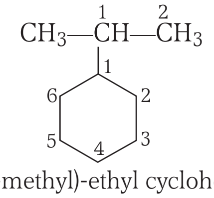
cyclopentane

Cycloalkanes are often represented by simple geometrical figures. It is understood that each corner represents —CH_2 groups. Remember that :

Cyclopropane is represented by a **triangle**
Cyclobutane is represented by a **square**
Cyclopentane is represented by a **pentagon**
Cyclohexane is represented by a **hexagon**

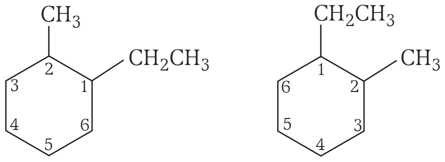
Following rules are considered while naming the alicyclic compounds :

1. Substituted cycloalkanes are named as alkylcycloalkanes. The substituents on the ring are named, and their positions are indicated by number.



1-(1-methyl)-ethyl cyclohexane

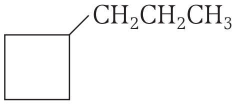
2. While numbering the C-atoms of the ring, the substituent which comes first in alphabetical order is given the lowest number provided that it does not violate the lowest sum rule. Remember there is no restriction in going clockwise or anticlockwise for numbering the C–atoms of ring. *e.g.,*



1-ethyl-2-methylcyclohexane

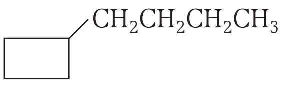
Since, 1-ethyl-2-methyl cyclohexane can have both of above written structures, both the above **written structures are similar.**

3. The alkyl group is designated as a substituent if the alkyl chain contains a lesser or equal number of C-atoms than the ring, *e.g.*,



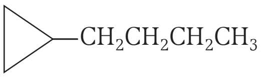
propylcyclobutane

and



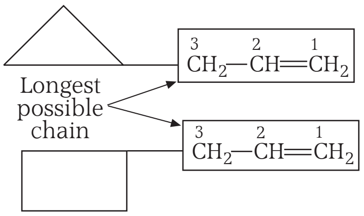
butylcyclobutane

4. The ring is designated as a substituent if the alkyl chain contains a greater number of C-atoms than the ring, *e.g.*,



cyclopropylbutane

5. However, if the side chain contains a multiple bond or a functional group, the ring is treated as a substituent irrespective of the size of ring.

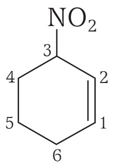


3-cyclopropylprop-1-ene

3-cyclobutylprop -1-ene

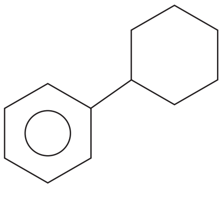
Such an exception is due to the rule *"the multiple bond/functional group if present in the compound should be included in the longest possible chain".*

6. If multiple bond and some other substituent are present in the ring, then the numbering should be done in such a manner so that the multiple bond gets the least possible number, *e.g.*,

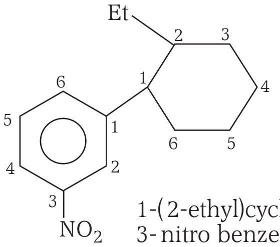


3-nitrocyclohex-1-ene

7. If a compound contains an alicyclic ring directly linked to the benzene ring, it is named as the derivative of benzene, *i.e.,* the compound having lowest state of hydrogenation, *e.g.*,

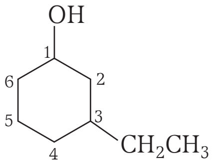


cyclohexyl benzene

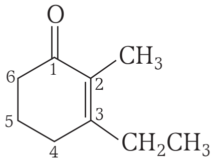


1-(2-ethyl)cyclohexyl 3-nitro benzene

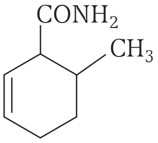
8. If some functional group alongwith other substituent groups are present in the ring, it is indicated by some appropriate prefix or suffix and its position is indicated by numbering the carbon atoms of the ring in such a way that the functional group gets the least possible number, *e.g.*,



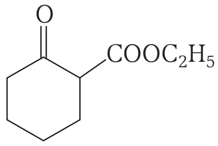
3-ethylcyclohexan-1-ol



3-ethyl-2-methyl cyclohex-2-en-1-one

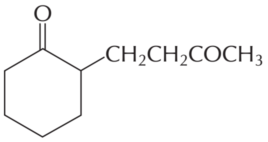


6-methylcyclohex -2-en-1-carboxamide



ethyl (2-oxo) cyclohexane 1-carboxylate

Sample **Problem 15** *The IUPAC name of*



is

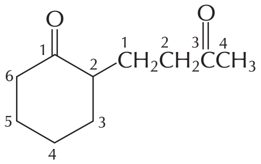
(a) 4-(2-oxobutyl) cyclohexan-1-one

(b) 4-(2-oxocyclohexyl) butan-2-one

(c) 1-(2-oxocyclohexyl) butan-3-one

(d) 2-(3-oxobutyl) cyclohexan-1-one

Interpret (*d*)

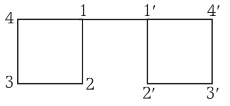


2-(3-oxobutyl) cyclohexan-1-one

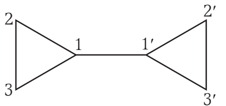
Naming the Bi and Polycyclic Compounds

1. Unbranched Assemblies Consisting of Two Identical Ring Systems

These assemblies are named by placing numerical prefix bi before the name of parent hydride, *e.g.,*



1,1′-bicyclo butane

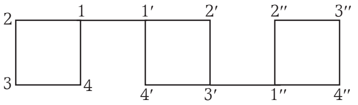


1,1′-bicyclo propane

Such assemblies can be identified by counting the C-atoms in them. The total number of C-atoms in such assemblies will be exactly double of the number of C-atoms present in a single ring.

2. Unbranched Assemblies Consisting of Three or More Identical Ring Systems

These are named by placing an appropriate numerical prefix like ter, quater, quinique etc., before the name of parent hydride corresponding to the repetitive unit, *e.g.,*

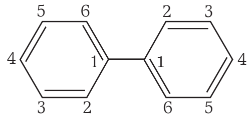


1,1′,3′,1″-tercyclobutane

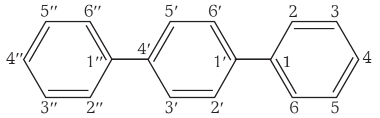
The following multiplying prefixes are used in names for unbranched assemblies of three or more identical repeating units :

2-bi-, 3-ter-, 4-quater-, 5-quiniques-, 6-sexi-, 7-septi-, 8-octi-, 9-novi-, 10-deci-

As exceptions, unbranched assemblies consisting of benzene rings are named by using the appropriate numerical prefix with the substituent prefix name phenyl, *e.g.,*



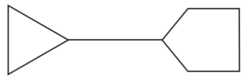
Biphenyl



1,1′4′,1″-terphenyl (preferred to *p*-terphenyl)

3. Unbranched Assemblies Containing Unidentical Rings

In such assemblies the smaller ring will be considered as substituent (written as cycloalkyl) while larger cycle will be considered as main chain, *e.g.,*



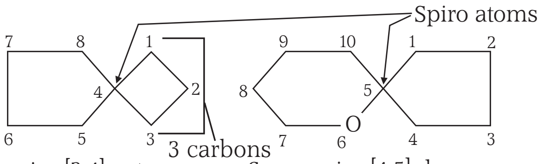
cyclopropyl cyclopentane

4. Spiro Parent Hydrides

A 'spiro union' is a linkage between two rings consisting of a single atom common to both. The common atom is designated as the 'spiro atom'. According to the number of spiro atoms present, the compounds are distinguished as monospiro, dispiro, trispiro, etc., ring systems. The following recommendations apply only to the naming of parent hydrides containing free spiro unions.

Monospiro parent hydrides are the hydrides consisting of two homogeneous saturated monocyclic rings and are named by placing 'spiro' before the name of the acyclic parent hydride with the same total number of skeletal atoms; heteroatoms, if any, in an otherwise hydrocarbon structure. The numbers of skeletal atoms linked to the spiro atom in each ring are indicated by arabic numbers separated by a full stop, cited in ascending order and enclosed in square brackets, this descriptor is placed between the spiro prefix and the name of the parent hydride.

Numbering starts with a ring atom next to the spiro atom and proceeds first through the smaller ring, if one is smaller, and then through the spiro atom and around the second ring, e.g.,

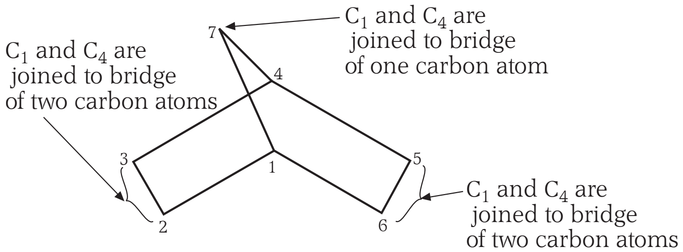


spiro [3.4] octane 6-oxo spiro [4.5] decane

Emphasis on ascending order of numerals was given in 1993 recommondations although it was not there according to 1979 recommondations of IUPAC.

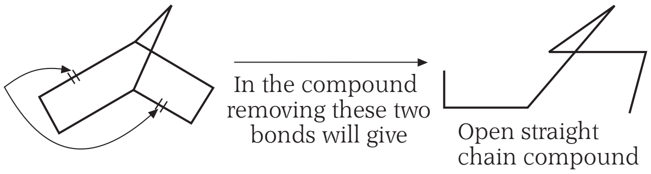
Polycyclic Ring Systems

Saturated homogeneous bicyclic systems having two or more atoms in common, are named by prefixing 'bicyclo-' to the name of the acyclic parent hydride that has the same total number of skeletal atoms. The number of the three acyclic atoms (bridges) connecting the two common atoms (bridgeheads) is given by arabic numbers cited in descending numerical order separated by full stops and enclosed in square brackets.

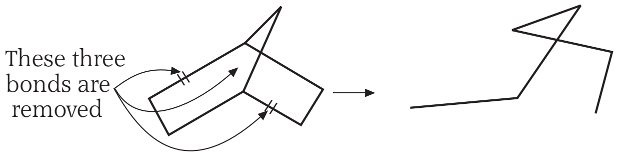


In these cases number or cycles can be guessed by practically observing minimum number of bonds removed so that the compound is converted into a continuous open chain compound.

Practically the minimum number of bonds removed
= Number of cycles present in the compound *e.g.,*



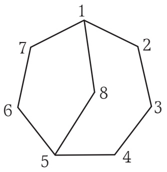
Hence, the above written compound is **bicyclo** (two bonds removed),



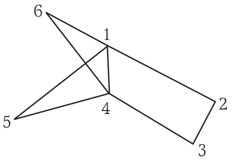
Open straight chain compound

Hence, the above written compound is **tricyclo** (3 bonds have to be removed).

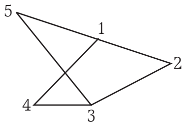
The system is numbered starting with one of the bridgeheads and proceeding through the longest bridge to the second bridgehead, continuing back to the first bridgehead by means of the longer unnumbered bridge, these two bridges constitute the 'main ring' of the system. Numbering is completed by numbering the remaining bridge (the shortest) beginning with the atom next to the first bridgehead, *e.g.,*



bicyclo [3.2.1] octane

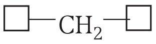


bicyclo [2.1.1] hexane



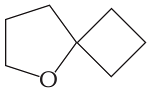
bicyclo [1.1.1] pentane

Sometimes it is difficult to name a compound which looks like simple but show a small deviation from a normal rule. *e.g.,* the compound  can be named as 1,1′ -bicyclo butane, but it is difficult to name:

 as a bivalent bridge is present in it. To name this compound we must know the name of bivalent bridges. In its 1993 recommondations, IUPAC provided the guidelines for such naming also. According to IUPAC the above compound can be named as "methano-1,1′-bicyclobutane". IUPAC gave the guidelines for usage of such simple bivalent bridges as **"such a bridge is named as a prefix derived from the hydrocarbon name by changing the final 'e' to 'o'.** The locant of a double bond, if present, is indicated in square brackets between the hydrocarbon prefix and the ending '–eno' –'dieno' etc. Some of such bridges can be named as :

$—CH_2—$ methano $—CH_2—CH_2—$ ethano
$—CH_2—CH_2—CH_2—$ propano
$—CH_2—CH_2—CH_2—CH_2—$butano
$—CH{=}CH—$ etheno
$—CH{=}CH—CH_2—$ prop[1] eno
$—CH{=}CH—CH_2—CH_2—$ but[1] eno
$—CH_2—CH{=}CH—CH_2—$ but[2] eno
$—CH{=}CH—CH{=}CH—$ buta[1,2] dieno

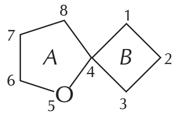
Sample **Problem 16** *The correct IUPAC name of the spiro compound,*



is

(*a*) 5-*oxaspiro* [3. 4] *octane*
(*b*) 1-*oxaspiro* [3. 4] *octane*
(*c*) 5-*oxaspiro* [4. 3] *octane*
(*d*) 1-*oxaspiro* [3. 4] *octane*

Interpret (a)



Number of atoms in ring *A* = 3 + 1 = 4
Number of atoms in ring *B* = 3
Total atoms in ring *A* and ring *B* + bridged *C* atom = 8

Numbering is done from smaller ring followed by spiro (common) carbon and larger ring.

Position of foreign element (O) is = 5

Thus, the IUPAC name of the compound is 5-oxaspiro [3. 4] octane.

13.10 Conversions Used in IUPAC System of Nomenclature

While writing IUPAC name, one should remember the following

1. **Locants** (numerals and/or letters) are placed immediately before the part of the name of which they relate, except in the case of traditional contracted forms. *e.g.,*

   hex-2-ene (formerly, 2-hexene)
   cyclohex-2-en-1-ol (formerly 2-cyclohexen-1-ol)

2. **Commas** are used to separate locants that refer to the same part of a name *i.e.*, locants of a series in names of fused ring systems, *e.g.,*

   1, 2-dichloroethane

3. **Full stops** (periods) separate numerical ring size indicators in names, constructed according to the von Baeyer system and in certain spiro names, *e.g.,*

   bicyclo [3.2.1] octane
4. **Colons** separate related sets of locants; if a higher level of separation is required, semicolons are employed, *e.g.,*

   1, 4, 5, 8-tetrahydro-1, 5 : 5, 8-dimethanoanthracene
5. **Hyphens** separate
   - (i) Locants from the words of syllables of a name.
   - (ii) Adjacent locants referring to different parts of the name (but preferably parentheses should be inserted).
   - (iii) The two parts of the designation for a primary fusion site in a name for a fused ring system.
   - (iv) A stereodescript or / and the name, *e.g.,*

     N-acetyl-N-(2-naphthyl) benzamide

     (preferred to N-acetyl-N-2-naphthyl-benzamide)
6. **Numerical** (multiplicative) **prefixes** are derived from Greek and Latin number names and are the principal method for describing a multiplicity of identical features of a structure in chemical nomenclature.
   - (i) **The simple numerical prefixes** di-, tri-, tetra-, etc., are of Greek derivation (except for nona- and undeca-, which are derived from Latin) and are used to indicate a multiplicity of substituent suffixes, *e.g.,*

     –diol
     –dicarboxylic acid
     –tricyclohexyl-
     –diamidodiaza
     ditetradecane-1, 4-diyl-
     tetra-2-naphthyl-
     dioxime
     ethylenedimino
   - (ii) **The numerical prefixes** 'bis-', 'tris-', 'tetrakis-', etc., which, except for 'bis-' and 'tris-', are derived by adding 'kis-' to the simple numerical prefixes are used to indicate a multiplicity of substituted prefixes or functional modification terms, *e.g.,* bis (2-aminoethyl). Such prefixes are also used when the use of 'di-', 'tri-', etc., is (or could be) ambiguous; this usually happens when an analogue of the term being multiplied begins with a simple numerical prefix.
   - (iii) **The numerical prefixes** 'bi-', 'ter-', 'quater-' etc., are derived from Latin number names and are used mainly in identical ring assembly names, *e.g.,*

     biphenyl, 2, 2' : 6', 2'' : 6'', 2'' -quaterpyridine

Check Point 2

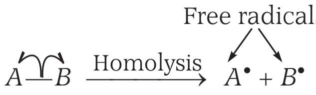
1. Is it always true that molecules with the general formula C_nH_{2n} are alkenes?
2. Write the formula for 1-phenyl-1-butanone. Explain why the designation "1-butanone is somewhat unusual,?
3. Is the name 2-methyl-3-butanol correct? Explain.
4. Which class of compounds is represented by the formula ROR'? Using CH_3 and C_2H_5 as a radical, write formula of three compounds which belong to this class.

13.11 Covalent Bond Fission

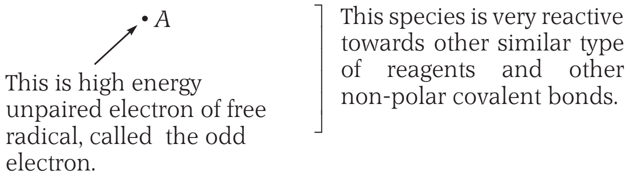
An organic reaction proceed through breaking of bonds and formation of bonds. A reaction is successful when the bond formed in the products are stronger than the bond broken. There are two possible ways through which a covalent bond can cleave.

Homolysis or Symmetrical Fission

If a covalent bond breakes in such a way that each atom takes away one electron of shared pair, the fission is called **homolysis,** *e.g.,*



The neutral chemical species, thus formed is called **free radical** and is represented as



Favourable factors for homolysis The factor which favours homolysis is zero or a small difference in electronegativity between *A* and *B*. Homolytic bond fission takes place in gaseous phase or in the presence of non-polar solvents (CCl_4, CS_2) .

Presence of peroxide, UV light, heat (≥ 500° C), electricity also favour homolysis. This process is known as initiation of free radical reaction.

Heterolysis or Asymmetrical Fission

If a covalent bond breakes in such a way that both the electrons of shared pair are taken away by one of the bonded atoms, the bond fission is called **heterolytic fission**, *e.g.*,

$$X\overset{\curvearrowright}{—}Y \xrightarrow{\text{Heterolysis}} X^+ + Y^-$$

(when X is less electronegative than Y)

$$X\overset{\curvearrowleft}{—}Y \xrightarrow{\text{Heterolysis}} X^- + Y^+$$

(when Y is less electronegative than X)

Such fission results in the formation of cation (positively charged) and anion (negatively charged). If positive charge is present on carbon then cation is termed as **carbocation** or if negative charge is present on carbon then anion is termed as **carbanion.** Cabocation or carbanion is the reaction intermediate.

Heterolysis is seen in polar covalent bonds and is favoured by polar solvents. *The energy required for the heterolytic bond fission is always greater than that for homolytic bond fission due to electrostatic force of attraction between ions.*

Sample Porblem 17 *Heterolysis of propane gives*

(*a*) *methyl and ethyl free radical*
(*b*) *methylium and ethylium ions*
(*c*) *methylium ion and ethyl anion*
(*d*) *methyl anion and ethylium ion*

Interpret (*d*) $CH_3CH_2CH_3 \xrightarrow{\text{Heterolysis}} \underset{\text{ethylium ion}}{CH_3CH_2^+} + \underset{\text{methyl anion}}{CH_3^-}$

or

$\underset{\text{ethyl anion}}{CH_3CH_2^-} + \underset{\text{methylium ion}}{CH_3^+}$

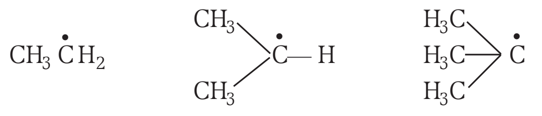
Here, the former products, *i.e.*, $CH_3CH_2^+$ ethylium ion and CH_3^- (methyl anion) are predominant as CH_3 is more electronegative as compared to CH_3CH_2 group.

13.12 Reaction Intermediates

Most of the chemical reactions require certain chemical species to occur. These species are generally short lived, highly reactive and are called **reactive intermediates**. *e.g.*, free radicals, carbocations, carbanions, carbenes, nitrenes etc.

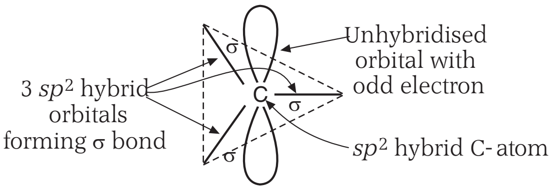
Free Radicals

The free radicals and their odd electron we have already discussed earlier under homolytic fission. These free radicals can be classified as primary (1°), secondary (2°) and tertiary (3°) depending upon the nature of carbon carrying odd electron *e.g.*,



primary or 1° secondary or 2° tertiary or 3°

These free radicals are **planar chemical species, *i.e.*, sp^2 hybridised.** Their unhybridised orbital contains an odd electron as seen below :



The order of the stability of free radicals is

$$(C_6H_5)_3\dot{C} > (C_6H_5)_2\dot{C}H > C_6H_5\dot{C}H_2$$
$$> CH_2 = CH — \dot{C}H_2 > 3° > 2° > 1° > CH_2 = \dot{C}H$$

The stability of free radicals depends upon bond dissociation energies (the energy associated with homolytic cleavage of covalent bond in a molecule). Generally, *lower the bond dissociation energy, more stable is the free radical.*

Reactions Involving Free Radicals

1. Wurtz reaction for alkanes
2. Substitution reactions of alkanes
3. Kolbe's electrolytic method
4. Anti-Markownikoff's addition reactions.

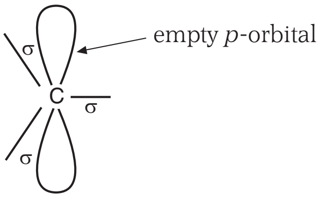
Caution Point *In substituted alkyl radicals, the s-character of these orbitals has been found to increase, thus tending to the pyramidal shape.*

$$\underset{\text{(planar)}}{\dot{C}H_3} < \dot{C}H_3F < \dot{C}H_2 < \underset{\text{(pyramidal)}}{\dot{C}F_3}$$

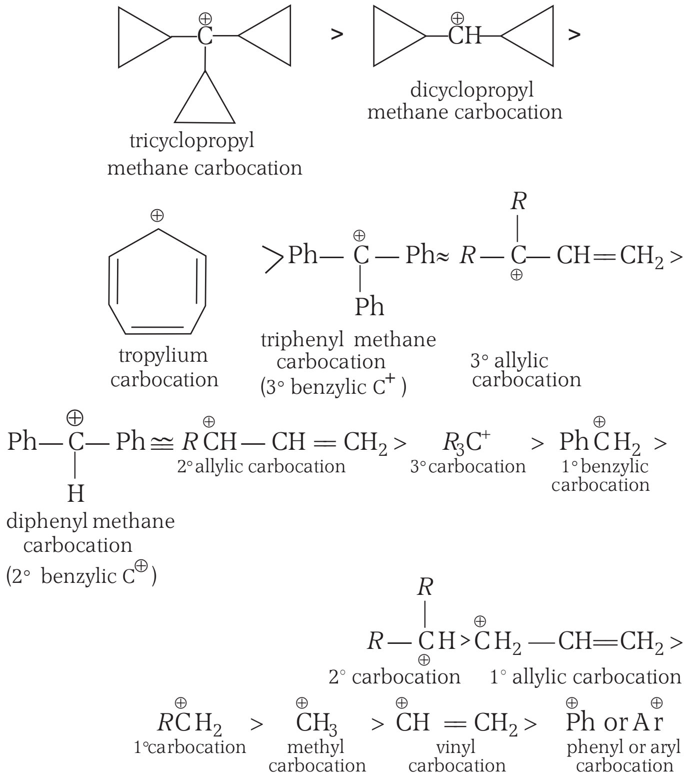
Carbocation

Carbon containing chemical species bearing a positive charge on carbon and carry 6 electrons in its valence shell are called **carbocations**. Just like free radicals these carbocations can also be categorised into primary (1°), secondary (2°) and tertiary (3°), depending upon the nature of carbon carrying positive charge.

Carbocations are also planar chemical species *i.e.*, sp^2 hybridised with an empty p-orbital as seen below



The decreasing order of the stabilities of carbocation

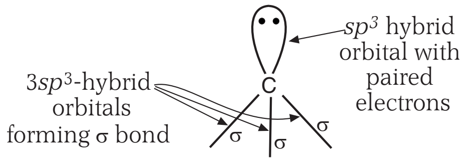


Caution Point $\overset{+}{C}H_5$, *an unusal ion, shares eight electrons among five bonds and is known as carbonium ion.* $\overset{+}{C}H_3, CH_3\overset{+}{C}H_2$ *etc., are termed as carbenium ion. For simplicity, we call both types as carbocations.*

Carbanions

Carbon containing chemical species bearing a negative charge on carbon atom and carrying 8 electrons in its valence shell is called **carbanion.** Just like free radicals and carbocations these can also be categorised into primary (1°), secondary (2°) and tertiary (3°).

The structure of simple carbanions is usually **pyramidal** with C-atom carrying the negative charge in sp^3 hybrid state and can be seen as



The order of stability of carbanions is as

$(C_2H_5)_2CH^- > (C_6H_5)_3\bar{C} > C_6H_5\bar{C}H_2 > \text{allyl} > \bar{C}H_3 >$
(1° > 2° > 3° carbanions)

Caution Point *Carbanions are* sp^3 *hydridised with pyramidal geometry. Due to steric hindrance of three phenyl* (Ph—) *groups, and to acquire pyramidal geometry, lots of energy is required due to which* Ph_3C^- *is less stable than* $Ph_3CH^{\ominus}$.

Reactions Involving Carbanion Intermediate

1. Aldol condensation
2. Cannizzaro reaction
3. Perkin's reaction
4. Knoevenagel reaction

Carbenes

The neutral divalent carbon species in which two non-bonding electrons are present along with 2 bonding pairs are called **carbenes**. These are generally produced either by **photolysis** (photo = light; lysis = breaking) *i.e.,* breaking by light or by **pyrolysis** *i.e.,* breaking by temperature, *e.g.,*

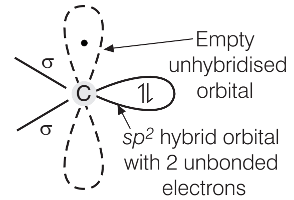
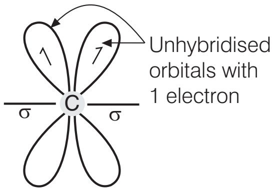
$$CH_2{=}C{=}O \xrightarrow[\text{or } \Delta]{h\nu} :CH_2 + :C{=}O$$

Carbenes are highly reactive chemical species with the tendency to gain electrons (as these have only 6 electrons in their valence shell), **thus behaving as Lewis acids or electrophiles.** These are, infact, neutral electrophiles.

Simplest carbene, *i.e.,* $\ddot{C}H_2$ is known as methylene. Hybridisation of the divalent carbon of carbene may be sp^2 as well as sp.

Carbenes can be categorised to singlet and triplet carbenes, the properties and structure of which is given in the table 13.4.

Table 13.4 **Distinguish Between Singlet and Triplet Carbenes**

S.No.	Singlet	Triplet
1.	With central C-atom sp^2 hybridised. The unhybridised orbital contains no electron and a hybridised orbital contains two electrons as shown below : 	With central C-atom *sp* hybridised. The unhybridised orbitals here contain 1 electron each in them as shown below : 
2.	The singlet carbene has bent structure *i.e.,* $\overset{\sigma}{\underset{\sigma}{>}}C\colon$	The triplet carbene has linear structure *i.e.,* $\overset{\sigma}{—}\ddot{C}\overset{\sigma}{—}$
3.	Less stable than triplet carbene.	More stable than singlet carbene.

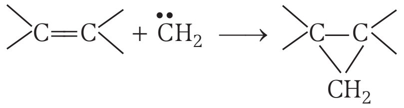
The decreasing order of stability of different types of singlet carbenes is as follows

$$\ddot{C}H_2 > \ddot{C}F_2 > \ddot{C}Cl_2 > \ddot{C}Br_2$$

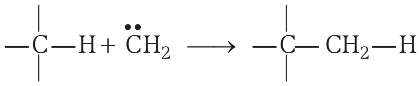
Reactions Given by Carbenes

Carbenes give following reactions.

(i) Addition with alkenes.

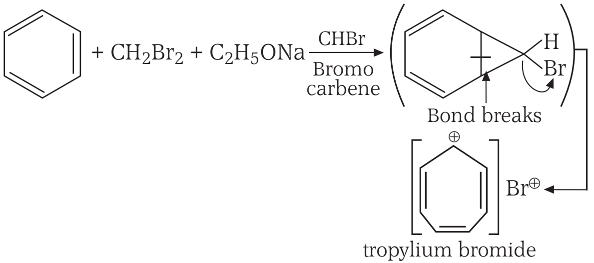


(ii) Insertion reaction between C—H bond.



$$-\overset{|}{\underset{|}{C}}-H + \ddot{C}H_2 \longrightarrow -\overset{|}{\underset{|}{C}}-CH_2-H$$

(iii) Ring expansion reactions *e.g.*, halogenated carbene produced by CHX_3/base adds to (C=C) bond, followed by ring expansion and gives product with one extra C atom ring.



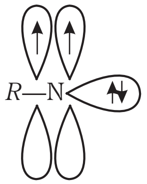
tropylium bromide
(stabilised due to aromatic character)

Nitrenes or Imidogenes

Neutral monovalent nitrogen species in which nitrogen has two unshared pair of electrons with a monovalent atom or group attached is called **nitrenes**, *i.e.*, $\overset{\sigma}{-}\ddot{N}:$

These are produced by thermolysis of azides and are very reactive just like carbenes.

In general, nitrenes obey Hund's rule and are ground state triplet with two degenerate *sp*-orbitals containing a single electron each.



sp-triplet nitrene

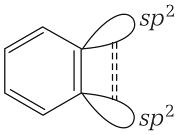
Reactions Involving Nitrene Intermediate

1. Hofmann bromamide rearrangement reaction
2. Lossen rearrangement reaction
3. Curtius rearrangement reaction
4. Schmidt rearrangement reaction

Arynes

A formal carbon-carbon triple bond containing aromatic molecule (in aromatic ring) is called aryne. The best known among these is benzyne.

In benzyne an additional bond is formed between two neighbouring C atoms by side ways overlapping of two sp^2 orbitals. The new bond orbital lies along with side of the ring and has little interaction with the π electron cloud lying above and below the ring. This sideways overlapping is weak and thus, makes the benzyne more reactive.



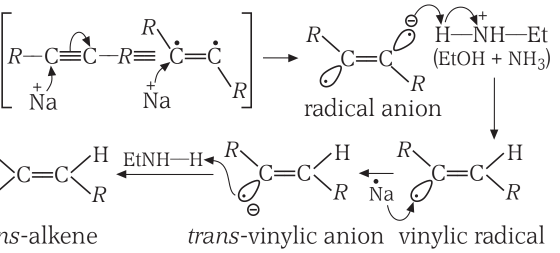
Radical Anions

Species carrying odd electron and negative charge are called radical anion.

These are of two types

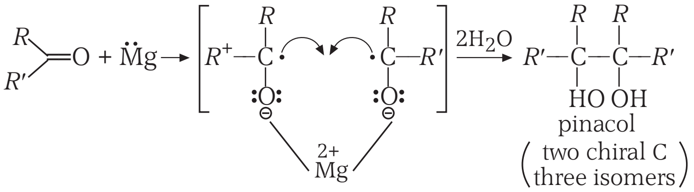
(a) Radical Anions of the Type ($R\dot{C}{=}\overset{\ominus}{\ddot{C}}R$)

These are formed as reactive intermediate in the reduction of (C≡C) bond to *trans* (C=C) bond.



(b) Radical Anions of the Type ($R_2\dot{C}{=}\overset{\ominus}{\ddot{O}}$:) Ketyl

These are formed in bimolecular reduction of carbonyl compounds to pinacol with Mg-Hg/H_2O.



13.13 Attacking Reagent or Species

An attacking reagent may be an organic or inorganic molecule or a part of them, *e.g.*, NaOH, Na in liquid NH_3, $RMgX$ etc. *Just like other organic molecules reagent can also show homolysis and heterolysis resulting in the formation of free radicals and ions respectively.*

The ions formed by heterolysis of a reagent are of utmost importance and can be categorised to

(i) Electrophiles (E^+),

(ii) Nucleophiles (Nu^-)

Electrophiles or **Electrophilic Reagents**

An electrophile is defined as **electron deficient species which attacks on electron rich areas.** Being electron deficient, the electrophiles behave as **Lewis acids**. *e.g.,* H^+, Cl^+, Br^+, I^+, NO_2^+, $\overset{+}{N}O$, $\overset{\oplus}{S}O_3H$ and carbocations.

The electrophiles can be seen in the form of neutral molecules also *e.g.,* carbenes ($:CR_2$), nitrenes ($\overset{\cdot\cdot}{N}R$), BF_3 etc. *The neutral electrophiles can be*

(i) All neutral covalent compounds in which central atom has incomplete octet, *e.g.,* $BeCl_2$, BH_3, $ZnCl_2$, AlX_3, FeX_3, $\dot{C}H_3$, $\overset{\cdot\cdot}{C}X_2$ etc.

(ii) All those compounds in which central atom has incomplete or expanded octet or unfilled *d*-subshell, *e.g.,* $SnCl_4$, $SiCl_4$, PCl_5, IF_7, etc.

(iii) All those compounds in which central atom is bonded by two or more than two electronegative atoms, *e.g.,* BX_3, AlX_3, FeX_3, PCl_3, PCl_5, etc.

Nucleophiles or Nucleophilic Reagents

A **nucleophile** or nucleophilic reagent is infact **an electron rich species that attacks on electron deficient areas.** Being electron rich, the nucleophiles behave as **Lewis bases.** *e.g.,* H^-, Cl^-, Br^-, I^- carbanions, etc., along with $\bar{O}H$, $\bar{O}R$, $\bar{S}R$. Nucleophiles can also be seen in the form of neutral molecules. Neutral covalent compounds in which central atom, has complete octet, has at least one lone pair of electrons and all atoms present on central atom are not be electronegative, is **neutral nucleophile**. *e.g.,*

$$H_2\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}},\ \overset{\cdot\cdot}{N}H_3,\ R\overset{\cdot\cdot}{N}H_2,\ R\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}H,\ R\underset{\cdot\cdot}{\overset{\cdot\cdot}{S}}H,\ R\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}H, \text{etc.}$$

Organic compounds containing carbon-carbon multiple bonds behave as the nucleophile, *e.g.,* alkene, alkyne, benzene, $CH_2{=}CH{-}CH{=}CH_2$, $CH_2{=}CH{-}C{\equiv}CH$, etc.

Sample Problem 18 *Choose the correct match of the underlined reagent with their nature (electrophile or nucleophile)* **[NCERT]**

(a) $CH_3COOH + \underline{HO^-} \longrightarrow CH_3COO^- + H_2O$ *Electrophile*

(b) $CH_3COCH_3 + \underline{CN^-} \longrightarrow (CH_3)_2C(CN)(OH)$ *Nucleophile*

(c) $C_6H_6 + \underline{CH_3CO^+} \longrightarrow C_6H_5COCH_3$ *Nucleophile*

(d) *All the above are correct*

Interpret (*b*) In the reaction given in option (a), OH^- carries negative charge and is an electron rich species so behaves as a nucleophile.

In the reaction given in option (b), CN^- carries negative charge and is also an electron rich species, so it is also a nucleophile.

In the reaction given in option (c), CH_3CO^+ carries positive charge and is an electron deficient species, so it acts as an electrophile.

Hot Spot 2

NUCLEOPHILICITY

It is a very important topic for JEE Main examination. By just following a few rules, you can answer questions based on nucleophilicity, which is more important and sometimes create confusion. So learn these rules and do practice.

Nucleophilicity is the theory of an element in a molecule/ion/species to donate its lone pair to an electrophile.

Following rules are considered while comparing the nucleophilicities of different nucleophiles.

(I) In case of same nucleophilic site, nucleophilicity parallels basicity, *i.e.,* as the basicity of nucleophile increases, its strength also increases. *e.g.,* the order of nucleophilicity is

$$RO^- > OH^- < ArO^- \quad (\text{Here, } R \neq CH_3)$$

This is because in all these, nucleophilic site is O. In RO^-, R group, being electron releasing, makes the O site more nucleophilic. OH^- is less nucleophilic because of the absence of any such group whereas ArO^- is least nucleophilic because of the presence of electron withdrawing Ar group.

The conjugate acid of above bases have the following order of acidity.

$$ROH > H_2O < ArOH$$

Hence, the order of basicity of their base is just opposite because conjugate base of a strong acid is weak or *vice-versa.*

Caution Points

(*i*) *Methanol is a stronger acid than* H_2O *but other alcohols are weaker than it.*

(*ii*) *If attacking atoms are different, nucleophilicity varies inversely with electronegativity. e.g., the order of nucleophilicity of halide ion is*

$$I^- > Br^- > Cl^- > F^-$$

(*this order is solvent dependent*)

Similary, sulphur being less electronegative than oxygen, is more nucleophilic. Similar is true in case of P *and* N.

The overall decreasing order of nucleophilicity for S_N2 *reaction in protic solvent is as follows.*

$$RS^- > ArS^- > I^- > CN^- > OH^- > N_3^- > Br^- > ArO^- > Cl^-$$

$$> \text{pyridine} > CH_3COO^- > H_2O$$

(III) A nucleophile carrying negative charge is more powerful nucleophile as compared to its conjugate acid *e.g.*, OH^- is a strong nucleophile as compared to H_2O and NH_2^- is strong nucleophile than NH_3.

***Sample* Problem 19** *The decreasing order of nucleophilicity of the following is*

I. CH_3S^- *II.* CH_3O^-
III. OH^- *IV.* EtO^-

(*a*) *IV > III > II > I*
(*b*) *I > II > III > IV*
(*c*) *IV > III > I > II*
(*d*) *II > I > III > IV*

Interpret (*c*) In II, III and IV nucleophilic site is same, so nucleophilicity follows the same order as basicity. The order of acidic character of conjugate acid of these base is

$$EtOH < H_2O < CH_3OH$$

So, the order of basicity of their base is opposite *i.e.*,

$$EtO^- > OH^- > CH_3O^-$$

Between I and II, CH_3S^- is more nucleophilic as S is less electronegative as compared to O. So the order of nucleophilicity is

$$\underset{IV}{EtO^-} > \underset{III}{OH^-} > \underset{I}{CH_3S^-} > \underset{II}{CH_3O^-}$$

Comparison between Electrophiles and Nucleophiles

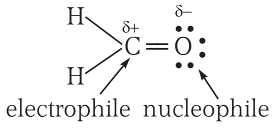
Electrophiles and nucleophiles differ in several aspects which are tabulated below.

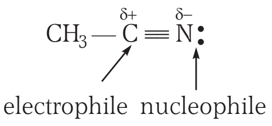
Table 13.5 **Comparison between Electrophiles and Nucleophiles**

S. No.	Electrophile	Nucleophile
1.	These are electron deficient species, usually cations.	These are electron rich species, usually anions.
2.	They possess an empty orbital in which they can accomodate an electron pair, thus behaves as Lewis acids.	They possess an unshared pair of electrons which they can donate easily, thus behaves as Lewis bases.
3.	They attack at the regions of high electron density.	They attack at the regions of low electron density.
4.	They are represented as E^+.	They are represented as $Nu\!:$.

Ambiphiles

Some molecules behave like both electrophiles and nucleophiles. These are called **ambiphiles.** Generally organic compounds containing a multiple bond between carbon and a more electronegative atom can act as ambiphiles. *e.g.*,



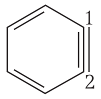


Isocyanides although cannot behave in these ways as their structure is

$$-\overset{+}{N}\equiv\overset{-}{C}\!:\longleftrightarrow -N=C\leftarrow \text{(bivalent)}$$

It is attacked by Nu as well as E^+.

Check Point 3

1. Propane on heterolysis gives methyl anion and ethyl carbocation but not ethyl carbocation. Explain.
2. Benzyne has following structure  the C_1 and C_2 are attached through triple bond but are sp^2 hybridised. Explain.
3. In between C and N atoms of isocyanides, multiple bond is present but they do not behave like ambiphiles. Explain.
4. Which one is more stable: singlet carbene or triplet carbon. Give reason.

13.14 Electronic Displacement in a Covalent Bond

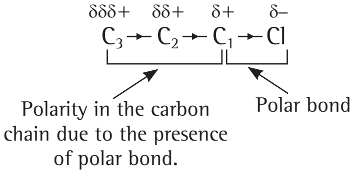
Presence of some atom or group in a molecule or presence of attacking reagent may lead to electronic displacement in a covalent bond. As a consequence of which, centres of different electron densities are generated. These centres are susceptible to attack by the reagents. The factors that create the centres of different electron densities are discussed below.

Hot Spot 3

INDUCTIVE Effect

It is the most important topic of the chapter for JEE Main examination. Questions are generally based on the application of inductive effect and their difficulty level is generally moderate (average).

The **inductive effect** is defined as **polarity produced in a molecule due to the presence of a polar bond.** *e.g.,* In a chain of carbon atoms with a chlorine atom joined to the last C-atom, due to higher electronegativity of chlorine atom, the electron distribution varies as



This induction of polarity due to the presence of polar bond in an organic molecule is called inductive effect.

The inductive effect is

(i) a permanent effect

(ii) operate through σ bonds

(iii) decreases in magnitude as we move away from the cause of polarity (*i.e.,* polar bond)

(iv) generally observed in saturated compounds.

For practical purpose the inductive effect is ignored after the second C-atom. It must be born in mind that the electron pairs although permanently displaced but they do not leave their valence shells.

Positive and Negative Inductive Effects

For measurement of relative inductive effects, atoms or groups having greater electron affinity than hydrogen are said to have $-I$ effect **(electron attracting).** Similarly, atoms or groups having smaller electron affinity than hydrogen are said to have $+I$ effect **(electron releasing or repelling).** Actually $-I$ group produce partial positive charge (*i.e.,* decrease in electron density due to more attracting power) while $+I$ groups produce partial negative charge (*i.e.,* increase in electron density due to less attracting power) on the carbon chain.

Some of the $-I$ effect producing groups in decreasing order of inductive effect are

$$R_3\overset{+}{N} > \overset{+}{N}H_3 > NO_2 > CN > SO_3H > CHO > CO > COOH >$$
$$COCl > COOR > CONH_2 > F > Cl > Br >$$
$$I > OH > OR > NH_2 > C_6H_5 > H$$

$-I$ power in decreasing order with respect to H

On the other hand alkyl groups, O and COO$^-$ are $+I$ groups. The $+I$ effect of different alkyl groups is as

$—O^- > —COO^- >$ tertiary alkyl group > secondary alkyl group > primary alkyl group $> —CH_3 > H$

$+I$ power of same type of alkyl groups varies directly with the number of C-atoms in the alkyl group *i.e.,*

$+I$ power $\propto$ number of C-atoms in same type of alkyl group

[The terminology ($+I$ and $-I$) is due to **Ingold,** while **Robinson** has suggested opposite signs. To avoid confusion, we shall use Ingold terminology throughout.]

Applications of Inductive Effect

The applications of inductive effect include

1. **In determining the stability of free radicals, carbocations and carbanions** following relationships are considered

(i) Stability of carbocation or free radical

$$\propto +I \text{ power of the group}$$
$$\propto \frac{1}{-I \text{ power of the group}}$$

Thus, the stability order for carbocations and free radicals is

$$1° < 2° < 3°$$

(ii) Stability of carbanions $\propto -I$ power of the group

$$\propto \frac{1}{+I \text{ power of the group}}$$

and the stability order for carbanions is

$$1° > 2° > 3°$$

2. **In determining the strength of acids and bases following relationships are considered**

(i) Strength of an acid $\propto K_a \propto \dfrac{1}{pK_a} \propto$ stability of acid anion

As stability of acid anion (or conjugate base)

$$\propto -I \text{ power of group present}$$
$$\propto \frac{1}{+I \text{ power of group present}}$$

Thus, **strength of acid increases with the attachment of group showing $-I$ effect and decreases with the attachment of group showing $+I$ effect.**

Although Ph group is $-I$ effect showing group, HCOOH (formic acid) is more acidic than benzoic acid (PhCOOH). This is because of $+R$ (resonance effect) of phenyl (Ph or C_6H_5) group.

(ii) Similarly strength of a base $\propto +I$ power of group present in the base $\propto K_b \propto \dfrac{1}{pK_b}$

$$\propto \frac{1}{-I \text{ power of group present in the base}}$$

However, this relation is not true for amines in their aqueous solutions as here the basicity is decided by combined effect of inductive effect, solvation effect and steric hindrance. The order of some of the amines are as

R of amine	Relative basic sterngth
CH_3—	2°>1°>3°> NH_3
C_2H_5—	$R_2NH > R_3N > RNH_2 > NH_3$
Me_2CH—	$RNH_2 > NH_3 > R_2NH > R_3N$
Me_3C—	$NH_3 > RNH_2 > R_2NH > R_3N$

The above two relations can be summarised as

Acid/Base	Group with +*I* effect	Group with –*I* effect
Acidic strength of acid	Decreases with this group	Increases with this group
Basic strength of base	Increases with this group	Decreases with this group

3. **In determining the reactivities of carbonyl compounds towards nucleophilic reagent** following relationship is considered

$$\text{Reactivity of carbonyl compound} \propto -I \text{ power of the group}$$
$$\propto \frac{1}{+I \text{ power of the group}}$$

4. Reactivity of alkyl halides is also determined by considering *I* effects.

Reactivity of alkyl halide towards S_N1 reaction is

$$3° > 2° > 1° \ \textit{i.e.}, \propto +I$$
$$\propto \frac{1}{-I}$$

Reactivity of alkyl halides towards S_N2 reactions follows reverse order of S_N1 reaction.

Sample Problem 20 *What is the correct order of decreasing stability of the following cations?*

$\underset{I}{CH_3—\overset{\oplus}{C}H—CH_3}$ $\underset{II}{CH_3—\overset{\oplus}{C}H—OCH_3}$

$\underset{III}{CH_3—\overset{\oplus}{C}H—CH_2—OCH_3}$ **[NCERT Exemplar]**

(a) *II* > *I* > *III* (b) *II* > *III* > *I*
(c) *III* > *I* > *II* (d) *I* > *II* > *III*

Interpret (a) $CH_3\overset{+}{C}H$ is same in all the cations, thus stability is affected by *Y* group in $CH_3\overset{+}{C}HY$

Stability of carbocation ∝ + *I* showing group.

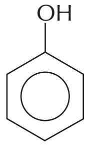
Order of + *I* effect of *Y* group is

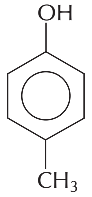
$$—OCH_3 > —CH_2OCH_3 > —CH_3$$

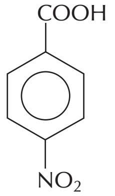
Thus, order of stability is

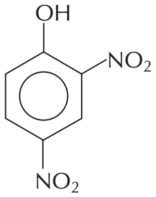
$$\underset{II}{CH_3\overset{+}{C}H\,OCH_3} > \underset{III}{CH_3\overset{+}{C}H\,CH_2OCH_3} > \underset{I}{CH_3\overset{+}{C}H\,CH_3}$$

Sample Problem 21 *The acidic strength of the following compounds is in the order*


(*I*)


(*II*)


(*III*)

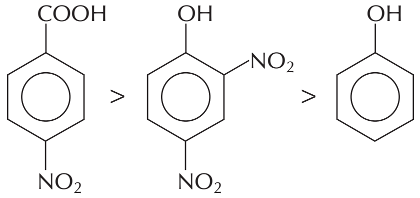

(*IV*)

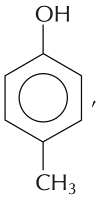
(a) (*II*) > (*I*) > (*III*) > (*IV*) (b) (*III*) > (*IV*) > (*I*) > (*II*)
(c) (*I*) > (*IV*) > (*III*) > (*II*) (d) (*IV*) > (*III*) > (*I*) > (*II*)

Interpret (*b*) Presence of electron withdrawing group, *i.e.*, the group showing –*I* effect, results in increased acidity while presence of electron releasing groups, *i.e.*, the group showing + *I* effect results in decreased acidity. —COOH, $—NO_2$, —OH all are electron withdrawing groups and the order of their –*I* effect is

$$—NO_2 > —COOH > —OH$$

Thus, the order of acidity is


(III) (IV) (I)


, however, is less acidic among the given compounds due to the presence of electron releasing $—CH_3$ group. Hence, the order of acidity is

III > IV > I > II

Sample Problem 22 *Arrange the following compounds in increasing order of acidity.*

I. $CH_3CH(Br)CH_2COOH$ *II*. $CH_3CH_2\,CH(Br)\,COOH$
III. $CH_3CH_2\,C(Br)_2\,COOH$ *IV*. $CH_3Br\,CH_2\,CH_2\,COOH$

(*a*) *II* > *III* > *I* > *IV*
(*b*) *III* > *IV* > *I* > *II*
(*c*) *III* > *II* > *I* > *IV*
(*d*) *III* > *I* > *II* > *IV*

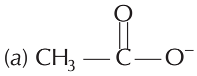
Interpret (*c*) As we know inductive effect decreases as we move away from the cause of polarity. Here Br group is the cause of polarity, so as the distance between Br and COOH increases inductive effect as well as acidity decreases. Thus, the order of acidity is

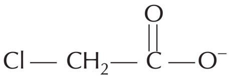
III > II > I > IV

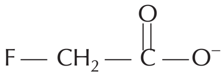
more -I group

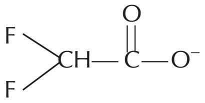
Remember! as the distance between +*I* showing group and —COOH increases, acidity increases.

Sample **Problem 23** *Ionic species are stabilised by the dispersal of charge. Which of the following carboxylate ion is the most stable?* **[NCERT** Exemplar]

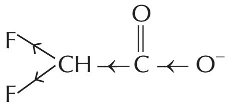
(*a*)

$CH_3—\overset{\overset{O}{\|}}{C}—O^-$

(*b*)

$Cl—CH_2—\overset{\overset{O}{\|}}{C}—O^-$

(*c*)

$F—CH_2—\overset{\overset{O}{\|}}{C}—O^-$

(*d*)


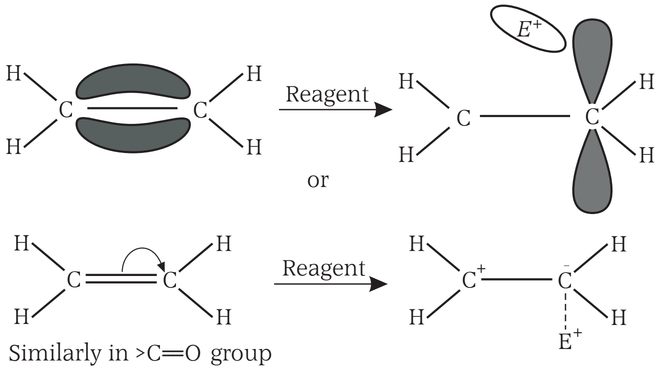
Interpret (*d*) Presence of two electron withdrawing – F atoms in $CF_2H – COO^-$ ion, makes the $\overset{\overset{O}{\|}}{C}—O^-$ carbon more electron deficient and hence, help in dispersal of negative charge.



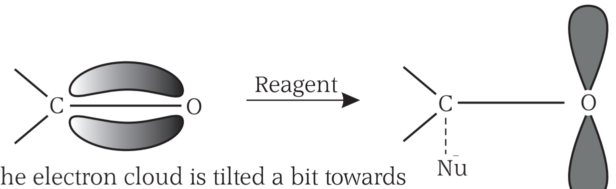
Electromeric Effect

The electromeric effect can be defined as *"Polarity produced in a multiple bonded compound as a reagent approaches it"* When a π bond is exposed to a reagent, the two π electrons are completely transferred to any of the one atom forming such a bond, thus producing polarity. *This is a temporary effect and brought into play only in the presence of attacking reagent.*

If π and σ bond both are present in a compound, the reagent always attacks the π electron cloud first because π electron cloud is always much more exposed than a σ electron cloud. *e.g.,* in ethylene molecule when an electrophile part of the reagent attacks the π bond, the symmetry of molecular orbital is disturbed as



Similarly in >C=O group

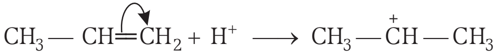


The electron cloud is tilted a bit towards oxygen due to its high electronegativity

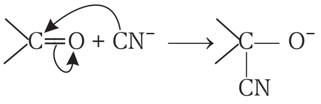
It is a strong effect because of the involvement of weak π bonds.

The electromeric effect is represented by means of a *curved arrow beginning at original position of the electron pair and denoting where the pair has migrated.* This effect may be of +*E* type or of – *E* type.

(1) If the electrons of the π-bond are transferred to that atom of the double bond to which the reagent gets finally attached, it is known as + *E* effect.


$CH_3—CH=CH_2 + H^+ \longrightarrow CH_3—\overset{+}{C}H—CH_3$

(2) If the electrons of the double bond are transferred to an atom of the double bond other than the one to which the reagent gets finally attached, the effect is known as – *E* effect.



Caution Point *In cases where inductive and electromeric effect both occur together, these may be aiding or opposing each other. Here it is not worthy that when these two effects are working in opposite directions, it is the electromeric effect that usually overcomes the inductive effect.*

Conjugation

A given atom or group is said to be in **conjugation** with an unsaturated system if it satisfies following two conditions

1. It has either π bond or any charge or odd electron or lone pair of electron.
2. It is directly linked to one of the atoms of multiple bond through a single bond. *e.g.,*

(i) $CH_2=CH—CH=CH_2$
(conjugation between 2π bonds)

(ii) $CH_2=CH—C\equiv N$
(conjugation between 2π bonds; one between 2 C-atoms and one between C and N)

(iii) $CH_2=\overset{+}{C}H—CH_2$
(conjugation between a π bond and a charge)

(iv) $CH_2=CH—\ddot{N}H_2$
(conjugation between a π bond and a lone pair)

Atoms or groups in conjugation with π electron should be at alternate position and in the same plane and at the same angle with each other.

Types of Conjugation

Conjugation can be of following types

(i) π-π conjugation
(ii) π and charge conjugation

(iii) π and odd electron conjugation
(iv) π and lone pair conjugation
(v) Lone pair and charge or odd electron conjugation

Consequences of Conjugation

Conjugation results in delocalisation of electrons which is visible through following observation

(i) Improper bond length, *i.e.,* bond length will not be as per expectations
(ii) The compound containing conjugated system will show extra stability (with antiaromatic compounds as exception).
(iii) As the compound will be extra stable that means its heat of formation will be greater than expected.

Conjugation in a Molecule

While looking for conjugation one must keep following points in mind

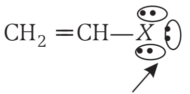
(i) **If any conjugate position has more than one π bond then only one π bond participates in conjugation** (See example (ii) above)

or in $CH_2{=}CH-C{\equiv}CH$

Here only one π bond out of two participates takes part in conjugation.

(ii) If any conjugate position has more than one lone pairs then only one lone pair participates in conjugation.

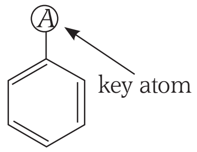
e.g.,



Here out of 3 lone pairs of halogen only one participates in conjugation.

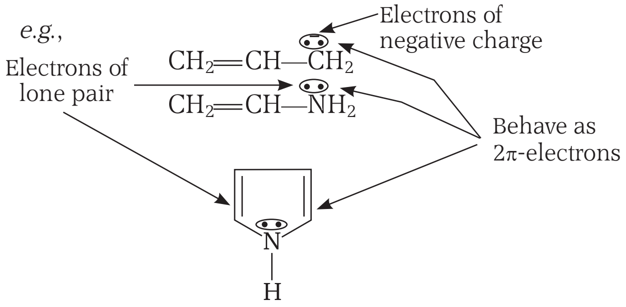
(iii) Key atom (atom other than hydrogen which is bonded with benzene ring) on aromatic ring will be in conjugate position if it has one of the following :

(i) A π bond
(ii) A charge
(iii) A lone pair
(iv) An odd electron

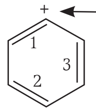


(iv) **Electrons of negative charge** or **lone pair** behaves as 2π electrons if these are in conjugation with 2π electrons.

e.g.,

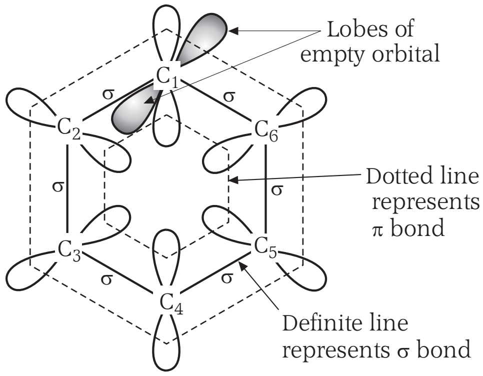


(v) Always remember alternate position and same plane with same angles for conjugation *e.g.,*



This charge does not conjugate with π bond as both of them are not in the same plane although the charge is in alternate position with π-bond number 3.

(Here, alternate position does not work but **same plane with same angle works.** Actually real conditions for conjugation are same plane with same angle while the alternate position is an assumption because these two conditions are normally fulfilled by this assumption.)



The orbitals of all the C-atoms with definite line are participating in conjugation (are in the same plane) while orbital with positive charge (empty orbital) of C_1 atom (here shown with dotted lines) cannot participates as it lies in different plane.

Resonance

Occassionally no reasonable electronic picture can be drawn for a molecule which could satisfactorily account for its observed properties. In such a condition, we assume several structures of the compound each one of which contribute to some of its observed properties but none of these structures satisfactorily account for all of its observed properties. The structure of such a compound is said to be resonance hybrid and the phenomenon is called resonance.

Thus, *"When several structures may be assumed to contribute to the true structure of the molecule but no one of them can be said to represent it uniquely, the molecule is referred to as a resonance hybrid and the phenomenon is termed as resonance". Such several structures are called canonical forms or resonating structures.*

It is hoped that the following crude functional similarity will help the reader to grasp the concept of resonance. "The mule is a hybrid of the jackass and the mare". It has inherited characteristics from both the parents, *e.g.,* it can carry load like an ass, and run faster like a mare. However when we look at the mule, we do not see a jackass at one glance and a mare at another, we see a mule always. In the similar way a resonance hybrid does not oscillate between its canonical forms. Its properties are fixed and these are the properties of the actual hybrid structure. It is hoped that you must have understood the meaning of word resonance. Now what are the chief conditions of resonance *i.e.,* in which conditions we can say that this hypothetical process is working. *The process of resonance can be said to occur only in one condition and that is when we are unable to explain all the observed properties of a compound with a single structure.*

In resonance,

1. *The arrangement of atoms must be identical or almost same in every formula.*
2. *The energy content of all the canonical forms must be nearly the same.*
3. *Each canonical form must have the same number of unpaired electrons.*

In a compound known to show resonance,

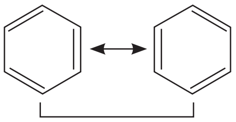
1. Heat of formation of resonance hybrid is abnormally high, *e.g.,* the observed heat of formation of CO_2(= 1590 kJ / mol) is greater than the calculated value (= 1464 kJ/mol) of the heat of formation of its most stable structure. The difference in heat of formation, *i.e.,*

   $$\underset{\text{(observed)}}{\text{Heat of formation}} - \underset{\text{(calculated)}}{\text{Heat of formation}}$$

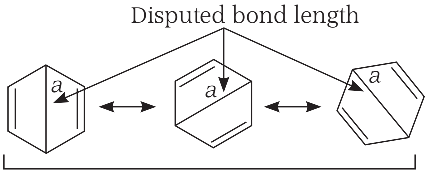
   is called the **resonance energy,** which is assumed to be the energy lost when a molecule acquires resonance hybrid formula.
2. The bond length in resonance hybrid is variable as compared to bond length in canonical forms.
3. The resonance hybrid is always stable than any of its canonical forms. *e.g.,*
   (i) CO_2 is said to have following canonical forms

   $$O{=}C{=}O \longleftrightarrow O^- — C{\equiv}O^+ \longleftrightarrow \overset{+}{O}{\equiv}C — O^-$$

   (ii) Benzene may be represented by following structures



Kekule structures



Dewar structures

In both the above examples the actual structure of CO_2 or benzene is more stable than either of the structures described.

(Later on Dewar structures were discarded as there one double bond (marked *a* in the figure above) is lengthy. Any π bond between 2 carbon atoms cannot have such length.)

Stability of a Canonical Form

Among the canonical forms the most stable canonical form can be judged by following rules

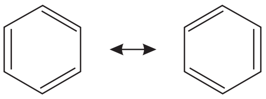
1. Among all the canonical forms **the form without charges will be the most stable one.**
2. Among the **charged forms**
   - (i) The structure with maximum number of covalent bonds is most stable one.
   - (ii) The structure with maximum charge separation comes second in number.
   - (iii) The structure with **conventionally correct charges** comes at third place (Here convention means the reason because of which charge arise)

Relation between Resonance and Bond Order

In compounds exhibiting resonance, bond order can be given by the formula

$$\text{Bond order} = \frac{\text{Total number of bonds between two atoms}}{\text{Total number of resonating structures}}$$

e.g., In benzene molecule with following canonical forms



$$\text{Bond order} = \frac{2+1}{2} = 1.5$$

Misconceptions Associated with Resonance

1. The canonical forms have no real existence.
2. There is no equilibrium between the canonical forms.
3. The molecule does not exist for a certain fraction of time in one canonical form and for other fractions of time in other canonical forms.

Sample **Problem 24** *Which of the following resonating structures of 1-methoxy-1,3-butadiene is least stable?*

(*a*) $\overset{\ominus}{C}H_2—CH{=}CH—CH{=}\overset{\oplus}{O}—CH_3$

(*b*) $CH_2{=}CH_2—\overset{\ominus}{C}H—CH{=}\overset{\oplus}{O}—CH_3$

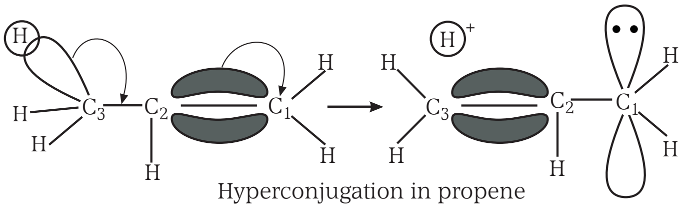
(*c*) $\overset{\ominus}{C}H_2—\overset{\oplus}{C}H—CH{=}CH—O—CH_3$

(*d*) $CH_2{=}CH—\overset{\ominus}{C}H—\overset{\oplus}{C}H—O—CH_3$

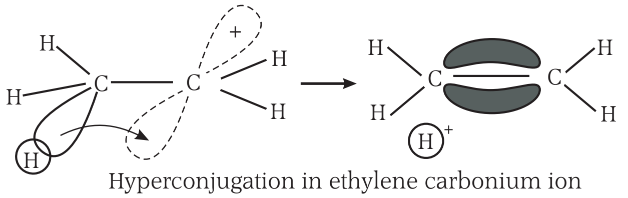
Interpret (c), In structures given in option (a) and (b), all the atoms have their complete octet. Moreover, these have more number of covalent bonds as compared to structure (c) and (d). In structure (d), the lone pair of electrons of adjacent oxygen atom compensates the electron deficiency of positively charged carbon whereas such neighbouring group support is not available in structure (c). Hence, it is the least stable resonating structure.

Hyperconjugation

It is shown by heat of hydrogenation data that alkenes are stabilized not only by conjugation but also by the presence of alkyl groups. Greater the number of alkyl groups attached to the doubly bonded carbon atoms, the more stable is the alkene, *e.g.*, propylene is more stable than ethylene. *Stabilization by alkyl group has been attributed to delocalisation of electrons due to overlapping between a π orbital and a σ bond orbital of the alkyl group* (C—H bond basically). *Such an overlapping is called hyperconjugation* which results to actually **no bond resonance.** This phenomenon is also helpful in stabilising carbonium ions and free radicals, *e.g.*,

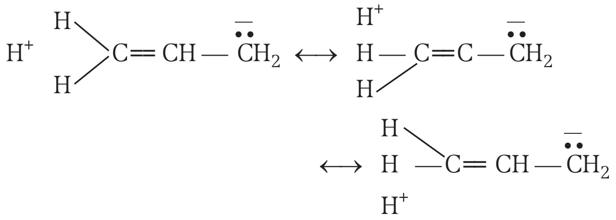


Hyperconjugation in propene

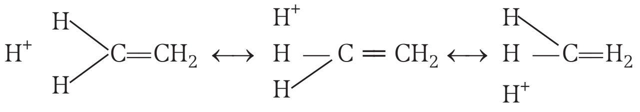


Hyperconjugation in ethylene carbonium ion

As in both the cases a methyl group is present near to the π bond (in propene) or (+)ve charge (in ethyl carbonium ion), all the three C—H bonds of it have equal probability of showing hyperconjugation. Thus, both of them have three hyperconjugative structures as



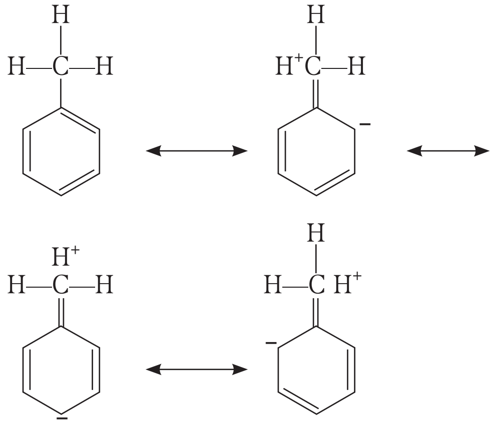
Hyperconjugative structures of propene



Hyperconjugative structures of ethyl carbonium ion

In both the above cases it is seen clearly that C—H bond of alkyl group possess a partial ionic character due to resonance *i.e.*, C—H covalent bond is not seen in resonating structure that's why the process is also called **no bond resonance** or **Baker Nathan effect**.

Hyperconjugation can also be seen in toluene as follows



Structure Requirements for Hyperconjugation

These are as follows

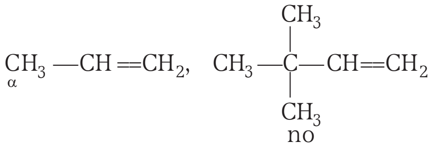
(i) Compound should have at least one sp^2 hybrid carbon of either alkene, alkyl carbocation or alkyl free radical.

(ii) α-carbon with respect to sp^2 hybrid carbon should have at least one hydrogen. *More the number of* H—C *bonds attached to the unsaturated system, more stable will be the alkene.*

Types of Hyperconjugation

Hyperconjugation is of three types

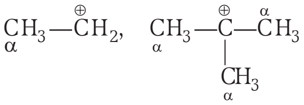
(i) **(C — H), π-conjugation** → This type of conjugation occurs in alkenes.



$$\underset{\alpha}{CH_3}-CH{=}CH_2,\quad CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH{=}CH_2$$

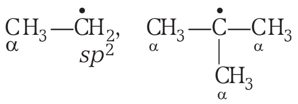
no hyperconjugation here

(ii) **(C — H), positive charge conjugation** → This type of conjugation occurs in alkyl carbocations.



$$\underset{\alpha}{CH_3}-\overset{\oplus}{C}H_2,\quad \underset{\alpha}{CH_3}-\overset{\oplus}{\underset{\underset{\alpha}{CH_3}}{C}}-\overset{\alpha}{CH_3}$$

(iii) **(C — H), odd electron conjugation** → This type of conjugation occurs in alkyl free radicals.



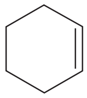
$$\underset{\alpha}{CH_3}-\underset{sp^2}{\dot{C}H_2},\quad \underset{\alpha}{CH_3}-\overset{\bullet}{\underset{\underset{\alpha}{CH_3}}{C}}-\underset{\alpha}{CH_3}$$

Applications of Hyperconjugation

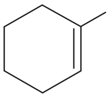
Following are the important applications of hyperconjugation.

(i) **The stability of alkene** can be determined on the basis of hyperconjugative structures. Always remember the more hyperconjugating structures an alkene possess, the more stable it is.

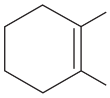
e.g., Out of



I



II

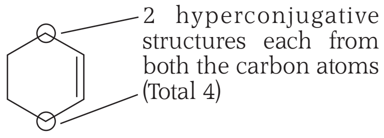


III

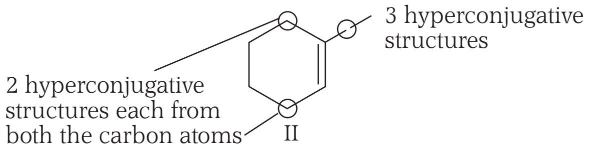
The stability order will be written as

$$\underset{\text{most stable}}{\text{III}} > \text{II} > \underset{\text{least stable}}{\text{I}}$$

The reason being I has minimum number of hyperconjugative structures (*i.e.,* 4) while 2nd have (7) and IIIrd have maximum number of hyperconjugative structures (*i.e.,* 10) as

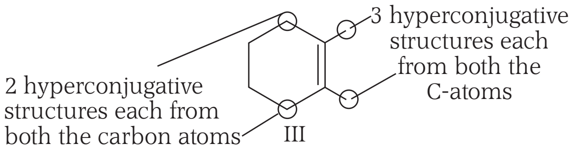


I



II

Total 4 + 3 = 7 structures

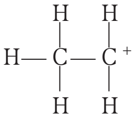


III

Total 6 + 4 = 10 structures

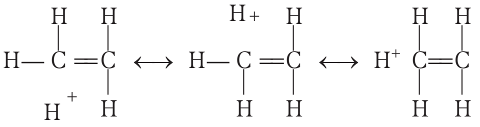
(ii) **Stability of alkyl free radicals and carbocations**

The stability of alkyl free radicals and carbocations can also be explained on the basis of hyperconjugation. Just like alkenes, *more the number of hyperconjugative structures seen in a free radical or carbonium ion more stable it is e.g.,* ethyl carbonium ion has following 3 hyperconjugative structures.



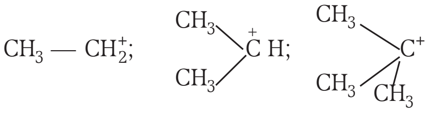
$$H-CH_2-\overset{+}{C}H_2$$

ethyl carbonium ion



hyperconjugative structures

Now, when we compare the stability of following ions



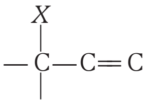
I II III

The I structure has 3 hyperconjugative structures, the II has 6 and the III has 9 hyperconjugative structures hence, the stability order of above three ions will be

$$\underset{\text{most stable}}{(CH_3)_3C^+} > (CH_3)_2CH^+ > \underset{\text{least stable}}{CH_3CH_2^+}$$

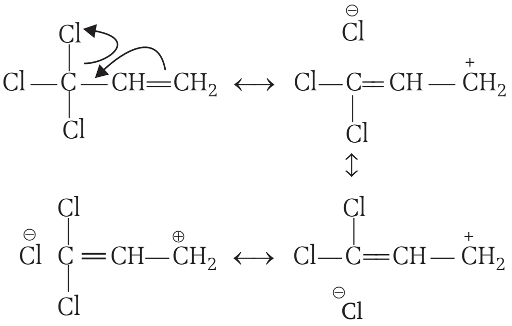
Reverse Hyperconjugation

The phenomenon of hyperconjugation is also observed in the system given below.



$$-\overset{X}{\underset{|}{\overset{|}{C}}}-C=C$$

In such system, the effect operates in the reverse direction. Hence, the hyperconjugation in such system is known as reverse hyperconjugation.



Check Point 4

1. Why is electromeric effect considered as a strong effect whereas *I* effect as a weak effect.
2. Why does a reagent attack first on the electron cloud as compared to σ electron clouds?
3. Explain why,
   (i) The central carbon-carbon bond in 1,3-butadiene is shorter than that of *n*-butane?
   (ii) Anilinium ion does not show mesomeric effect while aniline does?
4. Arrange the following in increasing order of their basic strength : $(C_6H_5)_3N$, $C_6H_5NH_2$, NH_3, RNH_2, R_3N, R_2NH, C_6H_5NHR, $C_6H_5CH_2NH_2$, $C_6H_5NHC_6H_5$.
5. Why benzyl carbocation is more stable than ethyl carbocation?
6. Which CX_2 (where, $X =$ F, Cl, Br, I) is the most stable singlet as compared to the corresponding triplet?

13.15 Common Types of Organic Reactions

The organic reactions can be categorised into following five categories

1. Substitution reactions
2. Addition reactions
3. Elimination reactions
4. Addition-elimination reactions
5. Rearrangement reactions

1. Substitution Reactions

A substitution reaction is that which involves the direct replacement (displacement or substitution) of an atom or a group of atoms in an organic molecule by another atom or group of atoms without any change in the remaining part of the molecule. The product obtained as a result of substitution is called the **substitution product** and the new atom or group of atoms which enters the molecule is called a **substituent,** *e.g.,*

$$R{-}CH_3 + X_2 \xrightarrow[520\text{–}670\text{ K}]{h\nu \text{ or}} \underbrace{R{-}CH_2\overset{\text{Substituent}}{\boxed{X}}}_{\text{substitution product}} + HX$$

Substitution reactions can further be classified into three categories on the basis of intermediate species which begins the reaction. These are

(i) Free Radical Substitution

Substitution reaction brought about by free radicals are called **free radical substitutions.** The best example of this kind of reactions is **halogenation of alkanes** in the presence of sunlight or heat *i.e.,*

$$\underset{\text{substrate-1}}{R{-}CH_3} + \underset{\substack{\text{substrate-2}\\ \text{or reagent}}}{X_2} \xrightarrow[\text{heat}]{\text{Sunlight}} \underset{\text{product-1}}{RCH_2X} + \underset{\text{product-2}}{HX}$$

Halogenation reactions are mainly given by those hydrocarbons which have at least one hydrogen on sp^3 hybrid carbon.

Free radical reactions run under following three steps (These reactions are infact chain reactions).

Step I **Chain initiation step** It involves the formation of free radicals from the reagent *i.e.,*

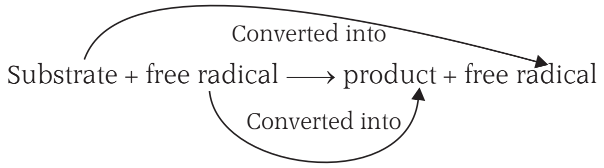
$$\text{Reagent} \xrightarrow[h\nu \text{ or free radical initiators}]{\text{Heat or}} \text{two free radicals}$$

e.g., for the above halogenation reaction

$$X_2 \xrightarrow[\text{free radical initiators}]{\text{Heat or } h\nu \text{ or}} X^{\bullet} + X^{\bullet}$$

This step can be recognised by the fact that free radicals are present on the product side i.e., after the arrow.

Step II **Chain propagation step** It Involves attack of radicals formed in step I on the substrate *i.e.,*



e.g., in the above reaction.

$$\underset{\text{substrate-1}}{R{-}CH_3} + \underset{\text{free radical}}{X^{\bullet}} \longrightarrow \underset{\text{free radical}}{R\dot{C}H_2} + \underset{\text{product-2}}{HX}$$

The free radical obtained continues the process as follows

$$\underset{\text{free radical}}{R{-}\dot{C}H_2} + \underset{\substack{\text{substrate-2}\\ \text{or reagent}}}{X_2} \longrightarrow \underset{\text{product-1}}{RCH_2X} + \underset{\text{free radical}}{X^{\bullet}}$$

This free radical formed further attacks on substrate-1

Thus, the steps continue repeating till one of the substrates is finished.

(*This step can be recognised by the presence of free radicals on both the sides of arrows.*)

Step III **Chain termination step** This step comes into action only when one of the substrates is finished. Here, the free radicals which are present combine at random, resulting to various kinds of products in traces *i.e.,* For the above reaction :

$$\dot{X} + \dot{X} \longrightarrow X_2$$

$$R{-}\dot{C}H_2 + R{-}\dot{C}H_2 \longrightarrow R{-}CH_2{-}CH_2{-}R$$

$$R{-}\dot{C}H_2 + \dot{X} \longrightarrow R{-}CH_2X$$

(*This step can be recognised by the presence of free radicals before the arrow only*)

Following is the decreasing order of reactivity of halogens (on the basis of electronegativity)

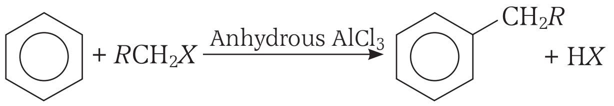
$$F_2 > Cl_2 > Br_2 > I_2$$

Following is the decreasing order of ease of abstraction of different kinds of hydrogens (on the basis of hyperconjugation and + *I* effect)

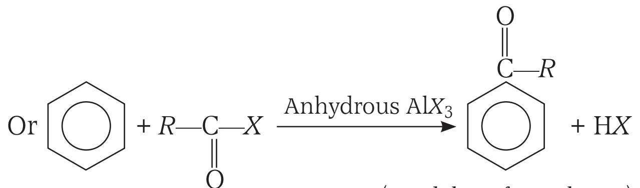
$$3^\circ \text{ hydrogen} > 2^\circ \text{ hydrogen} > 1^\circ \text{ hydrogen} > CH_3{-}H.$$

(ii) Electrophilic Substitution Reactions

The substitution reactions which are initiated by electrophiles, are called electrophilic substitution reactions. *These reactions are characteristics of aromatic compounds, e.g.,*



(Friedel Crafts' alkylation)



(Friedel-Crafts acylation)

Any electrophilic substitution reaction involves following three steps

***Step I* Liberation of electrophile from reagent**

$$[E^+Nu^-] + \text{catalyst} \longrightarrow \text{catalyst } Nu^-\text{complex} + E^+$$

Note This reagent can be any compound which is broken heterolytically

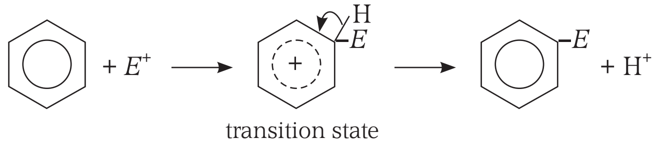
Note This can be any Lewis acid, *i.e.,* electron deficient compound

Thus, for the above reaction

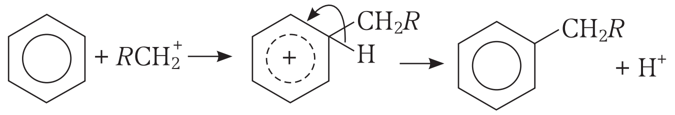
$$R\text{—}CH_2X + AlX_3 \longrightarrow \underset{\substack{Nu^- \text{ catalyst}\\ \text{complex}}}{AlX_4^-} + \underset{\text{electrophile}}{RCH_2^+}$$

***Step II* Attack of electrophile on benzene ring**

The electrophile formed in step I then attacks on the benzene ring as follows



Thus, in the above reaction



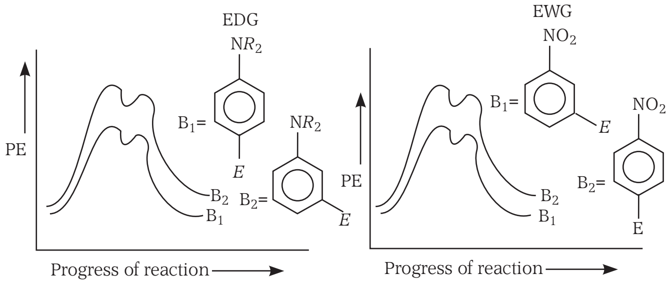
***Step III* Liberation of catalyst from catalyst Nu^- complex** The H^+ formed in step II attacks on catalyst Nu^- complex as

$$\text{Catalyst } Nu^- \text{ complex} + H^+ \longrightarrow H^+Nu^- + \text{catalyst}$$

Thus, in the above reaction

$$AlX_4^- + H^+ \longrightarrow HX + \underset{\text{catalyst}}{AlX_3}$$

Electron donating groups favour electrophilic substitution reactions whereas electron withdrawing groups disfavour them. Energy level diagram for such reactions is



Lower energy path for *p*-substitution
(a)

Lower-energy path for *m*-substitution
(b)

Fig. 13.1 Energy level diagram with (a) electron donating group (b) electron withdrawing group

Hot Spot 4

NUCLEOPHILIC Substitution Reactions

It is also an important topic for JEE Main examination point of view. Generally questions based on mechanism type and favourable factors are asked in the examination. The level of questions may vary from easy to difficult.

The reactions involving substitution which begins with attack of nucleophile are called **nucleophilic substitution reactions.** These are usually written as S_N (S-substitution, N = nucleophile) and are of two types, *i.e.,* **unimolecular** (shown as S_N1) and **bimolecular** (shown as S_N2)

These reactions are generally seen in alkyl halides and alcohols, *e.g.,*

$$RX + KOH(aq) \longrightarrow ROH + KX$$

1. **Bimolecular nucleophilic substitution (S_N2)** reaction is seen in primary alkyl halides and alcohols. The term bimolecular means, here, the rate of reaction depends upon the concentration of two molecule *i.e.,*

   Rate expression can be given as

   $$\text{Rate} \propto [A][B] \text{ for the reaction}$$

   $$A + B \longrightarrow C + D$$

   In specific words, we can say that the rate of reaction depends upon the concentration of substrate as well as of nucleophile and can be shown as

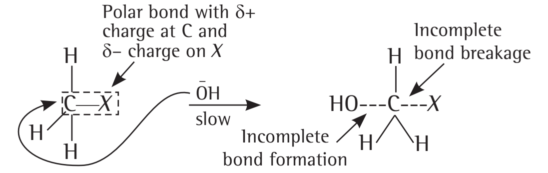
$$\text{Rate of reaction} \propto [\text{Substrate}]\,[Nu^-]$$

Let us consider the hydrolysis of any primary alkyl halide (say CH_3X) with aqueous KOH, *i.e.,*

$$CH_3X + KOH(aq) \longrightarrow CH_3OH + KX$$

The reaction is a multistep reaction and proceeds as

Step I

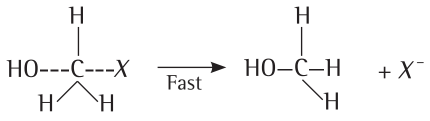


Here, C–X bond is polar thus negatively charged (electron dense) nucleophile is attracted towards δ+ carbon atom as shown

Transition state with incomplete C—OH bond formation and incomplete C—X bond breakage (both seen with dotted lines)

In this step, the OH^- cannot attack from the front side due to the przesence of electron rich *X* (halogen atom) on the front side which can repel OH^- and the transition state have all the C—H bonds in same plane.

Step II



transition state

product
Here the C—*X* bond gets fully broken and HO—C bond is fully formed

The alcohol formed here have opposite configuration to that of the parent alkyl halide (or has been inverted as an umbrella turns inside out in a high wind). This change in configuration is called **Walden's inversion.**

The step 1 of this reaction is slower step *i.e.,* formation of transition state is the rate determining step of this reaction. In the reaction step, involvement of both substrate and nucleophile (involvement can be judged by the presence of both in the transition state) suggest that

$$\text{Rate} \propto [\text{Alkyl halide}][\bar{O}H]$$

Hence, the reaction is considered as bimolecular.

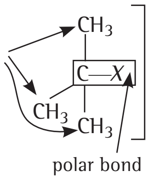
S_N2 **reactions are both stereospecific and stereoselective.** Some important facts related to this mechanism are

1. The order of reactivity of alkyl halide towards S_N2 mechanism is Me > 1° > 2° > 3°.
2. S_N2 reactions is catalysed by phase transfer catalysts *e.g.*, $R_4N^+X^-$ and by crown ethers.
3. If Nu (nucleophile) and reactant are uncharged, the rate increases with increase in solvent polarity.
4. If either one or both Nu and reactant are charged, the rate decreases with increase in solvent polarity.
5. In polar aprotic solvent the rate increases (DMSO >DMF > acetone), since such solvents leave the most reactive nucleophile free.
6. Rate of such reactions depends upon nucleophilicity. Greater the nucleophilicity, faster is the rate of reaction.

2. Unimolecular Nucleophilic Substitution

This reaction is the characteristic of tertiary alkyl halides and alcohols. In these molecules S_N2 reaction is not possible due to **steric hindrance** (steric = structure). Presence of three electron releasing alkyl groups along with an electron rich halide group or hydroxyl group hinders the reaction to occur through S_N2 pathway. This will be more clear if we examine a tertiary alkyl halide.

+*I* effect of these three groups reduces the $\delta+$ charge on C-atom attached to *X*.

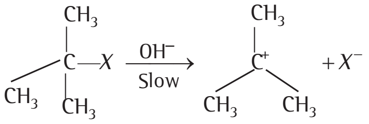


Target C-atoms for nucleophile, Note
1. Presence of $4e^-$ rich groups repel Nu^- to attack.
2. Reduced positive charge on C-atoms also does not favour S_N2 mechanism.
3. Alkyl groups being larger covered the target C-atom from sides.

Thus, in such cases the structure hinders the process to occur in accordance with S_N2 pathway that's why the reaction proceeds through another pathway, called S_N1 pathway or polar mechanism.

Here, the multistep reaction proceeds as

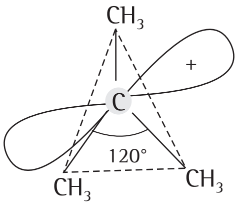
Step I



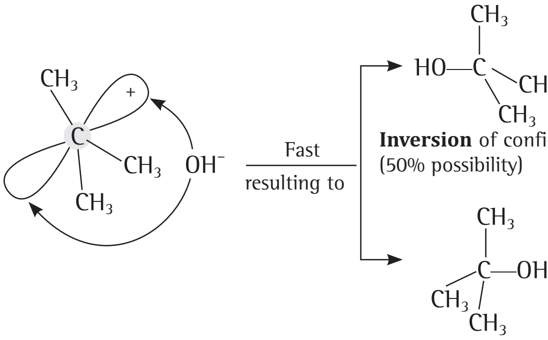
The C—*X* bond is broken due to the presence of nucleophile resulting to formation of a tertiary carbonium ion and X^- instead of transition state *i.e.*, ions are developed due to heterolysis in place of transition state.

During this step following changes take place

1. The bond angle between three alkyl groups come to 120° from 109°·28′ (in alkyl halide).
2. The empty orbital present in carbonium ion seems to present perpendicular to the plane of alkyl groups (as carbonium ion is sp^2 hybridised).



Step II The OH^- attacks on empty orbital as



Inversion of configuration (50% possibility)

Retention of configuration (50% possibility)

The alcohol formed here can have two possibilities

(i) 50% chances are there of *retention* in configuration.
(ii) 50% chances are there of *inversion* in configuration.

The rate determining step *i.e.,* step 1 of this reaction involves one molecule only *i.e.,* alkyl halide, hence,

$$\text{Rate of reaction} \propto [\text{Alkyl halide}]$$

S_N1 **reaction is non-stereospecific and non-stereoselective** as the attack of nucleophile is not specific and the products are a mixture of enantiomers.

Some Important facts about this mechanism are

(i) The order of reactivity of halides towards S_N1 reactions is

benzyl > allyl > 3°>2°>1°>Me

(ii) These reactions are catalysed by heavy metal ions, Lewis and Bronsted acids.

(iii) The rate of such reactions increases in polar solvents, *i.e.*, rate $\propto \alpha$-H bonding ability of solvent and dielectric constant.

(iv) The rate of such reactions remain unaffected by the concentration of nucleophile.

Caution Points

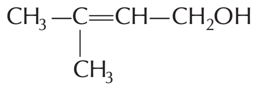
(*i*) *Secondary alcohols can proceed through either of these mechanisms.*

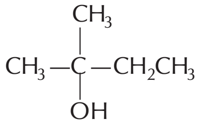
(ii) *Rearrangement of the carbocation (formed in S_N1 reaction) leading to more stable carbocation is also observed in S_N1 reaction.*

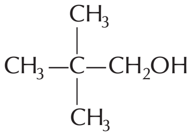
(iii) *High concentration of the nucleophile favours S_N2 reaction while low concentration favours S_N1 reaction.*

(iv) $(CH_3)_3CCH_2Br$ *shows S_N2 reaction with $C_2H_5O^-$, but S_N1 reaction with C_2H_5OH.*

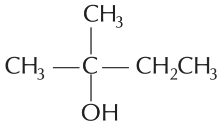
Sample **Problem 25** *Under S_N1 conditions the hydrolysis of neo-pentyl bromide gives*

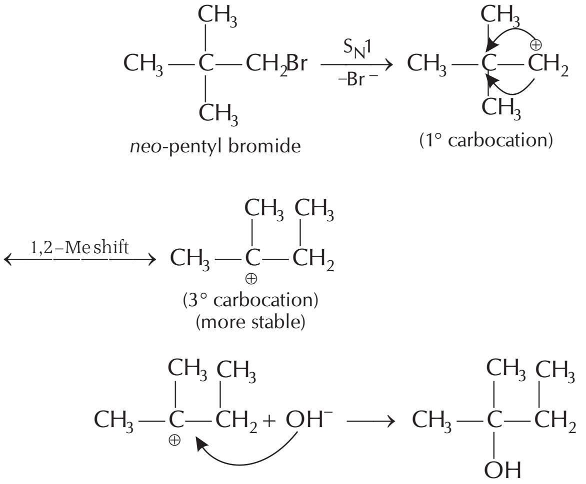
(*a*) 
$CH_3-\underset{CH_3}{C}=CH-CH_2OH$

(*b*) 
$CH_3-\overset{CH_3}{\underset{OH}{C}}-CH_2CH_3$

(*c*) 
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2OH$

(*d*) *None of these*

Interpret (*b*) 
$CH_3-\overset{CH_3}{\underset{OH}{C}}-CH_2CH_3$ is the major product of this reaction. The formation of the unexpected product is due to the rearrangement of the first formed 1°carbocation to the 3° carbocation as



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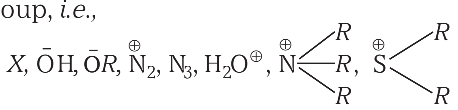
2. Elimination Reactions

An elimination reaction is one that involves the loss of two atoms or groups of atoms from the same or adjacent atoms of a substance leading to the formation of a multiple (double or triple) bond. Elimination reaction is given by those compounds which have a nucleophile as leaving group, *i.e.*,


$X, \bar{O}H, \bar{O}R, \overset{\oplus}{N}_2, N_3, H_2O^{\oplus}, \overset{\oplus}{N}R_3, \overset{\oplus}{S}R_2$

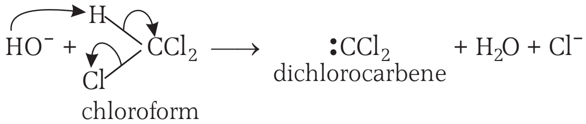
These reactions are generally endothermic and take place on heating. Moreover, **these are very common in alcohols and alkyl halides.**

In these reactions, there is loss of two σ bonds and gain of one π-bond, consequently, the product of such reactions is usually less stable than the reactant.

Elimination reactions are of two types

(i) α-elimination Reactions or 1,1-elimination Reactions

In these reactions, the loss of two atoms or groups occurs from the same atom of the substrate molecule, *e.g.*, base-catalysed dehydrohalogenation of chloroform to form dichlorocarbene



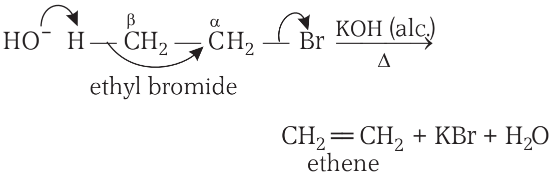
Dichlorocarbene is the reactive intermediate involved in carbylamine reaction and Reimer-Tiemann reaction.

(ii) β-elimination Reactions

In these reactions, the loss of two atoms or groups occurs from the adjacent atoms of the substrate molecule, *e.g.*, acid-catalysed dehydration of alcohols and base-catalysed dehydrohalogenation of alkyl halides

Acid-catalysed dehydration of alcohols

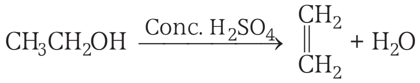
Base-catalysed dehydrohalogenation of alkyl halides



The β-elimination reactions proceed through two pathways just like nucleophilic substitutions. These are infact E_1 and E_2 pathways *i.e.*, unimolecular elimination and bimolecular elimination respectively.

(i) **Bimbolecular elimination (E_2) reactions are characteristic of primary alkyl halides and alcohols.** Just like S_N2 reaction pathway, here also a transition state is formed.

e.g., in the reaction



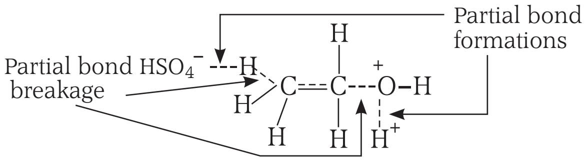
$$CH_3CH_2OH \xrightarrow{\text{Conc. } H_2SO_4} \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + H_2O$$

The reaction proceeds as

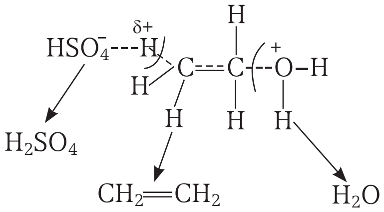
Step I H_2SO_4 gives H^+ and HSO_4^- as

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

Step II H^+ attacks on the oxygen of —OH group while HSO_4^- attacks on the H atom of adjacent C–atom to form the transition state. The transition state formed is explained with the help of hyperconjugation.



Step III The transition stage shows lysis as



In the above reaction as the transition state involves the participation of both alcohol and H_2SO_4 thus

$$\text{Rate of reaction} \propto [\text{alcohol}]\,[H_2SO_4]$$

Another example of such a reaction is dehydrohalogenation of primary alkyl halides.

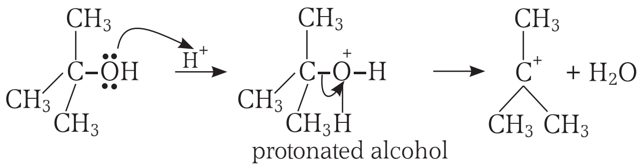
(ii) **Unimolecular elimination** (E_1) pathway is seen in tertiary alkyl halides and alcohols due to steric hindrance.

The unimolecular elimination proceeds as

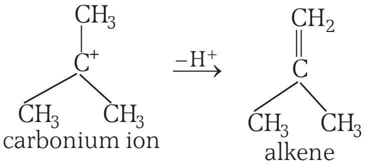
Step I H_2SO_4 dissociates as

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

Step II H^+ attacks on alcohol as



Step III The carbonium ion generated in step II stabilises itself with hyperconjugation to form alkene as



(This process is exactly as that of S_N1 pathway till the step II. The difference lies only in step III which involves substitution in S_N1 and elimination here in E_1.)

Substitution *Vs* Elimination Product

A good base favours elimination whereas a good nucleophile favours substitution reactions. The proportion of elimination and substitution products depends upon the following factors

(a) Nature of Substrate

The proportion of elimination increases with increase in the branching of carbon chain, *i.e.*, 1°→2°→3° because the alkenes formed on elimination are stabilised by hyperconjugation. Also the steric strain due to crowding is relieved on the formation of alkenes, whereas on substitution, the strain is reintroduced. Moreover, the substituted groups such as (C=C) and (Ph) in the substrate (which can stabilise the developing alkene) favour elimination. Thus, C_2H_5Br gives about 1% alkene while $PhCH_2CH_2Br$ gives about 99% $PhCH{=}CH_2$ (styrene).

(b) Nature of Base

1. Strong base favours elimination over substitution (in particular E2 over E1.
2. In low base concentration and in polar solvents, S_N1 reaction is favoured over E1.
3. High concentration of base in non-polar solvents favour E2 over S_N2. That's why alcoholic KOH favours elimination and aqueous KOH favours substitution.
4. Strong nucleophiles but weak bases promote substitution over elimination, whereas strong bases but weak nucleophiles promote elimination over substitution.
5. A large nucleophile favours elimination.

(c) Nature of Solvent

A more polar solvent increases the rate of S_N1 reactions and decreases S_N2 reactions. A less polar solvent although favours E2 over S_N2.

The change of hydroxylic solvents to aprotic solvents increases the base strength because the solvent layer around the base by H-bonding is absent. Thus, $Cl^{\ominus}$, $OH^{\ominus}$, $OR^{\ominus}$, etc., are very strong bases in DMF (dimethyl formamide) or DMSO (dimethyl sulphoxide).

The use of aprotic solvents may sometimes change the pathway from E1 to E2. *e.g.*, the nucleophilicity order increases with the decreasing basicity of elements. The nucleophilicity order of the halides is $I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$, but in aprotic solvents such as DMF or DMSO, the order is reversed, *i.e.*, $F^{\ominus} > Cl^{\ominus} > Br^{\ominus} > I^{\ominus}$.

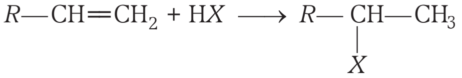
(d) Effect of Temperature

In elimination, the strong (C—H) bond has to break, hence high activation energy is required for elimination. High temperature favours elimination rather than substitution.

Caution Point *In general, elimination increases with strong base of high concentration, low polarity of solvent and high temperature. Substitution increases with the weak base of low concentration, high polarity of solvent, and low temperature.*

3. Addition Reactions

Reactions which involve combination between two reacting molecules to give a single molecule of the product are called addition reactions. Such reactions are typical of compounds containing multiple (double and triple) bonds, *e.g.*,



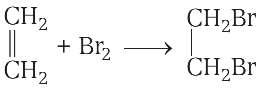
$$R—CH{=}CH_2 + HX \longrightarrow R—\underset{\displaystyle X}{\underset{|}{CH}}—CH_3$$

or $$R—CH{=}CH_2 + H_2 \xrightarrow{Ni-250°C} R—CH_2CH_3$$

Addition reactions can be further classified into following three categories on the basis of the intermediate species which begins the reaction.

(i) Electrophilic Addition Reactions

Here, the electrophilic part of reagents initiates the reaction, *e.g.*,

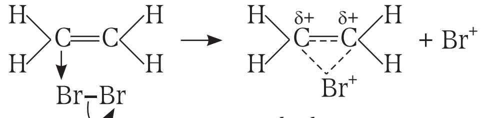


$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + Br_2 \longrightarrow \begin{matrix} CH_2Br \\ | \\ CH_2Br \end{matrix}$$

The reactions are normally seen in those compounds **where π electron cloud is evenly distributed** *i.e.,* alkenes and alkynes etc., (when π bonds is formed between two atoms of same or almost same electronegativity).

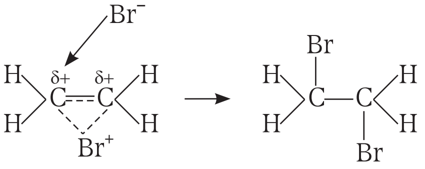
The reaction proceeds *via* the formation of a cyclic intermediate as under

Step I



cyclic bromonium ion

Step II Br^- attacks on either of the δ + charge containing carbonium ions as

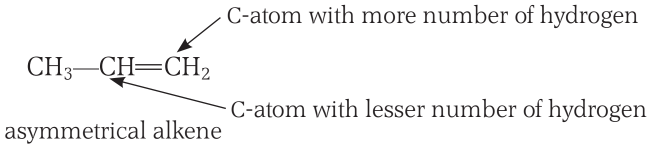


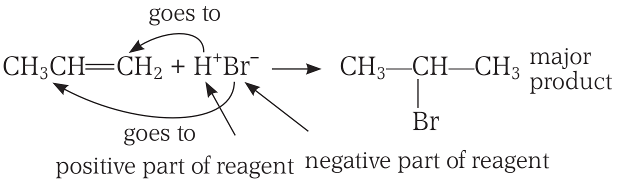
Caution Points

(*i*) *In anti addition like halogenation, cis alkene gives d and l products. trans alkene gives meso form.*

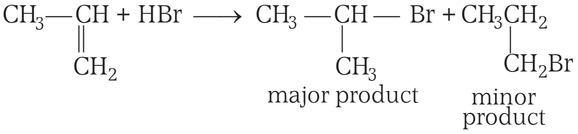
(*ii*) *In syn addition like hydrxylation cis alkene gives meso product trans alkene gives d and l products.*

Markownikoff's rule is useful in such conditions when an asymmetrical reagent is added to an asymmetrical alkene and says that in such additions positive part of reagent goes to that C–atom which have more number of hydrogens or negative part of reagent goes to that C–atom which have lesser number of hydrogens, In case, number of hydrogens are same, negative part goes to the carbon having more number of alkyl groups. If number of alkyl groups are also same then addition occur but this rule is not followed *e.g.,*





The Markownikoff's addition of HBr to propene also involves electrophilic addition and can be seen as



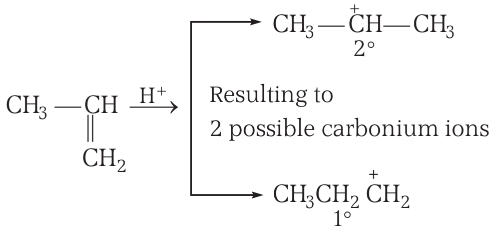
$$CH_3—\underset{\displaystyle CH_2}{\underset{\|}{CH}} + HBr \longrightarrow \underset{\text{major product}}{CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—Br} + \underset{\text{minor product}}{CH_3\underset{\displaystyle CH_2Br}{\underset{|}{CH_2}}}$$

The above reaction can be explained as

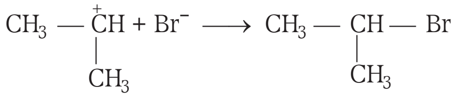
Step I HBr gives a H^+ and a Br^- ion, *i.e.*,

$$H—Br \longrightarrow H^+ + Br^-$$

Step II The H^+ attacks the π bond of propene to form carbonium ion as

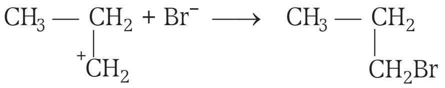


The 2° carbonium ion is more stable, thus



$$CH_3—\overset{+}{C}H(CH_3) + Br^- \longrightarrow CH_3—CH(CH_3)—Br$$

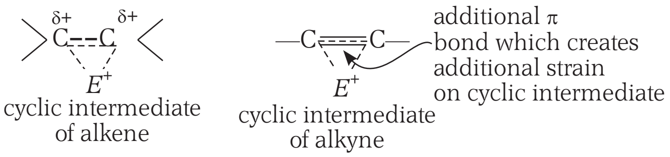
major product



$$CH_3—CH_2—\overset{+}{C}H_2 + Br^- \longrightarrow CH_3—CH_2—CH_2Br$$

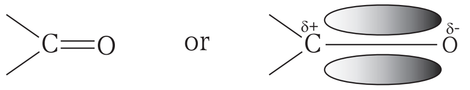
minor product

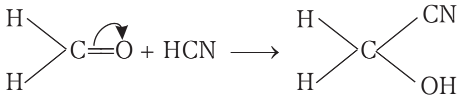
Alkenes are more reactive than alkynes as far as electrophilic additions are concerned although latter has more unsaturation than former. The reason for such a difference is more strained (less stable) cyclic intermediate in the case of alkynes due to the presence of additional π bond as



(ii) Nucleophilic Addition Reactions

In these reactions the nucleophilic part of reagent initiates the reaction. These additions are seen in those compounds which have unevenly distributed electron cloud, *i.e.*, have a π bond between two atoms of different electronegativity, *e.g.*, πe^- cloud in aldehydes and ketones, *i.e.*,





$$H_2C{=}O + HCN \longrightarrow H_2C(CN)(OH)$$

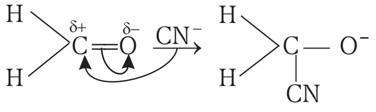
cyanohydrin

The reaction proceeds as follows

Step I HCN gives H^+ and CN^- as

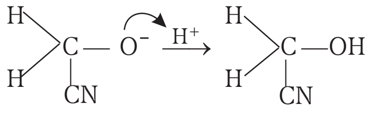
$$HCN \longrightarrow H^+CN^-$$

Step II CN^- attacks on carbon atom of carbonyl group to form corresponding anion as



$$H_2\overset{\delta+}{C}{=}\overset{\delta-}{O} \xrightarrow{CN^-} H_2C(CN)—O^-$$

Step III The proton attacks on anion to form the addition product as

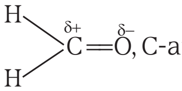


$$H_2C(CN)—O^- \xrightarrow{H^+} H_2C(CN)—OH$$

The reactivity of aldehydes and ketones towards **nucleophilic additions** follows the order

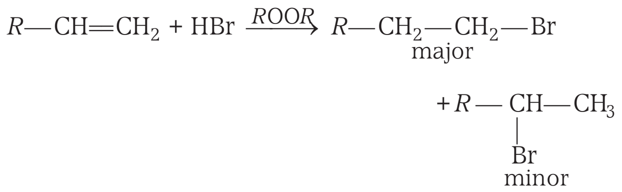
HCHO > other aldehydes > ketones

The reactivity in actual sense depends upon the magnitude of δ+ charge on the C-atom of >C═O group *i.e.*,

In  , C-atom bears maximum possible charge as in higher homologues, the magnitude of charge decreases due to the +*I* effect of an alkyl group attached in place of H. The magnitude further decreases in ketones as there the second hydrogen atom of HCHO is also replaced by another alkyl group.

(iii) Free Radical Addition Reactions

As addition reactions are commonly found in unsaturated compounds, the free radical additions involve additions through free radicals. The most common example of this type of reaction is addition of HBr to any asymmetric alkene in the presence of peroxide, *i.e.*,



$$R—CH{=}CH_2 + HBr \xrightarrow{ROOR} \underset{\text{major}}{R—CH_2—CH_2—Br} + \underset{\text{minor}}{R—CH(Br)—CH_3}$$

The reaction commonly called **Kharasch effect** or **peroxide effect** or **anti Markownikoff's** addition *i.e.*, here addition occurs opposite to Markownikoff's rule.

The free radical addition pathway in above written reaction proceeds as

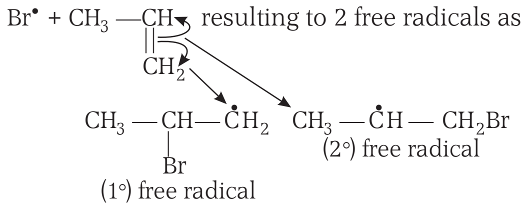
Step I Initiation step

$$R—O—O—R \xrightarrow{h\nu \text{ or high temperature}} 2RO^\bullet$$

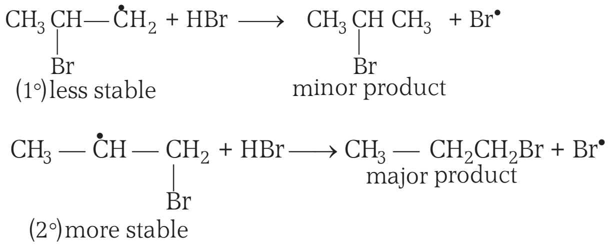
Step II Propagation steps

(i) $RO^\bullet + HBr \longrightarrow ROH + Br^\bullet$

(Homolytic fission of HBr by $RO^\bullet$ free radical)

(ii) 

Out of these two free radicals 2° free radical is more stable than 1° free radical.

(iii) 

$$CH_3\underset{\underset{Br}{|}}{CH}—\dot{C}H_2 + HBr \longrightarrow CH_3\underset{\underset{Br}{|}}{CH}CH_3 + Br^{\bullet}$$

(1°)less stable — minor product

$$CH_3 — \underset{\underset{Br}{|}}{\dot{C}H} — CH_2 + HBr \longrightarrow CH_3 — CH_2CH_2Br + Br^{\bullet}$$

(2°)more stable — major product

The stable intermediates give more product (major product) always due to following two reasons

(i) These lower the activation energy of the reaction.

(ii) These stay for a longer duration in the reaction.

Caution Point *The reaction is true for* HBr *only among halogen acids. The reason is* HF *and* HCl *bonds are so strong that their homolytic breakage is not possible with* $RO^{\bullet}$ *while* H—I *bond breakes easily but iodine free radicals are very unstable and generally combine to form* I_2 *molecule thus reducing the possibility of completion of reaction in this manner.*

4. Addition-Elimination Reactions

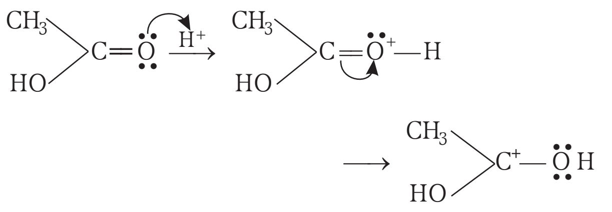
These reactions involve addition of two molecules with elimination of smaller molecules like H_2O. The best example of such a type of reaction is **esterification** *i.e.*,

$$C_2H_5OH + CH_3COOH \overset{H^+}{\rightleftharpoons} CH_3COOC_2H_5 + H_2O$$

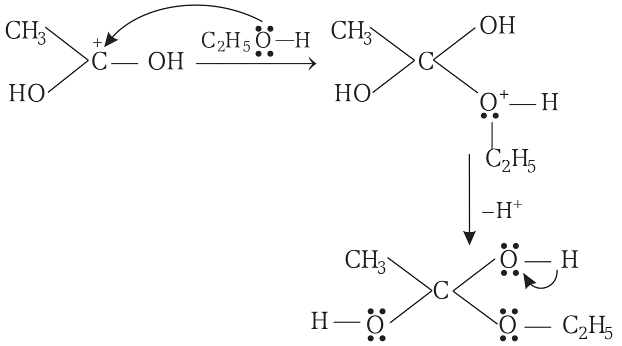
The reaction is said to proceed through **"nucleophilic addition-elimination"** and gives best result in the presence of mineral acids.

The **nucleophilic addition-elimination pathway with acid catalysed condition** for esterification can be said to proceed as follows

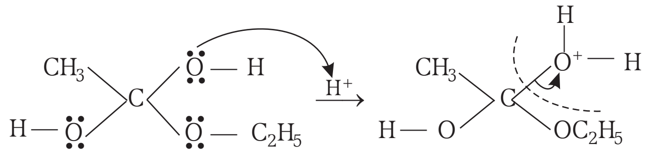
Step I Initially the H^+ of mineral acid attacks on O-atom of carbonyl part of —COOH group. Such an attack is said to create unit positive charge on C-atom of this group so that nucleophile can attack on it easily as



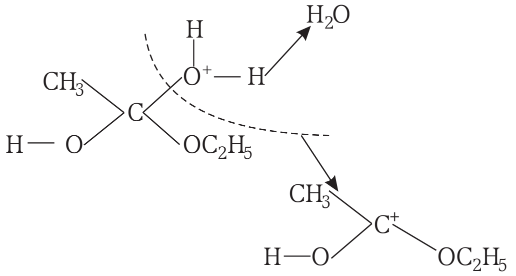
Step II Now the oxygen of alcohol donates its lone pair to positively charged C-atom of carbonium ion as



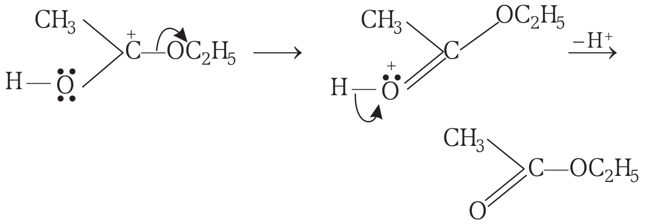
Step III The H^+ liberated in step II attacks on the oxygen of —OH group, taking the lone pair from it, thus



This results in liberation of water molecule and formation of another carbonium ion as



This carbonium ion stabilises itself as



(In this process the oxygen of alcohol remains intact and seen in ester itself. The process given above was fully worked out by **Fischer** in 1920, hence also called **Fischer Spierer** method commonly.)

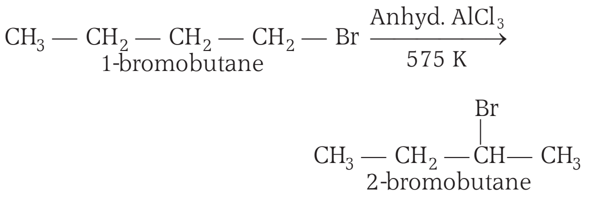
Two H^+ are used in the process and two are eliminated thus showing that H^+ is working as a catalyst **(During the reaction the concentration of catalyst remain unchanged).**

Other common examples of addition elimination reaction are addition of ammonia derivatives to aldehydes and ketones.

5. Rearrangement Reactions

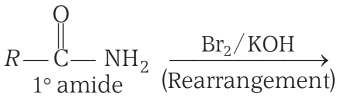
Reactions involving the migration of an atom or a group from one atom to another within the same molecule are called **rearrangement reactions,** *e.g.,*

(i) 1-bromobutane rearranges to 2-bromobutane in the presence of anhydrous $AlCl_3$ at 575 K.

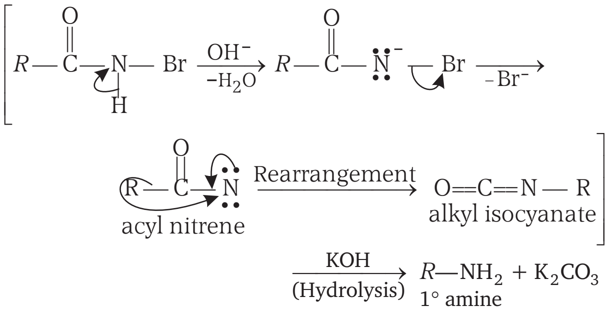


$$\underset{\text{1-bromobutane}}{CH_3—CH_2—CH_2—CH_2—Br} \xrightarrow[575\text{ K}]{\text{Anhyd. }AlCl_3} \underset{\text{2-bromobutane}}{CH_3—CH_2—\overset{Br}{\overset{|}{C}H}—CH_3}$$

(ii) **Hofmann bromamide reaction** involving the conversion of 1° amides to 1° amines on treatment with Br_2 in the presence of KOH.

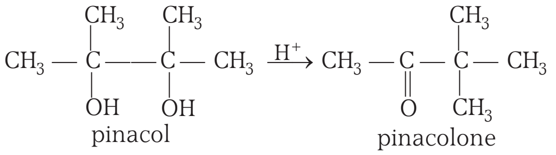


$$\underset{1°\text{ amide}}{R—\overset{O}{\overset{\|}{C}}—NH_2} \xrightarrow[\text{(Rearrangement)}]{Br_2/KOH}$$

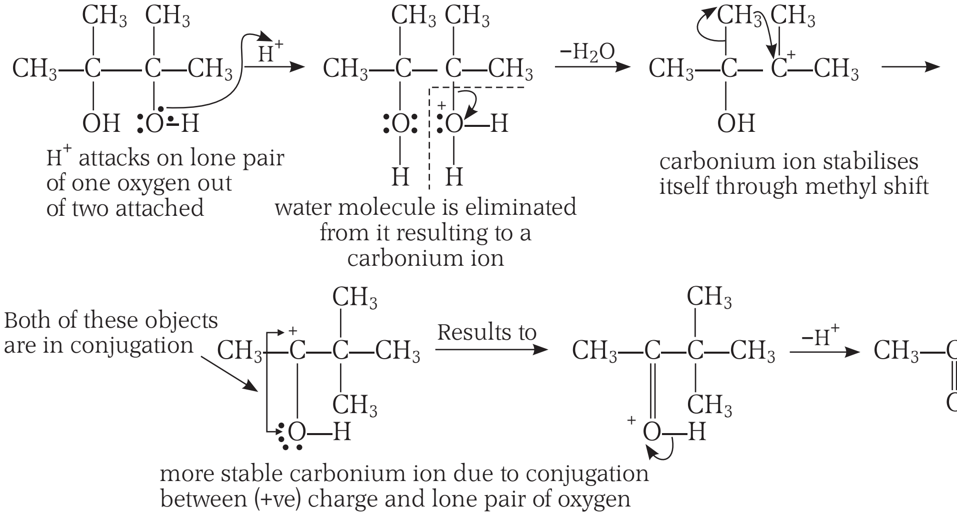


In this rearrangement reaction, the group *R* migrates from carbon to nitrogen to first give an alkyl isocyanate which upon hydrolysis gives a 1° amine with one carbon atom less than the original amide.

(iii) Another example of rearrangement reaction is a very common **pinacol-pinacolone** rearrangement which can be seen as



The reaction proceeds as

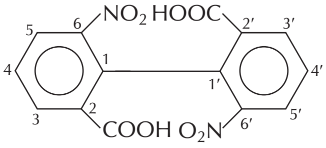


Check Point 5

1. Why allyl halides are more reactive than alkyl halides for S_N1 reaction?
2. Explain why carboxylic acids do not undergo substitution reaction under basic conditions?
3. Arrange benzene, toluene, methoxybenzene and chlorobenzene in increasing order of reactivity towards sulphonation.
4. Choose the reagent which will not give addition reactions with $CH_3—CH{=}CH_2$ and why?
   Br_2, HOCl, NaCl/HOH, NaOH, H_2, H*X*.
5. Arrange the following in increasing order of their nucleophilicity in a polar solvent. $\bar{N}_3$, $\bar{C}N$, OH^-, CH_3COO^-, Cl^-, H_2O. Also give the reason.

WORKED OUT Examples

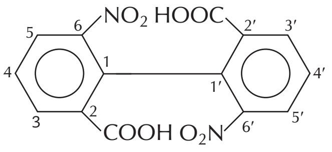
Example 1 *The IUPAC name of*



is

(*a*) 2, 2′-*dinitrodiphenic acid*
(*b*) 6, 6′-*dinitrodiphenic acid*
(*c*) 6, 6′-*dinitrophenyl*-2, 2′-*dicarboxylic acid*
(*d*) 2, 2′-*dinitrophenyl*-6, 6′-*dicarboxylic acid*

Solution (*c*)



6,6′-dinitrophenyl-2,2′-dicarboxylic acid

Example 2 *Consider the following compounds :*

(*i*) 1,2-*dichloroethene* (*ii*) *benzene*
(*iii*) 1,3-*butadiene* (*iv*) 1,3,5-*hexatriene*

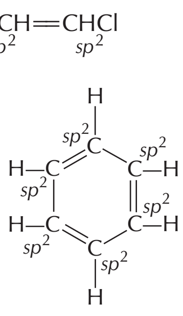
All the carbon atoms are sp^2 *hybridised in*

(*a*) (*i*), (*ii*), (*iii*) *only*
(*b*) (*i*), (*ii*) *only*
(*c*) (*i*) (*iii*), (*iv*) *only*
(*d*) *All of the above*

Solution (*d*) If a carbon atom forms three σ bonds, *i.e.*, attached through double bond, the hybridisation of the carbon is sp^2.

(i) $\underset{sp^2}{ClCH}=\underset{sp^2}{CHCl}$

(ii)



(iii) $\overset{sp^2}{CH_2}=\overset{sp^2}{CH}-\overset{sp^2}{CH}=\overset{sp^2}{CH_2}$

(iv) $\overset{sp^2}{CH_2}=\overset{sp^2}{CH}-\overset{sp^2}{CH}=\overset{sp^2}{CH}-\overset{sp^2}{CH}=\overset{sp^2}{CH_2}$

Example 3 *Which of the following is correctly connected for x and y ?*

$$\underset{\text{Bond length x Å}}{\underset{\downarrow}{CH_3-CH_2-\ddot{\underset{..}{Cl}}:}} \qquad \underset{\text{Bond length y Å}}{\underset{\downarrow}{CH_2=CH-\ddot{\underset{..}{Cl}}:}}$$

(*a*) $x = y$
(*b*) $x > y$
(*c*) $y > x$
(*d*) $x = 3y$

Solution (*b*) CH_3CH_2Cl is a non-conjugated compound, hence C—Cl bond will be pure single bond. $CH_2=CHCl$ is a conjugated compound, hence resonance effect works and a partial double bond character is developed between C and Cl and the bond length of a double bond is shorter as compared to that of a single bond. Thus, $x > y$.

Example 4 *Which of the following is the strongest nucleophile?*

(*a*) $CH_3-CH_2^-$
(*b*) $HC\equiv C^-$
(*c*) NH_2^-
(*d*) $H_2C=CH^-$

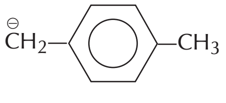
Solution (*a*) In case of same nucleophilic site, nucleophilicity parallels the basicity while in case of different sites, nucleophilicity varies inversely with electronegativity. Order of electronegativity, N > C.

Thus, the order of nucleophilicity C > N

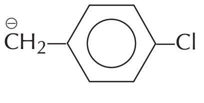
Among, $CH_3CH_2^-$, $HC\equiv C^-$ and $H_2C=CH^-$, $CH_3CH_2^-$ is the strongest nucleophile, as it is less electronegative (due to least *s*-character).

Example 5 *Which one of the following is most stable?*

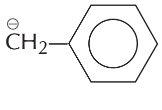
(*a*)



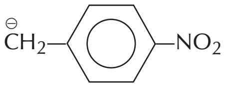
(*b*)



(*c*)



(*d*)



Solution (*d*) –*R* group present at *ortho* or *para* position increases the stability of carbanion.

Example 6 *Dichlorocarbene is generated by the action of potassium-1-butoxide on chloroform. This is an example of*

(*a*) *α-elimination reaction*
(*b*) *β-elimination reaction*
(*c*) *addition reaction*
(*d*) *rearrangement reaction.*

Solution (*a*) $\underset{\text{chloroform}}{CHCl_3} \xrightarrow{K(t\text{-butoxide})} \underset{\text{dichlorocarbene}}{:CCl_2}$

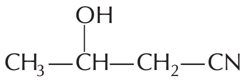
Since, the eliminating group, *i.e.,* hydrogen and chlorine,here are lost from the same carbon atom, it is an example of α-elimination reaction.

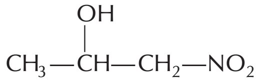
Example 7 *Which of the following is correctly matched?*

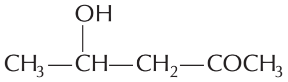
(*a*) CH_3CH_2OH	*Thermal elimination*
(*b*) $(CH_3)_3C\cdot OH$	*E*1 *reaction*
(*c*) $CH_3—CH_2—CH_2OH$	*$E1_{cb}$ reaction*
(*d*) *All of the above*	

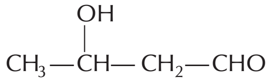
Solution (*b*) Tertiary alcohols usually favour *E*1 reactions.

Example 8 *Which alcohol will be most reactive for dehydration?*

(*a*) 
$CH_3—\overset{OH}{\overset{|}{C}}H—CH_2—CN$

(*b*) 
$CH_3—\overset{OH}{\overset{|}{C}}H—CH_2—NO_2$

(*c*) 
$CH_3—\overset{OH}{\overset{|}{C}}H—CH_2—COCH_3$

(*d*) 
$CH_3—\overset{OH}{\overset{|}{C}}H—CH_2—CHO$

Solution (*b*) More is the acidity of β-hydrogen, more will be the reactivity of alcohol for dehydration. Presence of electron withdrawing group increases the acidity, thus $CH_3CH(OH)CH_2NO_2$ is most reactive for dehydration.

Start Practice for JEE Main

Round I (Topically Divided Problems)

General Terms and Classification of Organic Compounds

1. The first organic compound prepared in the laboratory was
(a) acetic acid (b) acetylene
(c) urea (d) methane

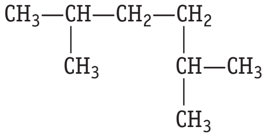
2. The huge number of organic compounds is due to the fact that
(a) carbon is tetravalent
(b) carbon possesses property of catenation
(c) carbon compounds exhibits polymerisation
(d) Both (a) and (b)

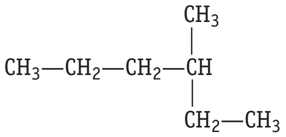
3. The alkane which has only primary hydrogen atom is
(a) pentane (b) *iso*-pentane
(c) *neo*-pentane (d) 2,2-dimethyl butane

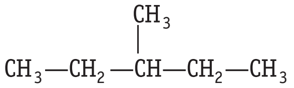
4. Alicyclic compounds are
(a) aromatic cyclic compounds
(b) aliphatic cyclic compounds
(c) Both (a) and (b)
(d) None of the above

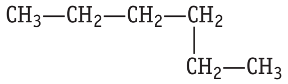
5. The number of tertiary C-atoms in 2,2,4,4-tetra methyl pentane is
(a) 1 (b) 2
(c) 3 (d) 4

6. Which of the following structure contain 9 primary and 6 secondary hydrogen atoms?

(a)

$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2-\underset{\underset{\displaystyle \underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3}{|}}{CH_2}$

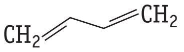
(b)

$CH_3-CH_2-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_2-CH_3}{|}}{CH}}$

(c)

$CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-CH_3$

(d)

$CH_3-CH_2-CH_2-\underset{\underset{\displaystyle CH_2-CH_3}{|}}{CH_2}$

7. Which of the following is a heterocyclic compound?
(a) Phenanthrene (b) Thiophene
(c) Phenol (d) Aniline

Bonding and Hybridisation in Organic Compounds

8. Which of the following represents the given mode of hybridisation $sp^2 - sp^2 - sp\text{-}sp$ from left to right?
(a) $CH_2{=}CH{-}C{\equiv}CH$ (b) $HC{\equiv}C{-}C{\equiv}N$
(c) $CH_2{=}C{-}C{=}CH_2$ (d)


9. How many sigma and pi bonds are there in the molecule of dicyanoethene $(CN{-}CH{=}CH{-}CN)$?
(a) 3 sigma and 3 pi (b) 5 sigma and 2 pi
(c) 7 sigma and 5 pi (d) 2 sigma and 3 pi

10. The enolic form of acetone contains
(a) 8σ bonds, 2π-bonds and 1 lone pair
(b) 9σ bonds, 1π-bond and 2 lone pairs
(c) 9σ bonds, 2π-bonds and 1 lone pair
(d) 10σ bonds, 1π-bond and 1 lone pair

11. In the dehydration reaction,

$CH_3CONH_2 \xrightarrow{P_2O_5} CH_3C{\equiv}N$, the hybridisation state of carbon changes from
(a) sp^3 to sp^2 (b) sp to sp
(c) sp^2 to sp (d) sp to sp^3

12. The shape of the π electron cloud in acetylene is
(a) linear (b) planar
(c) cylindrical (d) doughtnut

13. Electronegativity of carbon atoms depends upon their state of hybridisation. In which of the following compounds, the carbon marked with asterisk is most electronegative? **[NCERT Exemplar]**

(a) $CH_3—CH_2—{}^*CH_2—CH_3$
(b) $CH_3—{}^*CH{=}CH—CH_3$
(c) $CH_3—CH_2—C{\equiv}{}^*CH$
(d) $CH_3—CH_2—CH{=}{}^*CH_2$

14. The C—H bond distance is longest in

(a) C_2H_2
(b) C_2H_4
(c) C_2H_6
(d) $C_2H_2Br_2$

15. The maximum number of carbon atoms arranged linearly in the molecule, $CH_3—C{\equiv}C—CH{=}CH_2$ is

(a) 5
(b) 4
(c) 2
(d) 3

16. The basic strength of

$$\underset{\text{I}}{CH{\equiv}\bar{C}},\ \underset{\text{II}}{CH_2{=}\bar{C}H},\ \underset{\text{III}}{CH_3\bar{C}H_2}$$

will be in order

(a) I < II < III
(b) II < III < I
(c) III < II < I
(d) III < I < II

17. In the given structure, which carbon atom is most electronegative?

$$\underset{\text{(I)}}{CH_3}—\underset{\text{(II)}}{CH_2}—\underset{\text{(III)}}{CH}{=}\underset{\text{(IV)}}{\overset{\oplus}{C}H}$$

(a) (I)
(b) (II)
(c) (III)
(d) (IV)

Nomenclature of Organic Compounds

18. The incorrect statement for IUPAC system of nomenclature is

(a) in an organic compound, the longest carbon chain is always selected for assigning the root word
(b) there is no compound with the name 3-ethyl pentane
(c) out of $—NH_2$ and $—OH$ groups present in an organic compound, $—NH_2$ is treated as substituent
(d) different alkyl groups are written alphabetically while writing the IUPAC name

19. Which one is not correct for homologous series?

(a) All members are represented by same general formula
(b) All members have same chemical properties
(c) All members have same physical properties
(d) All members have same functional group

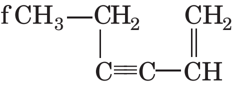
20. The correct statement related to IUPAC nomenclature is

(a) if two or more chains of equal length are seen in the compound then the chain with minimum number of side chains will be preferred
(b) if double and triple bonds are at symmetrical positions in a compound then triple bond gets lower preference
(c) correct IUPAC name of $CH_3COC_2H_5$ is ethyl methyl ketone
(d) as far as possible, the IUPAC name of a compound is written as a single word

21. Choose the option which show correct preferential order of groups among the following

(a) $—COOH, —CHO, —OH, —NH_2$
(b) $—NH_2, —OH, —CHO, —COOH$
(c) $—COOH, —OH, —NH_2, —CHO$
(d) $—COOH, —NH_2, —CHO, —OH$

22. The correct name of

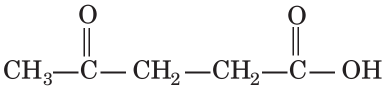


$$CH_3—CH_2—C{\equiv}C—CH{=}CH_2$$

is

(a) hex-3-yn-5-ene
(b) hex-5-en-3-yne
(c) hex-3-yn-1-ene
(d) hex-1-en-3-yne

23. The IUPAC name for

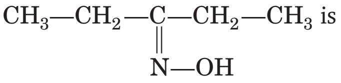


$$CH_3—\overset{\overset{\large O}{\|}}{C}—CH_2—CH_2—\overset{\overset{\large O}{\|}}{C}—OH$$

is **[NCERT Exemplar]**

(a) 1-hydroxypentane-1,4-dione
(b) 1, 4-dioxopentanol
(c) 1-carboxybutan-3-one
(d) 4-oxopentanoic acid

24. The IUPAC name of the compound

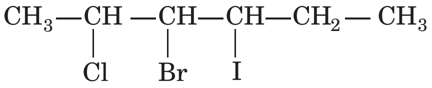


$$CH_3—CH_2—\underset{\underset{\large N—OH}{\|}}{C}—CH_2—CH_3$$

is

(a) N-hydroxy-3-aminopentane
(b) N-hydroxyaminopentane
(c) N-hydroxy-3-iminopentane
(d) None of the above

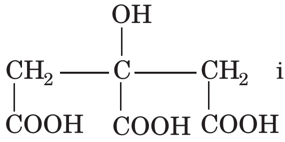
25. The correct IUPAC name of the compound is



$$CH_3—\underset{\underset{\large Cl}{|}}{CH}—\underset{\underset{\large Br}{|}}{CH}—\underset{\underset{\large I}{|}}{CH}—CH_2—CH_3$$

(a) 4-bromo-5-chloro-3-iodohexane
(b) 3-bromo-2-chloro-4-iodohexane
(c) 3-bromo-4-iodo-2-chlorohexane
(d) 2-chloro-3-bromo-4-iodohexane

26. The correct IUPAC name of

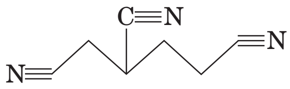


$$\begin{array}{ccccc} & & OH & & \\ & & | & & \\ CH_2 & — & C & — & CH_2 \\ | & & | & & | \\ COOH & & COOH & & COOH \end{array}$$

is

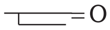
(a) 2-hydroxypropane-1, 2, 3-tricarboxylic acid
(b) 3-carboxy-3-hydroxypentane-1,5-dioic acid
(c) 2-carboxy-4 hydroxypentane-1,5-dioic acid
(d) 3-carboxy-3-hydroxyhexane-1,6-dioic acid

27. The IUPAC name of compound



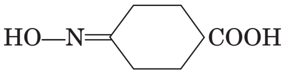
is

(a) hexane-1,2,5-tricarbonitrile
(b) hexane-1,3,6-tricarbonitrile
(c) butane-1,2,4-tricarbonitrile
(d) butane-1,3,4-tricarbonitrile

28. The IUPAC name of the compound  is

(a) butane-2-aldehyde
(b) 2-methylbutanal
(c) 2-ethylpropanal
(d) None of the above

29. The IUPAC name of



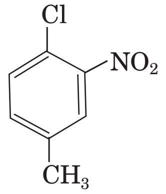
is

(a) 4-hydroxy amino benzene carboxylic acid
(b) 4-(N-hydroxy) imino benzene carboxylic acid
(c) 4-hydroxy imino cyclohexanoic acid
(d) 4-(N-hydroxy) imino cyclohexane-1-carboxylic acid

30. The correct IUPAC name of tartaric acid is

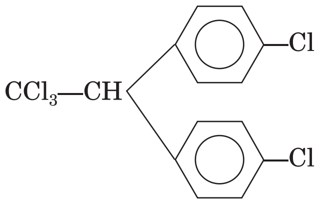
(a) 1,4-dicarboxy-2,3-dihydroxyethane
(b) α, α'-dihydroxybutane-1,4-dioic acid
(c) 1,4-dihydroxybutane-2,3-dioic acid
(d) 2,3-dihydroxybutane-1,4-dioic acid

31. The IUPAC name for **[NCERT Exemplar]**



(a) 1-chloro-2-nitro-4-methylbenzene
(b) 1-chloro-4-methyl-2-nitrobenzene
(c) 2-chloro-1-nitro-5-methylbenzene
(d) *m*-nitro-*p*-chlorotoluene

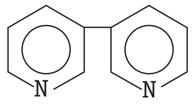
32. Correct IUPAC name of

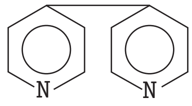


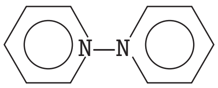
is

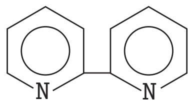
(a) gammexane
(b) dichloro diphenyl trichloroethane
(c) diparachlorophenyl trichloroethane
(d) 1,1,1-trichloro-2,2-bis (4-chlorophenyl) ethane

33. The compound 2,2′-bipyridine has the structure

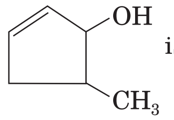
(a) 

(b) 

(c) 

(d) 

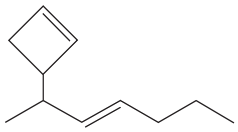
34. The IUPAC name of the compound

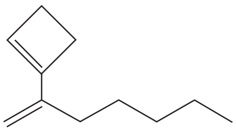


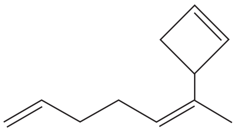
is

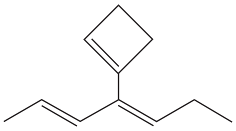
(a) 4-methylcyclopent-1-en-3-ol
(b) 5-methylcyclopent-2-en-1-ol
(c) 2-methylcyclopent-4-en-1-ol
(d) 3-methylcyclopent-1-en-2-ol

35. Which is the structure of compound 2-(1-cyclobutenyl)- 1-hexene?

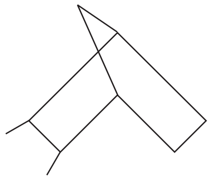
(a) 

(b) 

(c) 

(d) 

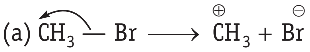
36. Write the IUPAC name of the compound

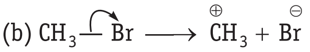


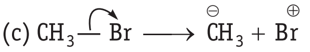
(a) 5,6-dimethyl bicyclo [2.2.1] heptane
(b) 2,3-dimethyl bicyclo [2.2.1] heptane
(c) 2,3-dimethyl bicyclo[1.2.2] heptane
(d) 3,4-dimethyl bicyclo [2.1.2] heptane

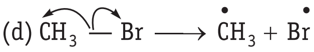
Bond Fission and Reaction Intermediates

37. Covalent bond can undergo fission in two different ways. The correct representation involving a heterolytic fission of CH_3 — Br is **[NCERT Exemplar]**

(a) 
$CH_3—Br \longrightarrow \overset{\oplus}{C}H_3 + \overset{\ominus}{Br}$

(b) 
$CH_3—Br \longrightarrow \overset{\oplus}{C}H_3 + \overset{\ominus}{Br}$

(c) 
$CH_3—Br \longrightarrow \overset{\ominus}{C}H_3 + \overset{\oplus}{Br}$

(d) 
$CH_3—Br \longrightarrow \overset{\bullet}{C}H_3 + \overset{\bullet}{Br}$

38. Heterolysis of $CH_3CH_2CH_3$ results in the formation of

(a) $\overset{\oplus}{C}H_3$ and $\bar{C}_2H_5$ (b) $\overset{\bullet}{C}H_3$ and $\overset{\bullet}{C}_2H_5$

(c) $\bar{C}H_3$ and $\overset{\oplus}{C}_2H_5$ (d) CH_3 and C_2H_5

39. Which of the following is an electrophile?

(a) $:CCl_2$ (b) CO_2

(c) H_2O (d) NH_3

40. Which of the following is not a nucleophile?

(a) BF_3 (b) CN^- (c) OH^- (d) NH_3

41. Among the following the strongest nucleophile is

(a) C_2H_5SH (b) CH_3COO^-

(c) CH_3NH_2 (d) $NCCH_2^-$

42. Which behaves both as a nucleophile as well as an electrophile?

(a) CH_3OH (b) CH_3NH_2

(c) CH_3CN (d) CH_3Cl

43. Correct order of nucleophilicity is

(a) $I^- > Br^- > Cl^- > F^-$ (b) $F^- > Cl^- > Br^- > I^-$

(c) $Cl^- > F^- > Br^- > I^-$ (d) $I^- > Cl^- > Br^- > F^-$

44. The stability of a carbonium ion depends upon

(a) the bond angle of the attached group

(b) the substrate with which it reacts

(c) the inductive effect and hyper-conjugative effect of the attached group

(d) None of the above

45. The most stable carbonium ion among the following is

(a) $C_6H_5CH_2\overset{+}{C}H_2$ (b) $CH_3\overset{+}{C}H_2$

(c) $C_6H_5\overset{+}{C}HC_6H_5$ (d) $C_6H_5\overset{+}{C}H_2$

46. The stability of the free radicals; allyl, benzyl, 3°, 2°, 1° and CH_3 is in the order

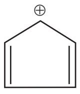
(a) benzyl > allyl > 3° > 2° > 1° > CH_3

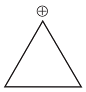
(b) allyl > 3° > benzyl > 2° > 1° > CH_3

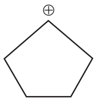
(c) 3° > 2° > 1° > CH_3 > allyl > benzyl

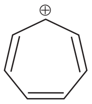
(d) 3° > 2° > 1° > CH_3 > allyl = benzyl

47. The most stable carbocation is

(a) 

(b) 

(c) 

(d) 

48. Arrange the following carbocations in order of stability

I. benzyl, II. allyl, III. methyl, IV. vinyl

(a) IV > III > II > I (b) I > II > III > IV

(c) II > IV > III > I (d) III > II > I > IV

49. Correct order of stability is

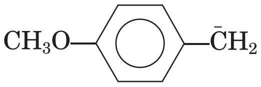
(a) $HC{\equiv}\bar{C} > CH_2{=}\bar{C}H > CH_3{—}\bar{C}H_2$

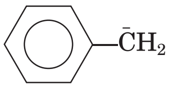
(b) $CH_3{—}\bar{C}H_2 > CH_2{=}\bar{C}H > CH{\equiv}\bar{C}$

(c) $CH_3{—}\bar{C}H_2 > CH{\equiv}CH \cong CH_2{=}\bar{C}H$

(d) All are equally stable

50. Consider the following carbanions

I.  II. 

III. 

Correct order of stability is

(a) I > II > III (b) III > II > I

(c) II > III > I (d) I > III > II

51. Which of the two : $O_2NCH_2CH_2O^-$ or $CH_3CH_2O^-$ is expected to be more stable? **[NCERT]**

(a) $O_2NCH_2CH_2O^-$

(b) $CH_3CH_2O^-$

(c) Both are equally stable

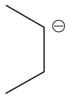
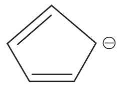
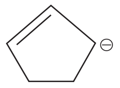
(d) Cannot say anything

52. State the hybridisation of carbon present in triplet carbene.

(a) sp^3 (b) sp^2

(c) sp (d) None of these

53. The order of stability of the following carbanion is

$CH_3\overset{\ominus}{C}H_2$   

I II III IV

(a) I > II > III > IV (b) I > III > II > IV

(c) IV > III > II > I (d) III > IV > I > II

54. With a change in hybridisation of the carbon bearing the charge, the stability of a carbanion increase in the order

(a) $sp < sp^3 < sp^2$ (b) $sp < sp^2 < sp^3$

(c) $sp^2 < sp < sp^3$ (d) $sp^3 < sp^2 < sp$

Electronic Displacement in Organic Compounds

55. The inductive effect

(a) implies the atom's ability to cause bond polarization

(b) increases with increase of distance

(c) implies the transfer of lone pair of electrons from more electronegative atom to the lesser electronegative atom in a molecule

(d) implies the transfer of lone pair of electrons from lesser electronegative atom to the more electronegative atom in a molecule

56. In which of the following compounds, the carbon marked with asterisk is expected to have greatest positive charge? **[NCERT Exemplar]**

(a) $^*CH_3—CH_2—Cl$ (b) $^*CH_3—CH_2—Mg^+Cl^-$

(c) $^*CH_3—CH_2—Br$ (d) $^*CH_3—CH_2—CH_3$

57. Hyperconjugation involves overlap of the following orbitals

(a) σ-σ (b) σ-*p*

(c) *p*-*p* (d) π-π

58. Alkyl groups act as electron donors when attached to a π-system because of **[NCERT]**

(a) resonance (b) mesomeric effect

(c) hyperconjugation (d) Both (b) and (c)

59. Which of the following orders is not correct regarding the –*I* effect of the substituents?

(a) $—I < —Cl < —Br < —F$ (b) $—\overset{+}{N}R_3 < —\overset{+}{O}R_2$

(c) $—\overset{+}{N}R_2 < —OR < —F$ (d) $—SR < —OR < —\overset{+}{O}R_2$

60. Which of the following orders is correct regarding the acidity of carboxylic group?

(a) $CH_3CH_2CH(Cl)COOH > CH_3CH(Cl)CH_2COOH > ClCH_2CH_2CH_2COOH$

(b) $CH_3CH_2CH(Cl)COOH < CH_3CH(Cl)CH_2COOH < ClCH_2CH_2CH_2COOH$

(c) $CH_3CH_2CH(Cl)COOH > CH_3CH(Cl)CH_2COOH < ClCH_2CH_2CH_2COOH$

(d) $CH_3CH_2CH(Cl)COOH < CH_3CH(Cl)CH_2COOH > ClCH_2CH_2CH_2COOH$

61. Correct gradation of basic character is

(a) $NH_3 > CH_3NH_2 > NF_3$ (b) $CH_3NH_2 > NH_3 > NF_3$

(c) $NF_3 > CH_3NH_2 > NH_3$ (d) $CH_3NH_2 > NF_3 > NH_3$

62. The order of stability of the alkenes is

$$\underset{\text{I}}{R_2C{=}CR_2},\ \underset{\text{II}}{R_2C{=}CHR},\ \underset{\text{III}}{R_2C{=}CH_2},$$

$$\underset{\text{IV}}{RCH{=}CHR},\quad \underset{\text{V}}{RCH{=}CH_2}$$

(a) I > II > IV > III > V (b) I = II > III > IV > V

(c) II > I > IV > III > V (d) V > IV > III > I > II

63. Which of the following does not show electromeric effect?

(a) Alkenes (b) Ethers

(c) Aldehyde (d) Ketones

64. Stability of which intermediate is not governed by hyperconjugation?

(a) Carbon cation (b) Carbon anion

(c) Carbon free radical (d) None of these

65. Delocalised electrons are present in

(a) 1, 3-butadiene (b) C_6H_6

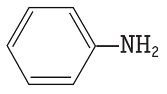
(c) 1, 3, 5-hexatriene (d) All of these

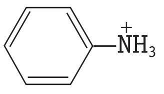
66. Resonance energy is more for

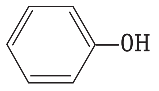
(a) C_6H_6 (b) cyclohexene

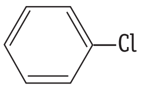
(c) cycloheptene (d) cyclohexa-1,2,3-triene

67. In which of the following molecules, the resonance effect is not present?

(a) 

(b) 

(c) 

(d) 

68. Polarisation of electron in acrolein may be written as

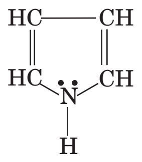
(a) $\overset{-\delta}{C}H_2{=}CH—\overset{+\delta}{C}H{=}O$

(b) $\overset{-\delta}{C}H_2{=}CH—CH{=}\overset{+\delta}{O}$

(c) $\overset{-\delta}{C}H_2{=}\overset{+\delta}{C}H—CH{=}O$

(d) $\overset{+\delta}{C}H_2{=}CH—CH{=}\overset{-\delta}{O}$

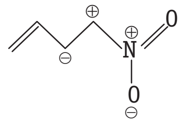
69. How many delocalised π-electrons are there in the compound

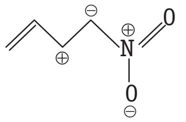


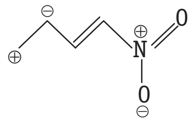
(a) 8 (b) 2

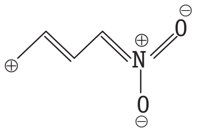
(c) 4 (d) 6

70. Among the following, the least stable resonance structure is

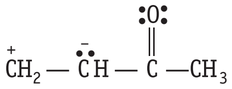
(a) 

(b) 

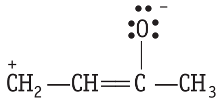
(c) 

(d) 

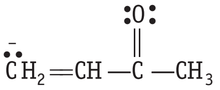
71. One of the stable resonating forms of methyl vinyl ketone is

(a) 

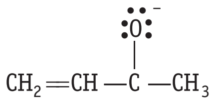
$\overset{+}{C}H_2 - \overset{-}{\ddot{C}}H - \overset{:\ddot{O}:}{\overset{\|}{C}} - CH_3$

(b) 

$\overset{+}{C}H_2 - CH = \overset{:\ddot{O}:^-}{\overset{|}{C}} - CH_3$

(c) 

$\overset{-}{\ddot{C}}H_2 = CH - \overset{:\ddot{O}:}{\overset{\|}{C}} - CH_3$

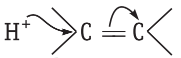
(d) 

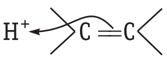
$CH_2 = CH - \overset{:\ddot{O}:^-}{\overset{|}{C}} - CH_3$

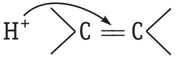
72. The oxygen atom in phenol
(a) exhibits only inductive effect
(b) exhibits only resonance effect
(c) has more dominating resonance effect than inductive effect
(d) has more dominating inductive effect than the resonance effect

Types of Organic Reaction

73. The addition of HCl to an alkene proceeds in two steps. The first step is the attack of H^+ ion to $>C=C<$ portion which can be shown as **[NCERT Exemplar]**

(a) 

(b) 

(c) 

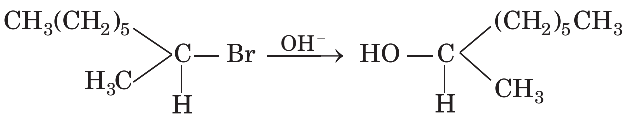
(d) All of these

74. Electrophilic addition reactions proceed in two steps. The first step involves the addition of an electrophile. Name the type of intermediate formed in the first step of the following addition reaction.

$H_3C - HC{=}CH_2 + H^+ \longrightarrow ?$ **[NCERT Exemplar]**

(a) 2° carbanion
(b) 1° carbocation
(c) 2° carbocation
(d) 1° carbanion

75. The following reaction is described as



(a) S_E2
(b) S_N2
(c) S_N1
(d) S_N0

76. Which one is least reactive in a nucleophilic substitution reaction?
(a) CH_3CH_2Cl
(b) $CH_2{=}CHCH_2Cl$
(c) $CH_2{=}CHCl$
(d) $(CH_3)_3CCl$

77. *t*-butyl chloride reacts with OH^- by S_N1 mechanism and rate $\propto$ [*t*-butyl chloride]. One of the reasons for this is that
(a) stereochemical inversion takes place
(b) *t*-butyl carbocation is first formed which is more stable
(c) the product *t*-butyl alcohol is more stable
(d) the intermediate *t*-butyl carbocation is stabilized by solvation

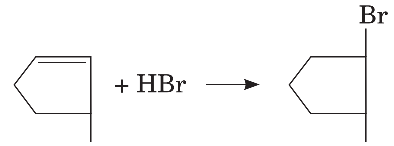
78. Which one of the following explain, why does propene undergo electrophilic addition with HBr, but not with HCN ?
(a) Br^- is better nucleophile than CN^-
(b) HBr being better source of proton as it is stronger acid than HCN
(c) HCN attacks preferentially *via* lone pair of nitrogen
(d) The C—Br bond being stronger is formed easily as compared to C—CN bond

79. Which of the following is most reactive towards elimination reaction?
(a) $RCOO^-$
(b) CN^-
(c) NO_3^-
(d) RO^-

80. Examine the following statements regarding S_N2 reaction
(1) The rate of reaction is independent of concentration of nucleophile
(2) The nucleophile attacks the carbon atom on the side of molecule opposite to the group being displaced
(3) The reaction proceeds with simultaneous bond formation and rupture

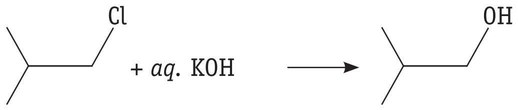
Which of the above written statements are correct?
(a) 1, 2
(b) 1, 3
(c) 1, 2, 3
(d) 2, 3

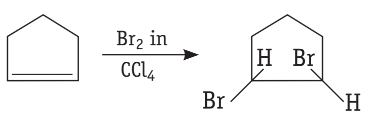
81. The reaction,

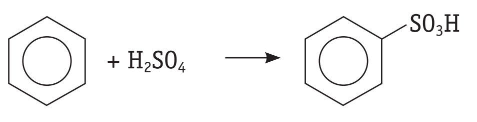


is an example of
(a) nucleophilic substitution
(b) electrophilic addition
(c) elimination reaction
(d) nucleophilic addition

82. The addition reaction among the following is

(a)


(b)


(c)


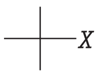
(d) All of the above

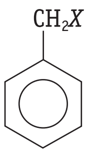
83. Consider the following reaction

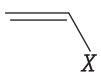
$$>C{=}O + H_2NOH \longrightarrow >C{=}NOH + H_2O$$

It is an example of
(a) substitution
(b) elimination
(c) addition
(d) addition-elimination

84. Which of the following cannot show S_N1 reaction?

(a)


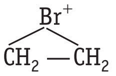
(b)


(c)


(d)


85. Which of the following types of reaction occurs when a substituent has got a double bond with evenly distributed π electron cloud ?
(a) Electrophilic addition
(b) Nucleophilic addition
(c) Any of the (a) and (b)
(d) None of the above

86. During addition of bromine on ethene, the first species formed is

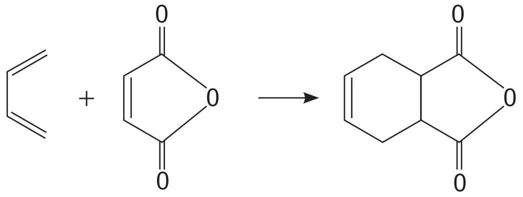
(a)

$\overset{Br^+}{CH_2—CH_2}$

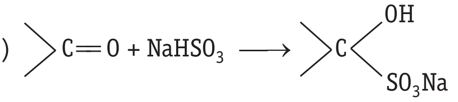
(b) $C_2H_4OH^+$

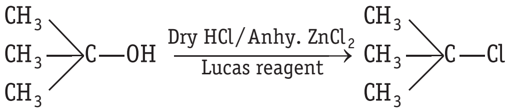
(c) $\overset{+}{C}H_2CH_2Br$

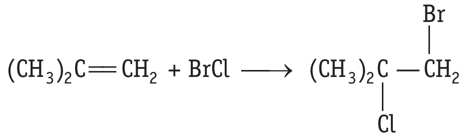
(d) $C_2H_5^+$

87. The substitution reaction among the following is

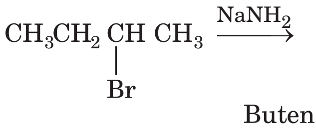
(a)


(b)


(c)


(d)

$(CH_3)_2C{=}CH_2 + BrCl \longrightarrow (CH_3)_2\underset{Cl}{C}—\overset{Br}{CH_2}$

88. The reaction,


$$CH_3CH_2\underset{Br}{CH}CH_3 \xrightarrow{NaNH_2}$$

Butene -1 and butene-2 (major)

The correct statement(s) are
(a) 2-butene is Saytzeff product
(b) 1-butene is Hofmann(s) product
(c) the elimination reaction follows Saytzeff rule
(d) All of the above

89. List the following alkoxide nucleophile in decreasing order of their S_N2 reactivity

1. Me_3CO^- 2. MeO^- 3. $MeCH_2O^-$

4. Me_2CHO^- 5.


(a) 2 > 3 > 5 > 4 > 1
(b) 5 > 3 > 2 > 1 > 4
(c) 1 > 5 > 2 > 3 > 4
(d) 3 > 5 > 1 > 2 > 3

90. Consider the following reactions. Which of these does not involve attack of a nucleophile in first step? **[NCERT]**

(a) $CH_3CH_2Br + HS^- \longrightarrow CH_3CH_2SH + Br^-$
(b) $(CH_3)_2C{=}CH_2 + HCl \longrightarrow (CH_3)_2CCl — CH_3$
(c) $CH_3CH_2Br + HO^- \longrightarrow CH_2{=}CH_2 + H_2O + Br^-$
(d) $(CH_3)_2C — CH_2OH + HBr \longrightarrow (CH_3)_2\ CBrCH_2CH_3 + H_2O$

Round II (Mixed Bag)

Only One Correct Option

1. In which of the compounds given below there is more than one kind of hybridisation (*sp*, sp^2, sp^3) for carbon?

(I) $CH_3CH_2CH_2CH_3$

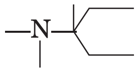
(II) $CH_3CH{=}CH-CH_3$

(III) $CH_2{=}CH-CH{=}CH_2$

(IV) $H-C{\equiv}C-H$

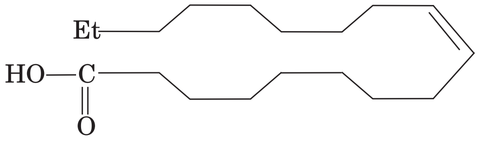
(a) (II) and (IV) (b) (I) and (IV)
(c) (II) and (III) (d) (II) only

2. The IUPAC name of following compound is



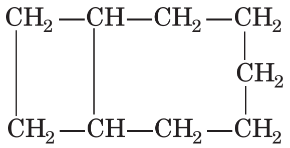
(a) N,N-dimethyl- 3-methylpentan-3-amine
(b) 3-N,N-dimethyl, 3-methyl pentanamine
(c) 3-methyl-3-N,N-dimethyl pentane
(d) 3-methyl-3-N,N-dimethyl butane

3. The compound



have its IUPAC name as
(a) octa dec-9-enoic acid
(b) oleic acid
(c) ethyl hexadec-9-enoic acid
(d) All of the above

4. The IUPAC name of the compound

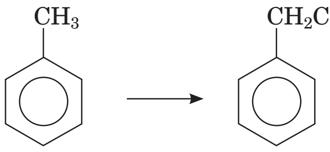


is

(a) bicyclo [2.5.0] nonane (b) bicyclo [5.0.2] nonane
(c) bicyclo [5.2.0] nonane (d) bicyclo [0.2.5] nonane

5. The nodal plane in the π-bond of ethene is located in
(a) the molecular plane
(b) a plane parallel to the molecular plane
(c) a plane perpendicular to the molecular plane which bisects the carbon-carbon sigma bond at right angle
(d) a plane perpendicular to the molecular plane which contains the carbon-carbon sigma bond

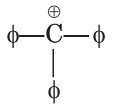
6.



The above reaction proceeds through
(a) free radical substitution
(b) nucleophilic substitution
(c) electrophilic substitution
(d) None of the above

7. Which of the following species is paramagentic in nature?
(a) Carbonium ion (b) Free radical
(c) Carbene (d) Nitrene

8. (1)

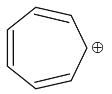


$\phi-\underset{\substack{|\\ \phi}}{\overset{\oplus}{C}}-\phi$

(2) $\phi-\overset{\oplus}{C}H_2$

(3) $CH_2{=}CH-\overset{\oplus}{C}H_2$

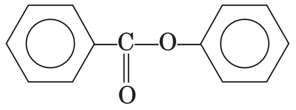
(4)



Correct order of stability is
(a) 1 > 4 > 2 > 3
(b) 1 > 2 > 3 > 4
(c) 1 > 2 > 4 > 3
(d) 1 > 3 > 4 > 2

9. Formation of ethylene from acetylene is an example of
(a) elimination reaction (b) substitution reaction
(c) condensation reaction (d) addition reaction

10. In



electrophilic substitution occurs at
(a) *ortho*/*para* at first ring
(b) *meta* at first ring
(c) *ortho* /*para* at second ring
(d) *meta* at second ring

11. An S_N2 reaction at an asymmetric carbon of a compound always gives
(a) a mixture of diastereomers
(b) a single stereoisomer
(c) an enantiomer of the substrate
(d) a product with opposite optical rotation

12. Identify the most stable species in the following sets of ions. **[NCERT Exemplar]**

(i) $\overset{\oplus}{C}H_3, \overset{\oplus}{C}H_2Br, \overset{\oplus}{C}HBr_2, \overset{\oplus}{C}Br_3$

(ii) $\overset{\ominus}{C}H_3, \overset{\ominus}{C}H_2Cl, \overset{\ominus}{C}HCl_2, \overset{\ominus}{C}Cl_3$

(a) $\overset{+}{C}Br_3, \overset{-}{C}Cl_3$ (b) $\overset{+}{C}H_3, \overset{-}{C}H_3$
(c) $\overset{+}{C}H_2Br, \overset{-}{C}H_3$ (d) $\overset{+}{C}H_3, \overset{-}{C}Cl_3$

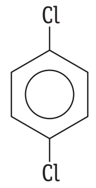
13. SO_3 acts as an electrophile because **[NCERT Exemplar]**

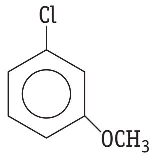
(a) S is an electron deficient element
(b) O is highly electronegative
(c) S is larger in size
(d) All of the above

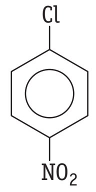
14. Amino group is *ortho*/*para*- directing for aromatic electrophilic substitution. On nitration of aniline, a good amount of *m*-nitroaniline is obtained. This is due to

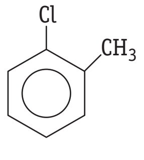
(a) the fact that in nitration mixture, *ortho, para*-activity of NH_2 group is completely lost
(b) $-NH_2$ becomes $-NH_3^+$, which is *m*-directing
(c) $-NH_2$ becomes $-NH^+SO_4^-$; which is *m*-directing
(d) $-NH_2$ becomes $-NH^-NO_2^+$, which is *m*-directing

15. Which of the following would react most readily with nucleophiles?

(a)


(b)


(c)


(d)


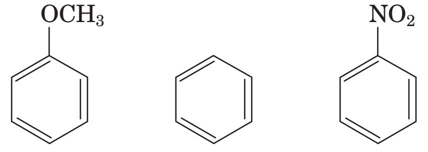
16. Which of the following statement is not characteristic of free radical chain reaction?

(a) It gives major products derived from most stable free radical
(b) It is usually sensitive to change in solvent polarity
(c) It proceeds in three main steps like initiation, propagation and termination
(d) It may be initiated by UV light

17. Arrange *p*-toluidine (I) N,N-dimethyl-*p*-toluidine (II) *p*-nitroaniline (III) and aniline (IV) in order of decreasing basicity

(a) I > IV > III > II
(b) I > II > III > IV
(c) II > I > IV > III
(d) III > I > II > IV

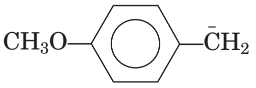
18. Among the following compounds (I – III) the correct order of reaction with electrophilic reagent is

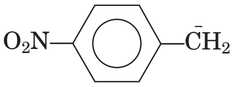


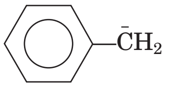
I II III

(a) II > III > I (b) III < I < II
(c) I > II > III (d) I = II > III

19. Consider the following carbanions

(I)


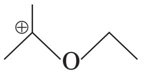
(II)


(III)


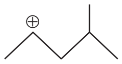
Correct order of stability is

(a) I > II > III (b) III > II > I
(c) II > III > I (d) I > III > II

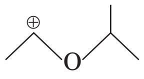
20. The correct stability order for the following species is



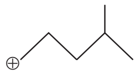
(I)



(II)



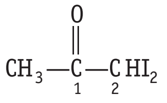
(III)

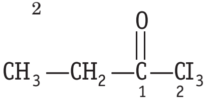


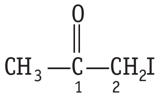
(IV)

(a) (II) > (IV) > (I) > (III) (b) (I) > (II) > (III) > (IV)
(c) (II) > (I) > (IV) > (III) (d) (I) > (III) > (II) > (IV)

21. Which of the following compounds yields most stable carbanion after rupture of $(\underset{1}{C}-\underset{2}{C})$ bond?

(a)

$CH_3-\underset{1}{\overset{\overset{O}{\|}}{C}}-\underset{2}{C}HI_2$

(b)

$CH_3-CH_2-\underset{1}{\overset{\overset{O}{\|}}{C}}-\underset{2}{C}I_3$

(c)

$CH_3-\underset{1}{\overset{\overset{O}{\|}}{C}}-\underset{2}{C}H_2I$

(d) None of these

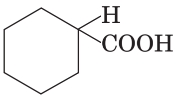
22. Match the following

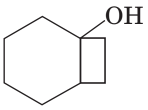
Column I

A. cyclohexane carboxylic acid
B. 2,3,5-trimethyl hexane
C. trimethyl bismuthane
D. Bicyclo [4.2.0] octane 1-ol

Column II

(i) $CH_3-CH(CH_3)CH_2-CH(CH_3)-CH(CH_3)-CH_3$

(ii)


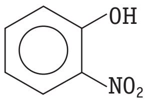
(iii) 

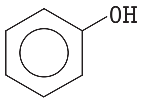
(iv) $(CH_3)_3Bi$

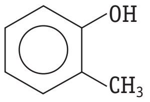
	A	B	C	D
(a)	(iv)	(i)	(ii)	(iii)
(b)	(i)	(ii)	(iv)	(iii)
(c)	(ii)	(i)	(iv)	(iii)
(d)	(iii)	(ii)	(iv)	(i)

23. Which one of the following compounds is most acidic?

(a) $Cl—CH_2—CH_2—OH$

(b) 

(c) 

(d) 

24. Which of the following is singlet carbene?

(a) $CH_3\ddot{C}HCH_3$ (b) $C_2H_5\ddot{C}—H$

(c) $CH_2=CH—\overset{\oplus}{C}H_2$ (d) $(CH_3)_3C^+$

25. Which of the following applies in the reaction $CH_3CHBrCH_2CH_3 \xrightarrow{\text{Alco. KOH}} ?$

(I) $CH_3CH=CHCH_3$ (Major product)

(II) $CH_2=CHCH_2CH_3$ (Minor product)

(a) Hofmann's rule (b) Saytzeff's rule

(c) Kharasch effect (d) Markownikoff's rule

26. A solution of D(+)-2-chloro-2-phenylethane in toluene racemises slowly in the presence of small amount of $SbCl_5$ due to the formation of

(a) carbanion (b) carbene

(c) free radical (d) carbocation

27. Which of the following statements is incorrect?

(a) The rate of reaction increases with increase in water concentration in the hydrolysis of tertiary butyl bromide in methanol and water

(b) The relative nucleophilicity in protic solvent is

$$CN^- > I^- > \bar{O}H > Br^- > Cl^- > F^- > H_2O$$

(c) In S_N2 reactions, the order of reactivity of alkyl halides is in the order

methyl > primary > secondary > tertiary

(d) S_N2 reaction involves carbonium ions

28. Which of the following statement(s) is (are) not true?

(a) Carbanions and carbonium ions, usually exist in ion pairs or else solvated

(b) Acidity increases and basicity decreases in going from left to right across a row of periodic table

$$CH_4 < NH_3 < H_2O < HF \text{ (acidity)}$$

$$CH_3^- > NH_2^- > OH^- > F^- \text{ (basicity)}$$

(c) $RCOOH$ like $RCOR$ reacts with H_2NOH to give an oxime

(d) Decreasing order of ionizing power of solvents is

$$CF_3COOH > HCOOH > H_2O > CH_3COOH > CH_3OH > C_2H_5OH > (CH_3)_2SO > CH_3CN$$

29. Match the terms mentioned in Column I with the terms in Column II and choose the correct answer using the codes given below **[NCERT Exemplar]**

	Column I		Column II
A.	Carbocation	1.	Cyclohexane and I- hexene
B.	Nucleophile	2.	Conjugation of electrons of C—H σ bond with empty *p*-orbital present at adjacent positively charged carbon.
C.	Hyperconjugation	3.	*sp*^{2} hybridised carbon with empty *p*-orbital
D.	Isomers	4.	Ethyne
E.	*sp* hybridisation	5.	Species that can receive a pair of electrons
F.	Electrophile	6.	Species that can supply a pair of electrons

Codes

	A	B	C	D	E	F
(a)	1	2	3	4	5	6
(b)	3	6	2	1	4	5
(c)	2	3	6	5	4	1
(d)	6	3	2	1	4	5

More than One Correct Option

30. Which of the following are cyclic compounds?

(a) Borazole (b) Pyrrole

(c) Anthracene (d) Isobutylene

31. Electrophiles are electron seeking species. Which of the following groups contain only electrophiles? **[NCERT Exemplar]**

(a) BF_3, NH_3, H_2O (b) $AlCl_3, SO_3, NO_2^+$

(c) $NO_2^+, \overset{+}{C}H_3, CH—\overset{+}{C}=O$ (d) $C_2H_5^-, \dot{C}_2H_5, C_2H_5^+$

32. Hyperconjugation involves delocalisation of **[NCERT Exemplar]**

(a) electrons of carbon-hydrogen σ bond of an alkyl group directly attached to an atom of unsaturated system.

(b) electrons of carbon-hydrogen σ bond of an alkyl group directly attached to the positively charged carbon atom.

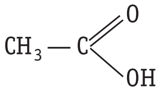
(c) π-electrons of carbon-carbon bond

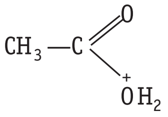
(d) lone pair of electrons

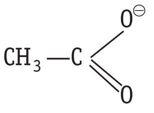
33. Br has a low reactivity in $CH_2{=}CH{-}Br$ because
(a) Br is electronegative
(b) of the $+M$ effect of bromine
(c) the C—Br bond has a partial double bond character
(d) Br shows + I effect

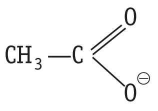
34. Which of the following species are planar?
(a) *Iso*-propyl carbanion
(b) Nitromethyl carbanion
(c) Singlet carbene
(d) Triphenylmethyl carbocation

35. Which of the following structures have resonance stability?

(a) 

(b) 

(c) 

(d) 

Assertion and Reason

Directions (Q. Nos. 36 to 40) *Each of these questions contains two statements : Statement* I (*Assertion*) *and Statement* II (*Reason*). *Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes* (*a*), (*b*), (*c*), (*d*) *given below :*

(a) Statement I is true; Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true; Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

36. Statement I The IUPAC name for the compound, $NCCH_2CH_2COOH$ is 3-cyano propanoic acid.

Statement II —COOH is considered as substituent group while —CN is considered as the principal functional group.

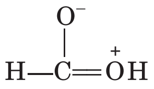
37. Statement I All the carbon atoms in $H_2C{=}C{=}CH_2$ are sp^2-hybridised.

Statement II In this molecule all the carbon atoms are attached ot each other by double bonds.

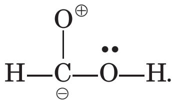
38. Statement I The order of stability of carbocations are

$$R_3C^+ > R_2\overset{+}{C}H > R\overset{+}{C}H_2 > \overset{+}{C}H_3.$$

Statement II The stability of carbocations is influenced by both resonance and inductive effects.

39. Statement I 

$H{-}\underset{}{\overset{O^-}{\overset{|}{C}}}{=}\overset{+}{O}H$ is more stable than



$H{-}\underset{\ominus}{\overset{O^{\oplus}}{\overset{|}{C}}}{-}\ddot{O}{-}H.$

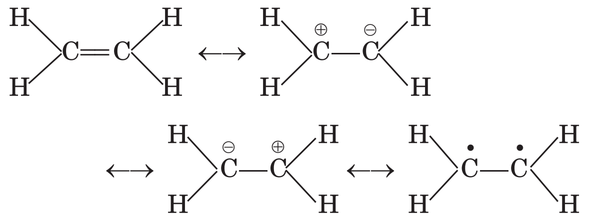
Statement II Compound in which the positive and negative charges reside on the most electropositive and most electronegative atoms of the species respectively is more stable.

40. Statement I Energy of resonance hybrid is equal to the average of energies of all canonical forms.

Statement II Resonance hybrid cannot be presented by a single structure. [**NCERT** Exemplar]

Comprehension Based Questions

Directions (Q. Nos. 41 to 43) Resonance effects are encountered mainly in molecule with multiple, *i.e.*, π bonds. Except in a few special molecules, the σ-bond framework is not involved in significant resonance interactions. This fact can be rationalized by noting that electron in π bonds are higher in energy than those in σ-bonds, making the π-bonding electrons more reactive and also more polarizable than σ-bonding electrons. For example, here four structures we might write for ethylene.



41. Which of the following compounds shows resonance?
(a) Ethyne (b) Ethane
(c) Toluene (d) Cyclohexene

42. Naphthalene is an example of
(a) alicyclic compound
(b) heterocyclic compound
(c) aliphatic compound
(d) polynuclear aromatic hydrocarbon

43. In benzene, all the C—C bonds have the same length because of
(a) isomerism
(b) tautomerism
(c) resonance
(d) inductive effect

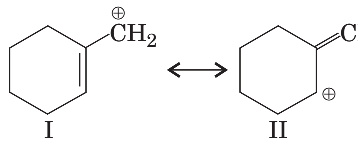
Directions (Q. Nos. 44 to 47) Stability of carbocations depends upon the electron releasing inductive effect of groups adjacent to positively charged carbon atom involvement of neighbouring groups in hyperconjugation and resonance. [**NCERT** Exemplar]

44. From the following resonance structures of $CH_3 — \ddot{\underset{\bullet\bullet}{O}} — \overset{+}{C}H_2$ predict which of the structures is more stable?

(a) $CH_3O — \overset{+}{C}H_2$ (b) $CH_3 — \underset{\bullet\bullet}{\overset{+}{O}} = CH_2$

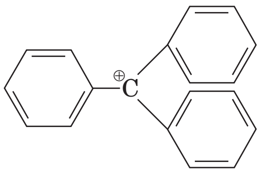
(c) $CH_2 = \overset{-}{O} — CH_3$ (d) All are equally stable

45. Which of the following ions is more stable?



(a) I
(b) II
(c) Both are equally stable
(d) Unpredictable

46. The structure of triphenylmethyl cation is given below. This is very stable and someof its salts can be stored for months. The cause of high stability of this cation, is [**NCERT** Exemplar]

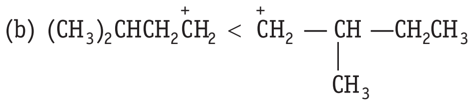


(a) hyperconjugation (b) mesomeric effect

(c) resonance (d) Both (b) and (c)

47. Arrange the various carbocations that can be obtained from 2-methylbutane in order of increasing stability. [**NCERT** Exemplar]

(a) $(CH_3)_2CHCH_2\overset{+}{C}H_2 < (CH_3)_2CH\overset{+}{C}HCH_3 < (CH_3)_2\overset{+}{C}CH_2CH_3 < \overset{+}{C}H_2(CH_3)CHCH_2CH_3$



(b) $(CH_3)_2CHCH_2\overset{+}{C}H_2 < \overset{+}{C}H_2 — \underset{\underset{CH_3}{|}}{CH} — CH_2CH_3 < (CH_3)_2H\overset{+}{C}HCH_3 < (CH_3)_2\overset{+}{C}CH_2CH_3$

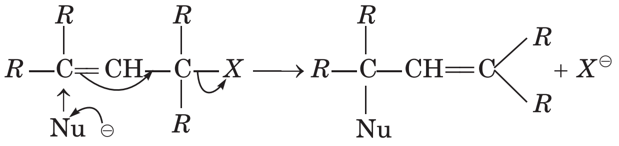
(c) $(CH_3)_2CHCH_2\overset{+}{C}H_2 < (CH_3)_2CH\overset{+}{C}HCH_3 < \overset{+}{C}H_2CH(CH_3)CH_2CH_3 < (CH_3)_2\overset{+}{C}CH_2CH_3$

(d) $(CH_3)_2CHCH_2\overset{+}{C}H_2 < (CH_3)_2\overset{+}{C}CH_2CH_3 < \overset{+}{C}H_2CH(CH_3)CH_2CH_3 < (CH_3)_2CH\overset{+}{C}HCH_3$

Directions (Q. Nos. 48 and 49) Nucleophilic substitution at an allylic carbon may also takes place by S_N2 mechanism without allylic rearrangement. This mechanism operates with primary allyl halides in the presence of polar aprotic solvents.

$$CH_2 = CH — CH_2 — Br \xrightarrow[\text{Acetone}]{\text{NaI}} CH_2 = CH — CH_2 — I$$

However, allylic rearrangement can also take place under S_N2 conditions through the following mechanism in which nucleophile attacks at the γ-carbon instead of at the usual position. This mechanism is also called S_N2 mechanism and is an allylic rearrangement. S_N2 mechanism takes place under S_N2 conditions where α-substitution sterically retards the normal S_N2 mechanism.



48. Which one of the halide is most reactive for S_N2 reaction?

(a) $C_6H_5CH_2Cl$ (b) $CH_3—O—CH_2—Cl$

(c) $CH_2 = CH—CH_2—Cl$ (d) $CH_3—CO—CH_2—Cl$

49. For the reaction,

$$CH_3 — I + Nu^{\ominus} \longrightarrow CH_3 — Nu + I^{\ominus}.$$

the rate will be maximum when $Nu^{\ominus}$ is

(a) $Br^{\ominus}$ (b) $N_3^{\ominus}$

(c) $CH_3O^{\ominus}$ (d) $C_6H_5O^{\ominus}$

Previous Years' Questions

50. Consider thiol anion ($RS^{\ominus}$) and alkoxy anion ($RO^{\ominus}$). Which of the following statements is correct? [AIEEE 2011]

(a) ($RS^{\ominus}$) is less basic and less nucleophilic than ($RO^{\ominus}$)

(b) ($RS^{\ominus}$) is less basic but more nucleophilic than ($RO^{\ominus}$)

(c) ($RS^{\ominus}$) is more basic and more nucleophilic than ($RO^{\ominus}$)

(d) ($RS^{\ominus}$) is more basic and more nucleophilic than ($RO^{\ominus}$)

51. The correct order of increasing basicity of the given conjugate bases ($R = CH_3$) is [AIEEE 2010]

(a) $RCO\bar{O} < HC \equiv \bar{C} < \bar{R} < \bar{N}H_2$

(b) $\bar{R} < HC \equiv \bar{C} < RCO\bar{O} < \bar{N}H_2$

(d) $RCO\bar{O} < \bar{N}H_2 < HC \equiv \bar{C} < \bar{R}$

(d) $RCO\bar{O} < HC \equiv \bar{C} < \bar{N}H_2 < \bar{R}$

52. Arrange the carbanions, $(CH_3)_3\bar{C}, \bar{C}Cl_3$,$(CH_3)_2\bar{C}H$, $C_6H_5\bar{C}H_2$ in order of their decreasing stability. **[AIEEE 2009]**

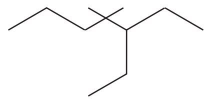
(a) $C_6H_5\bar{C}H_2 > \bar{C}Cl_3 > (CH_3)_3\bar{C} > (CH_3)_2\bar{C}H$
(b) $(CH_3)_2\bar{C}H > \bar{C}Cl_3 > C_6H_5\bar{C}H_2 > (CH_3)_3\bar{C}$
(c) $\bar{C}Cl_3 > C_6H_5\bar{C}H_2 > (CH_3)_2\bar{C}H > (CH_3)_3\bar{C}$
(d) $(CH_3)_3\bar{C} > \bar{C}Cl_3 > C_6H_5\bar{C}H_2 > (CH_3)_2\bar{C}H$

53. The IUPAC name of *neo*-pentane is **[AIEEE 2009]**

(a) 2-methylbutane (b) 2,2-dimethylpropane
(c) 2-methylpropane (d) 2,2-dimethylbutane

54. The correct decreasing order of priority for the functional groups of organic compounds in the IUPAC system of nomenclature is **[AIEEE 2008]**

(a) —COOH, SO_3H,—$CONH_2$,—CHO
(b) —SO_3H,—COOH,—$CONH_2$,—CHO
(c) —CHO,—COOH,—SO_3H — $CONH_2$
(d) —$CONH_2$, CHO,—SO_3H,—COOH

55. The IUPAC name of  is **[AIEEE 2007]**

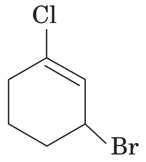
(a) 1, 1-diethyl-2, 2-dimethylpentane
(b) 4, 4-dimethyl-5, 5-diethylpentane
(c) 5, 5-diethyl-4, 4-dimethylpentane
(d) 3-ethyl-4, 4-dimethylheptane

56. Which of the following is the correct order of decreasing S_N2 reactivity? **[AIEEE 2007]**

(X = a halogen)

(a) $RCH_2X > R_3CX > R_2CHX$ (b) $RCH_2X > R_2CHX > R_3CX$
(c) $R_3CX > R_2CHX > RCH_2X$ (d) $R_2CHX > R_3CX > RCH_2X$

57. The IUPAC name of the compound shown below is **[AIEEE 2006]**



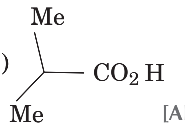
(a) 2-bromo-6-chlorocyclohex-1-ene
(b) 6-bromo-2-chlorocyclohexene
(c) 3-bromo-1-chlorocyclohexene
(d) 1-bromo-3-chlorocyclohexene

58. The increasing order of stability of the following free radicals is **[AIEEE 2006]**

(a) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_2\dot{C}H < (C_6H_5)_3C$
(b) $(C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$
(c) $(C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C} < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$
(d) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H$

59. The correct order of increasing acid strength of the compounds

(*A*) CH_3CO_2H (*B*) $MeOCH_2CO_2H$

(*C*) CF_3CO_2H (*D*) 

[AIEEE 2006]

(a) $B < D < A < C$ (b) $D < A < C < B$
(c) $D < A < B < C$ (d) $A < D < C < B$

60. Due to the presence of an unpaired electron, free radicals are **[AIEEE 2005]**

(a) cations (b) anions
(c) chemically inactive (d) chemically reactive

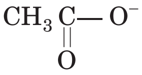
61. Tertiary alkyl halides are practically inert to substitution by S_N2 mechanism because of **[AIEEE 2005]**

(a) steric hindrance (b) inductive effect
(d) instability (d) insolubility

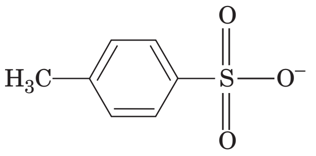
62. Among the following acids which has the lowest pK_a value?

(a) CH_3CH_2COOH (b) $(CH_3)_2CH_2$—COOH
(c) HCOOH (d) CH_3COOH

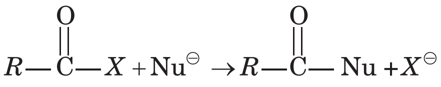
63. The decreasing order of nucleophilicity among the nucleophiles

(*A*) 
$$CH_3\underset{\underset{O}{\|}}{C}—O^-$$
(*B*) CH_3O^-

(*C*) CN^-

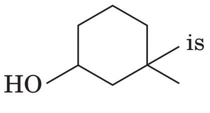
(*D*)  is **[AIEEE 2005]**

(a) *C,B,A,D* (b) *B,C,A,D* (c) *D,C,B,A* (d) *A,B,C,D*

64. The reaction 
$$R—\overset{\overset{O}{\|}}{C}—X + Nu^{\ominus} \rightarrow R—\overset{\overset{O}{\|}}{C}—Nu + X^{\ominus}$$
is fastest when X is **[AIEEE 2005, 2004]**

(a) OCOR (b) OC_2H_5
(c) NH_2 (d) Cl

65. The IUPAC name of the compound **[AIEEE 2004]**



is

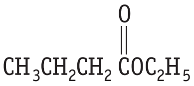
(a) 3, 3-dimethyl-1-hydroxy cyclohexane
(b) 1, 1-dimethyl-3-hydroxy cyclohexane
(c) 3, 3-dimethyl-1-cyclohexanol
(d) 1, 1-dimethyl-3-cyclohexanol

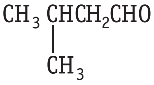
66. Which one of the following dose not have sp^2 hybridised carbon? [AIEEE 2004]
(a) Acetone (b) Acetic acid
(c) Acetonitrile (d) Acetamide

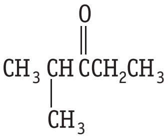
67. The IUPAC name of $CH_3COCH(CH_3)_2$ is [AIEEE 2003]
(a) *iso*-propylmethyl ketone
(b) 2-methyl-3-butanone
(c) 4-methyl *iso*-propyl ketone
(d)3-methyl-2-butanone

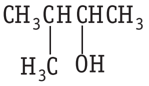
68. In the anion, $HCOO^-$ the two carbon-oxygen bonds are found to be of equal length . What is the reason for it? [AIEEE 2003]
(a) Electronic orbits of carbon atom are hybridised
(b) The C$=$O bond is weaker than the C—O bond
(c) The anion, $HCOO^-$ has two reasonationg structures
(d) The anion is obtained by removal of a proton from the acid molecule

69. Which of the following compounds has incorrect IUPAC nomenclature? [AIEEE 2002]

(a) 
$CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}OC_2H_5$
ethyl butanoate

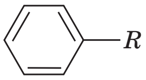
(b) 
$CH_3\underset{CH_3}{\underset{|}{CH}}CH_2CHO$
3-methyl butanal

(c) 
$CH_3\underset{CH_3}{\underset{|}{CH}}\overset{O}{\overset{\|}{C}}CH_2CH_3$
2-methyl-3-pentanone

(d) 
$CH_3\underset{H_3C}{\underset{|}{CH}}\underset{OH}{\underset{|}{CH}}CH_3$
2-methyl-3-butanol

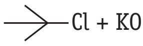
70. Underlined carbon is sp^3 hybridised in [AIEEE 2002]
(a) $CH_3\underline{C}H{=}CH_2$
(b) $CH_3\underline{C}H_2NH_2$
(c) $CH_3\underline{C}ONH_2$
(d) $CH_3CH_2\underline{C}N$

71. In the following benzyl/allyl system

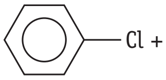
R—CH$=$CH$_2$ or 

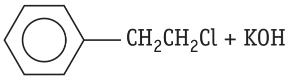
(R is alkyl group)
decreasing order of inductive effect is [AIEEE 2002]
(a) $(CH_3)_3C— > (CH_3)_2CH— > CH_3CH_2—$
(b) $CH_3CH_2— > (CH_3)_2CH— > (CH_3)_3C—$
(c) $(CH_3)_2CH_2— > CH_3CH_2— > (CH_3)_3C—$
(d) $(CH_3)_2C— > CH_3CH_2— > (CH_3)_3CH—$

72. S_N1 reaction is feasible in [AIEEE 2002]

(a)  $+ \text{KOH} \longrightarrow$

(b)  $+ \text{KOH} \longrightarrow$

(c)  $+ \text{KOH} \longrightarrow$

(d)  $+ \text{KOH} \longrightarrow$

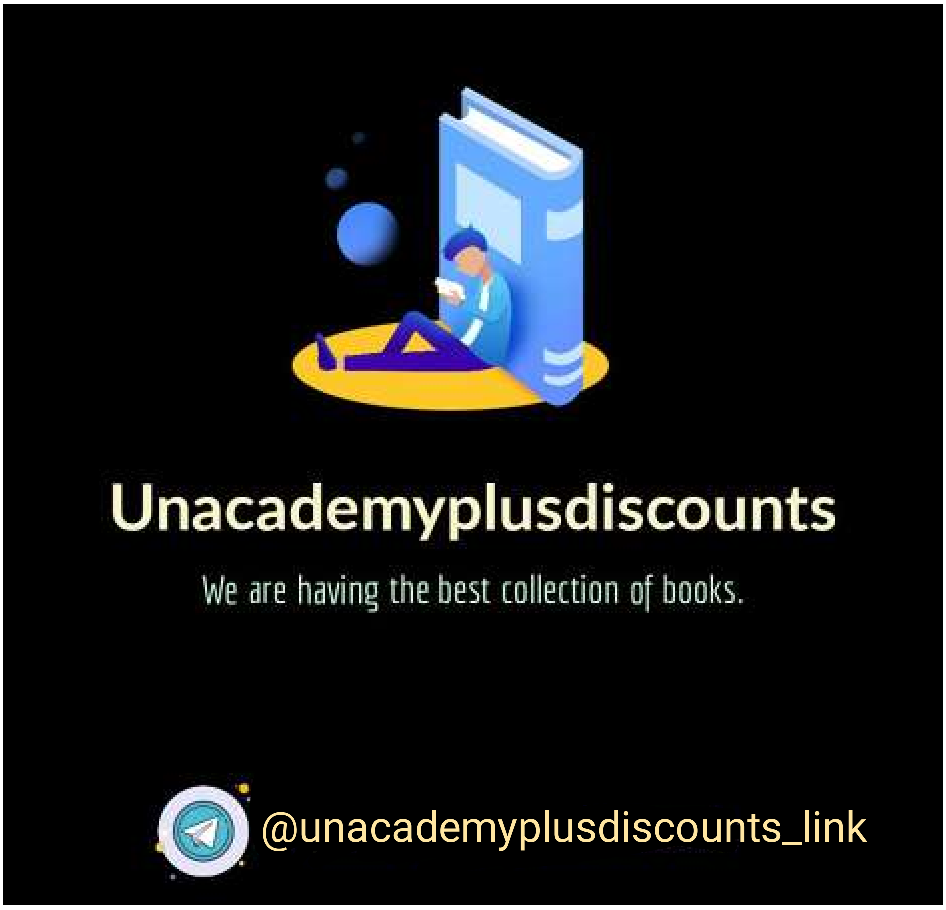
Answers

Round I

1. (c)	**2.** (d)	**3.** (c)	**4.** (b)	**5.** (b)	**6.** (b)	**7.** (b)	**8.** (a)	**9.** (c)	**10.** (b)
11. (c)	**12.** (c)	**13.** (c)	**14.** (c)	**15.** (c)	**16.** (a)	**17.** (d)	**18.** (b)	**19.** (c)	**20.** (d)
21. (a)	**22.** (d)	**23.** (d)	**24.** (c)	**25.** (b)	**26.** (a)	**27.** (c)	**28.** (b)	**29.** (d)	**30.** (d)
31. (b)	**32.** (d)	**33.** (d)	**34.** (b)	**35.** (b)	**36.** (b)	**37.** (b)	**38.** (c)	**39.** (a)	**40.** (a)
41. (a)	**42.** (c)	**43.** (a)	**44.** (c)	**45.** (c)	**46.** (a)	**47.** (d)	**48.** (b)	**49.** (a)	**50.** (c)
51. (a)	**52.** (c)	**53.** (d)	**54.** (d)	**55.** (a)	**56.** (a)	**57.** (b)	**58.** (c)	**59.** (a)	**60.** (a)
61. (b)	**62.** (a)	**63.** (b)	**64.** (b)	**65.** (d)	**66.** (a)	**67.** (b)	**68.** (d)	**69.** (d)	**70.** (a)
71. (b)	**72.** (c)	**73.** (b)	**74.** (c)	**75.** (b)	**76.** (c)	**77.** (b)	**78.** (b)	**79.** (d)	**80.** (d)
81. (b)	**82.** (b)	**83.** (d)	**84.** (c)	**85.** (a)	**86.** (a)	**87.** (c)	**88.** (d)	**89.** (a)	**90.** (b)

Round II

1. (d)	**2.** (a)	**3.** (a)	**4.** (c)	**5.** (c)	**6.** (a)	**7.** (b)	**8.** (a)	**9.** (d)	**10.** (c)
11. (b)	**12.** (d)	**13.** (b)	**14.** (b)	**15.** (c)	**16.** (b)	**17.** (c)	**18.** (c)	**19.** (c)	**20.** (d)
21. (b)	**22.** (c)	**23.** (b)	**24.** (b)	**25.** (b)	**26.** (d)	**27.** (d)	**28.** (c)	**29.** (b)	**30.** (a,b,c)
31. (b,c)	**32.** (a,b)	**33.** (b,c)	**34.** (b,c)	**35.** (c,d)	**36.** (c)	**37.** (d)	**38.** (c)	**39.** (a)	**40.** (d)
41. (c)	**42.** (d)	**43.** (c)	**44.** (b)	**45.** (a)	**46.** (c)	**47.** (b)	**48.** (d)	**49.** (c)	**50.** (b)
51. (d)	**52.** (c)	**53.** (b)	**54.** (a)	**55.** (d)	**56.** (b)	**57.** (c)	**58.** (a)	**59.** (c)	**60.** (d)
61. (a)	**62.** (c)	**63.** (b)	**64.** (d)	**65.** (c)	**66.** (c)	**67.** (d)	**68.** (c)	**69.** (d)	**70.** (b)
71. (a)	**72.** (a)								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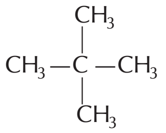
the Guidance

Round I

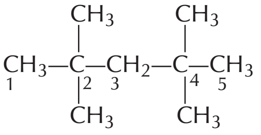
3. 

$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

neo-pentane

The structure shows that all the hydrogen atoms are attached to primary C-atoms hence, these are primary hydrogens.

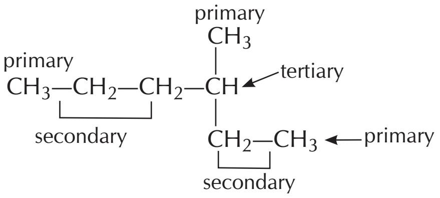
4. Carbocyclic compounds which resemble aliphatic compounds in their properties are called alicyclic compounds.

5. 

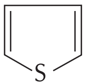
$$\underset{1}{CH_3}-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{\overset{}{C}_2}}-\underset{3}{CH_2}-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C_4}}-\underset{5}{CH_3}$$

2, 2, 4, 4-tetramethyl pentane

There are two carbon atoms, *i.e.,* C-2 and C-4 which are tertiary in nature.

6. 

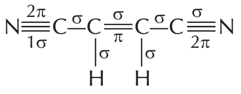
$$CH_3-CH_2-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_2-CH_3}{|}}{CH}}$$

7. 

thiophene

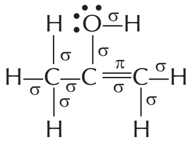
It is a heterocyclic compound as it contains foreign element (element other than C and H) in the cyclic chain.

8. $\underset{sp^2}{\underset{\downarrow}{CH_2}}=\underset{sp^2}{\underset{\downarrow}{CH}}-\underset{sp}{\underset{\downarrow}{C}}\equiv\underset{sp}{\underset{\downarrow}{CH}}$

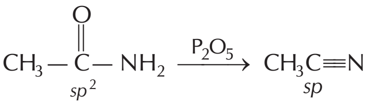
9. 

$$N\underset{1\sigma}{\overset{2\pi}{\equiv}}C\overset{\sigma}{-}\underset{\underset{H}{|\sigma}}{C}\underset{\pi}{\overset{\sigma}{=}}\underset{\underset{H}{|\sigma}}{C}\overset{\sigma}{-}C\underset{2\pi}{\overset{\sigma}{\equiv}}N$$

7 sigma and 5 pi

10. 

enolic form of acetone
9σ bonds, 1π bond, 2 lone pairs

11. 

$$CH_3-\underset{sp^2}{\overset{\overset{O}{\|}}{C}}-NH_2\xrightarrow{P_2O_5}\underset{sp}{CH_3C\equiv N}$$

12. The shape of π electron cloud in acetylene is cylindrical.

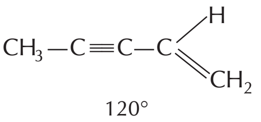
13. Electronegativity depends upon *s*-character and increases with increase in *s*-character. In $CH_3-CH_2-C\equiv\overset{*}{C}H$ the *s*-character of carbon marked with asterisk is 50% (as it is *sp* hybridised). So, it is the most electronegative.

Note In sp^2, *s*-character is 33.3% and in sp^3 it is 25%.

14. Order of bond length.

$$\sigma\text{ bond }(sp^3)>\sigma\text{ bond }(sp^2)>\sigma\text{ bond }(sp)$$

C_2H_6	C_2H_4 Or $C_2H_2Br_2$	C_2H_2

15. 

The C-atoms attached to the triple bond lie in a straight line while the carbon of the CH_2 group is inclined at an angle of 120°. Therefore, only 2 carbon atoms are linearly arranged.

16. Weak base ⟶ strong conjugate acid

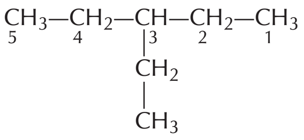
$$\underset{\text{(weakest base)}}{CH\equiv C^-}\longrightarrow\underset{\text{(strongest acid among the given)}}{CH\equiv CH}$$

$$\underset{\text{(strongest base)}}{CH_3-CH_2^-}\longrightarrow\underset{\text{(weakest acid)}}{CH_3CH_3}$$

17. $\underset{sp^3}{CH_3}-\underset{sp^3}{CH_2}-\underset{sp^2}{CH}=\underset{sp}{\overset{\oplus}{C}H}$

Electronegativity of different hybrid and unhybrid orbitals in decreasing order is as follows

$$s>sp>sp^2>sp^3>p$$

18. 

$$\underset{5}{CH_3}-\underset{4}{CH_2}-\underset{\underset{\underset{CH_3}{|}}{\underset{CH_2}{|3}}}{CH}-\underset{2}{CH_2}-\underset{1}{CH_3}$$

3-ethyl pentane

This compound exists.

20. According to IUPAC system, the IUPAC name of a compound is written as single word as far as possible.

21. The choice of principal functional group is made on the basis of the following order

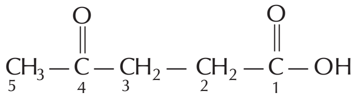
Carboxylic acid > sulphonic acid > anhydride > esters > acid halide > acid amide > nitrile > aldehyde > ketone > alcohol > amine

22. $\underset{6}{CH_3}-\underset{5}{CH_2}-\underset{4}{C}\equiv\underset{3}{C}-\underset{2}{CH}=\underset{1}{CH_2}$

hex-1-en-3-yne

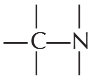
[∵ Double bond is preferred over ≡ bond while naming.]

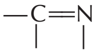
23.

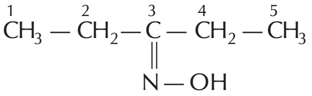


$\underset{5}{CH_3}-\underset{4}{\overset{O}{\overset{\|}{C}}}-\underset{3}{CH_2}-\underset{2}{CH_2}-\underset{1}{\overset{O}{\overset{\|}{C}}}-OH$

4-oxo pentanoic acid

24.  $-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{N}}$ group is called amino

while  $-\underset{|}{C}=\underset{|}{N}$ group is called imino.

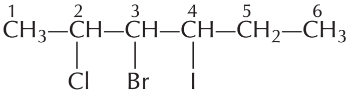


$\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{3}{\underset{\underset{N-OH}{\|}}{C}}-\overset{4}{CH_2}-\overset{5}{CH_3}$

N-hydroxy-3-iminopentane

25. The decreasing order of priority of prefix in numbering the carbon chain of an organic compound is

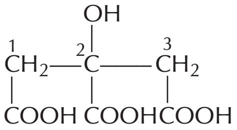
Bromo > Chloro > Iodo.



$\overset{1}{CH_3}-\underset{\underset{Cl}{|}}{\overset{2}{CH}}-\underset{\underset{Br}{|}}{\overset{3}{CH}}-\underset{\underset{I}{|}}{\overset{4}{CH}}-\overset{5}{CH_2}-\overset{6}{CH_3}$

3-bromo-2-chloro-4-iodohexane

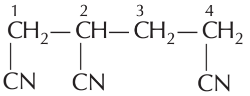
26.



$\underset{\underset{COOH}{|}}{\overset{1}{CH_2}}-\underset{\underset{COOH}{|}}{\overset{\overset{OH}{|}}{\overset{2}{C}}}-\underset{\underset{COOH}{|}}{\overset{3}{CH_2}}$

2-hydroxy propane-1,2,3-tricarboxylic acid

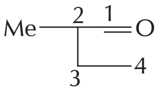
27.



$\underset{\underset{CN}{|}}{\overset{1}{CH_2}}-\underset{\underset{CN}{|}}{\overset{2}{CH}}-\overset{3}{CH_2}-\underset{\underset{CN}{|}}{\overset{4}{CH_2}}$

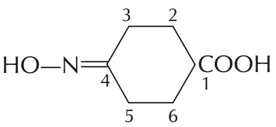
butane-1,2,4-tricarbonitrile

28.



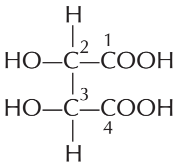
2-methylbutanal

29.



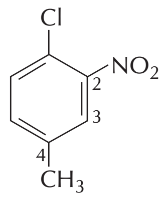
4-(N-hydroxy) imino cyclohexane-1-carboxylic acid

30. Tartaric acid is



2,3-dihydroxybutane-1,4-dioic acid

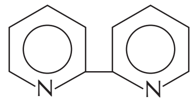
31.



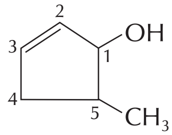
1-chloro-4-methyl-2-nitrobenzene

[Because the order of preference is $Cl > NO_2$]

33. The structure of the compound 2,2′-bipyridine is

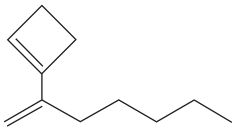


34.



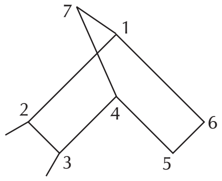
5-methyl cyclopent-2-en-1-ol

35.



2-(1-cyclobutenyl)-1-hexene

36.



2,3-dimethyl bicyclo [2.2.1] heptane

37. During the fission of a covalent bond, species that loses its electron, acquires positive charge and other one with which the electron of previous species gone, acquires a negative charge. Thus,

$$CH_3 \overset{\curvearrowright}{-} Br \longrightarrow \overset{\oplus}{C}H_3 + \overset{\ominus}{Br}$$

38. In heterolysis, the covalent bond is broken in such a way that one species (less electronegative) is deprived of its own electron, while the other species gain both the electrons.

$$CH_3CH_2CH_3 \longrightarrow \overset{\ominus}{C}H_3 + \overset{\oplus}{C}_2H_5$$

because $\overset{\oplus}{C}H_3$ is less stable than $\overset{\oplus}{C}_2H_5$.

39. Electron deficient species or electron acceptor are called electrophiles. For example

$$\dot{C}H_3, \ddot{C}H_2, \ddot{C}X_2 \qquad \text{(where, } X = Cl, Br, I)$$

40. All neutral covalent compound in which central atom has incomplete octet are electrophiles. For example

$$BF_3, BeCl_2, BH_3, ZnCl_2, AlCl_3$$

41. Nucleophiles are those substances which can donate a pair of electrons. They can be neutral or negatively charged. The nucleophilic power depends on the tendency of species to donate the electrons. Due to the presence of $+I$ effect, it increases. Hence, higher the $+I$ effect, higher the nucleophilic power.

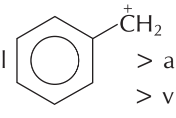
42. CH_3NH_2 and CH_3OH are nucleophiles, CH_3-Cl is an electrophile. But $CH_3-\overset{\delta+}{C}\equiv\overset{\delta-}{N}\colon$ is a nucleophile due to the presence of a lone pair of electrons on N and is an electrophile due to the presence of a partial positive charge on C.

43. Nucleophilicity increases on moving down in a group of the Periodic Table.

$$I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$$

45. $C_6H_5\overset{+}{C}HC_6H_5$ is the most stable since the positive charge can be delocalise on both the phenyl rings.

47. It is with maximum conjugative structures (or resonating structures) among them.

48. Benzyl 

$>$ allyl $CH_2{=}CH{-}\overset{+}{C}H_2 >$ methyl CH_3 $>$ vinyl $CH_2{=}\overset{+}{C}H$

This order is based on conjugative and hyperconjugative structures.

49. Stability of alkyl carbanion $\propto \dfrac{1}{\text{magnitude of negative charge}}$

and magnitude of negative charge $\propto +I$ power of the group. Hence, acetylenic carbanion is more stable than vinylic carbanion which is more stable than alkyl carbanion.

50. $-NO_2$ group shows $-M$ effect while CH_3O- group shows $+M$ effect ($-M$ effect stabilises an anion).

51. Stability of a carbanion increases in the presence of electron withdrawing group but decreases in the presence of electron releasing group.

$O_2N-CH_2-CH_2O^-$ is expected to be more stable than $CH_3-CH_2O^-$ because $-NO_2$ group has $-I$ effect, this leads to the dispersal of negative charge. On the other hand, $-CH_3$ group has $+I$ effect, this leads to the intensification of the negative charge. Dispersal of the charge leads to the stability of ion while intensification of negative charge leads to the unstability of ion.

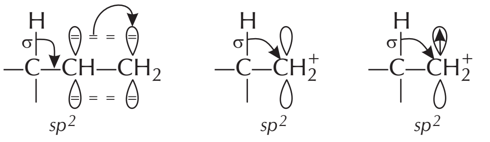
$$\underset{\text{more stable}}{O_2N\leftarrow CH_2\leftarrow CH_2\leftarrow O^-} \qquad \underset{\text{less stable}}{CH_3\rightarrow CH_2\rightarrow O^-}$$

53. The order of stability of carbanion is 1° > 2° > 3°. Moreover, III is resonance stabilised and IV also exists in two resonating forms. Thus, the order of stability is III > IV > I > II.

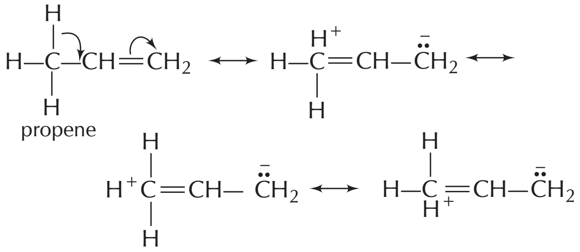
54. Stability of carbanions increase with increase in *s*-character of hybrid orbitals of carbon bearing charge therefore, the order is $sp^3 < sp^2 < sp$.

56. Cl is more electronegative than Br thus, $C-Cl$ bond is more polar and hence greatest positive charge is expected in $\overset{*}{C}H_3CH_2-Cl$.

57. Hyperconjugation is one kind of delocalisation of σ(C—H) bonded electron to unshared *p*-orbital.



58. Due to hyperconjugation, alkyl groups act as electron donors when attached to a π-system as shown below.



59. $-I$ power of groups in decreasing order with respect to the reference H is.

$$-NO_2 > -CHO > -COOR > -F > -Cl$$
$$> -Br > -I > -OH > -OR > -NH_2.$$

60. Presence of —I showing group like —Cl increases the acidic character of carboxylic acids and the acidity reduces with increase in the distance between —COOH and —I showing group.

61. In gas phase, tertiary amines are more basic than secondary amines which are more basic than ammonia.

$-I$ group present on central atom decreases electron density, hence decreases basicity. Thus, the correct order is

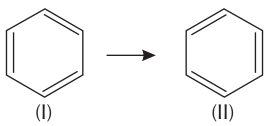
$$CH_3NH_2 > NH_3 > NF_3$$

62. As the number of hyperconjugative structures increases, stability of alkenes increases. Thus, the correct order is I > II > IV > III > V

63. Electromeric effect implies complete transfer of π-electrons in the presence of a reagent. Since, simple ethers do not contain a multiple bond, therefore, they do not show electromeric effect.

64. Stability of carbanion is not governed by hyperconjugation. Its stability depends on the $+I$ or $-I$ group.

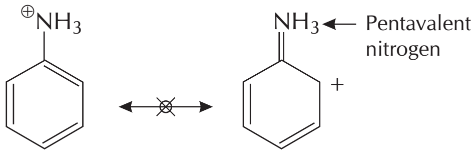
65. Delocalised electrons are present in benzene, 1,3-butadiene and 1,3,5-hexatriene.



(I) (II)

66. Benzene is the most stable and we know that resonance energy is a direct measure of the stability of a molecule.

67. If positive charge is present on nitrogen then positive charge will not be in conjugation to the ring because in this case nitrogen will become pentavalent.



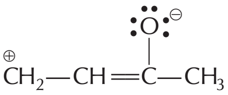
68. Due to –*R* effect of —CHO group, oxygen carries –δ charge while the terminal carbon carries +δ, *i.e.,*

$$\overset{+\delta}{C}H_2{=}CH{-}CH{=}\overset{-\delta}{O}$$

69. In the given compound four π-electrons of double bond and 1 lone pair on N atom leads to delocalisation of six electrons.

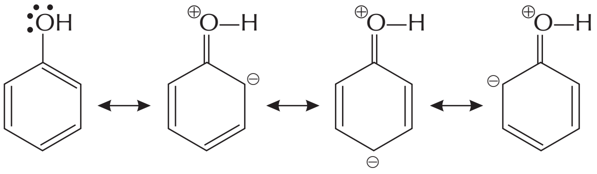
70. Two positive charges present at the adjacent place, elevates the energy, thus lowers the stability most.

71. The most stable one is that in which the positive and negative charges reside on the most electropositive and most electronegative atoms of the species respectively like



$$\overset{\oplus}{C}H_2{-}CH{=}C(\ddot{O}^{\ominus}){-}CH_3$$

72. The oxygen atom in phenol has more dominating resonance effect than inductive effect. Increase in charge separation decreases the stability of a resonating structure.



(I) (II) (III) (IV)

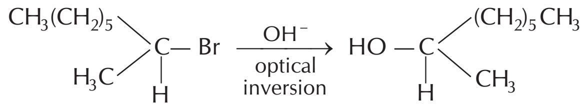
Stability of resonating structures in decreasing order will be

$$I > II \equiv IV > III$$

74. $H_3C{-}HC{=}CH_2 + H^+ \longrightarrow H_3C{-}HC^+{-}CH_3$

2° carbocation
(more stable)
+
$CH_3CH_2CH_2^+$
1° carbocation
(less stable)

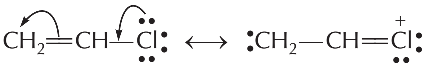
75.



$$CH_3(CH_2)_5{-}C(H_3C)(H){-}Br \xrightarrow[\text{optical inversion}]{OH^-} HO{-}C(H)((CH_2)_5CH_3)(CH_3)$$

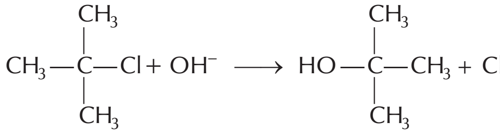
In this reaction, inversion takes place. Hence, it is an example of S_N2 reaction. In this mechanism the attack of OH^- ions take place from the back side while the Br^- ion leaves from the front side.

76. Vinyl chloride is least reactive for S_N reaction due to resonance stabilisation of C—Cl bond.



$$CH_2{=}CH{-}\ddot{\underset{..}{Cl}}{:} \longleftrightarrow {:}\bar{C}H_2{-}CH{=}\overset{+}{Cl}{:}$$

77.



$$CH_3{-}C(CH_3)_2{-}Cl + OH^- \longrightarrow HO{-}C(CH_3)_2{-}CH_3 + Cl^-$$

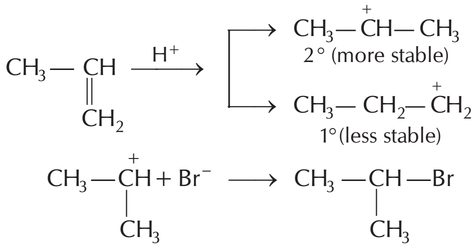
Rate ∝ [*t* - butyl chloride]

Tertiary butyl carbocation is first formed which is more stable.

78. HBr is a better source of proton. It gives H^+ and Br^- ions.

$$HBr \longrightarrow H^+ + Br^-$$

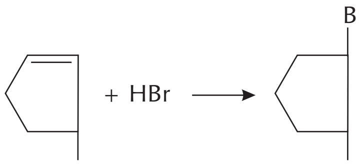
Thus, H^+ attacks the π-bond of propene to form carbonium ion as



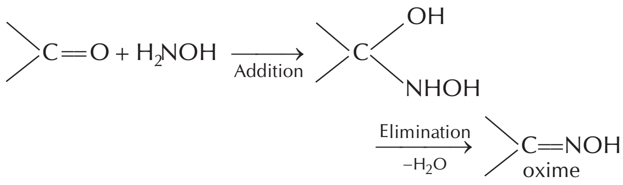
(major product)

79. With the increasing basicity of the added base, the rates of the elimination reactions have been found to increase. Thus, RO^- is most reactive.

81. A hydrogen halide containing a highly polar H—*X* bond can easily lose $\overset{\oplus}{H}$ to the pi bond of an alkene. The result of the attack of $H^{\oplus}$ is an intermediate carbocation, which quickly undergoes reaction with the negative halide ion (X^-) to yield an alkyl halide.

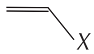


83. The reaction occurs as

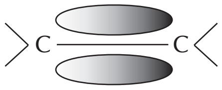


$$>C{=}O + H_2NOH \xrightarrow{\text{Addition}} >C(OH)(NHOH) \xrightarrow[-H_2O]{\text{Elimination}} >C{=}NOH$$

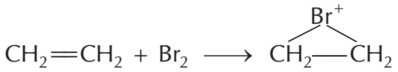
oxime

84. Primary and secondary alkyl halides give S_N2 reaction. Substrates that give stable carbocation generally undergo S_N1 reaction. Vinyl carbocation is least stable so  does not give this reaction.

85. Such a condition is seen when π-bond is formed between similar atoms *i.e.,*



86. Addition of Br_2 on ethene follow electrophilic addition.

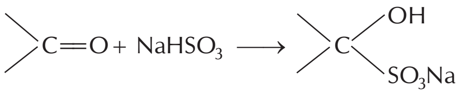


$CH_2{=}CH_2 + Br_2 \longrightarrow \overset{Br^+}{CH_2-CH_2}$

Intermediate is cyclic bromonium ion.

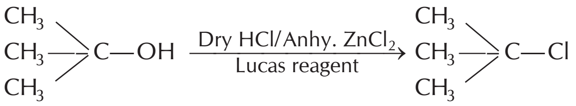
87. (a) It is Diels Alder's reaction (cyclo addition).

(b)



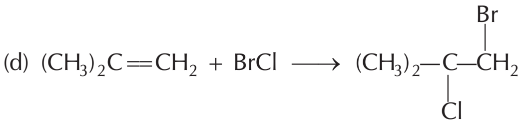
It is a nucleophilic addition reaction.

(c)



It is a nucleophilic substitution reaction.

(d)

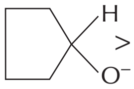


$(CH_3)_2C{=}CH_2 + BrCl \longrightarrow (CH_3)_2-\overset{Br}{\underset{Cl}{C}}-CH_2$

It is an electrophilic addition reaction.

88. The elimination takes place according to Saytzeff rule. The most substituted alkene (butene-2) is called Saytzeff product whereas less substituted alkene (butene-1) is called Hofmann product.

89. Epoxide is ambidentate substrate for nucleophilic substitution reactions. In protonated epoxide carbon-2 and carbon-3 both aquire some positive charge due to the highly electronegative atom.

$MeO^- > MeCH_2O^- >$  $> Me_2CHO^- > Me_3CO^-$

90. (a) Nucleophilic substitution reaction

(b) Electrophilic addition reaction, involve attack of electrophile

(c) β-elimination reaction

(d) Nucleophilic substitution reaction with rearrangement.

Round II

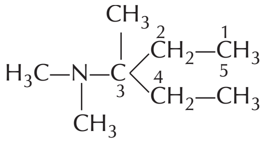
1. (I) $\overset{sp^3}{C}H_3-\overset{sp^3}{C}H_2-\overset{sp^3}{C}H_2-\overset{sp^3}{C}H_3$ only sp^3 hybridised carbon

(II) $\overset{sp^3}{C}H_2-\overset{sp^2}{C}H=\overset{sp^2}{C}H-\overset{sp^3}{C}H_3$ both sp^2 and sp^3 hybridised carbon.

(III) $\overset{sp^2}{C}H_2=\overset{sp^2}{C}H-\overset{sp^2}{C}H=\overset{sp^2}{C}H_2$ only sp^2 hybridised carbon.

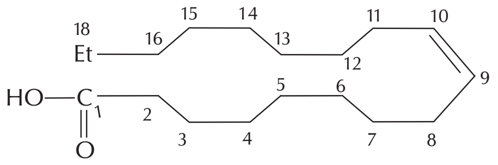
(IV) $H-\overset{sp}{C}\equiv\overset{sp}{C}-H$ only *sp*-hybridised carbon.

2.



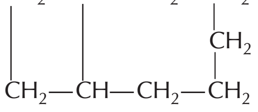
N,N-dimethyl-3-methylpentan-3-amine

3.



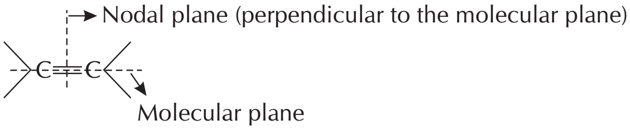
octa dec-9-enoic acid

4.

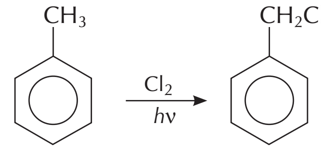


This compound contains 9 carbon atoms thus, corresponding alkane is nonane. Three bridges contain 5, 2 and 0 carbon atoms respectively. Therefore, the name of the compound is bicyclo [5.2.0] nonane.

5.

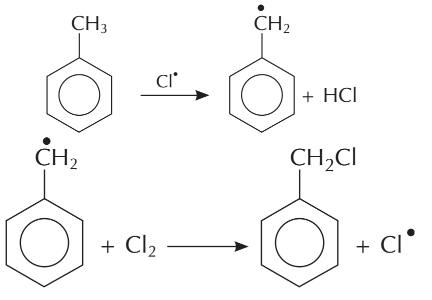


6.



This reaction proceeds through free radical substitution.

$$Cl_2 \xrightarrow{h\nu} 2Cl^\bullet$$

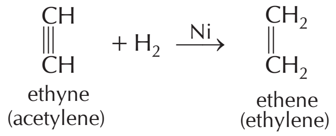


7.

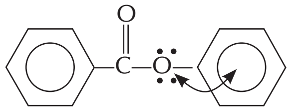
Species	Valence electrons	Magnetic behaviour
Carbonium ion	6	Diamagnetic
Free radical	7	Paramagnetic
Carbene	6	Diamagnetic
Nitrene	6	Diamagnetic

8. ϕ is phenyl group, and stability is based on the number of conjugative structures. Thus, the correct order is 1 > 4 > 2 > 3

9. Formation of ethylene from acetylene is an example of addition reaction.



10. Second ring is in conjugation with lone pair of oxygen, thus electrophilic substitution occur at *o*/*p* position of second ring.

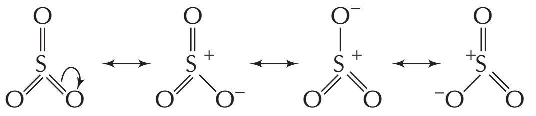

conjugation

11. In S_N2 reactions, the nucleophile attaches itself from the direction opposite to that of the nucleophile already present in the second step, the previous nucleophile is removed and a single stereoisomer is obtained.

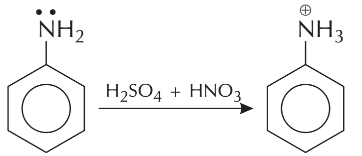
12. $\overset{\oplus}{C}H_3$ is the most stable species because the replacement of H by Br increases positive charge on carbon atom and destabilises the species.

$\overset{\ominus}{C}Cl_3$ is the most stable species because on replacing H by Cl, negative charge on carbon is reduced and species is stabilised.

13. In SO_3, three highly electronegative oxygen atoms are attached to sulphur atom. It makes sulphur atom electron deficient. Further, due to resonance, sulphur acquires positive charge. Both these factors make SO_3 an electrophile.

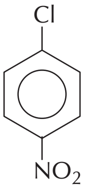


14. On direct nitration of aniline, lone pair of electrons present at nitrogen atom will accept proton from the nitrating mixture to give anilinium ion which is *meta*-directing.



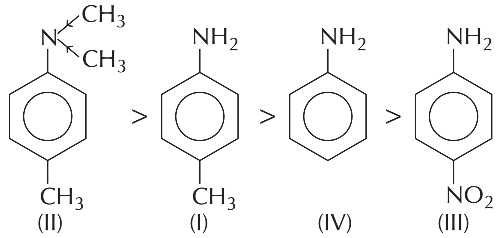
anilinium ion

15. Nucleophile always attacks on electron deficient site. Presence of electron withdrawing groups such as NO_2, CHO etc., decreases the electron density on benzene nucleus, hence such groups activate the ring towards nucleophilic attack. While presence of electron releasing groups such as *R* or O*R* increases the electron density, thus deactivates the nucleus towards nucleophilic attack.

NO_2 group activates the ring more than Cl towards nucleophilic attack, hence  reacts readily with nucleophile.

16. Free radical chain reaction is initiated by UV light. It proceeds in three main steps like initiation, propagation and termination. It gives major product derived from most stable free radical.

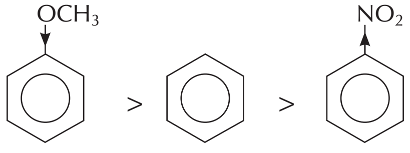
17.



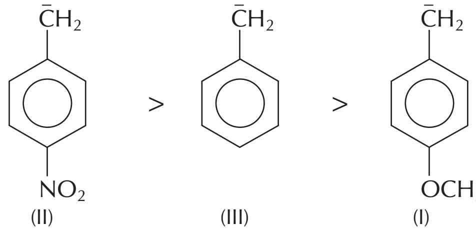
order of basicity

The reason for the above order of basicity is the presence of electron releasing —CH_3 group in II and I which facilitates the donation of lone pair by increasing electron density over N atom.

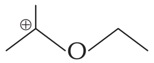
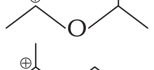
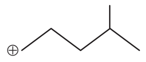
18. Methoxy group is electron releasing group so it increases electron density at benzene nucleus while —NO_2 group is electron withdrawing group, so it decreases the electron density of benzene nucleus. Thus, the order of reaction with electrophilic reagent is

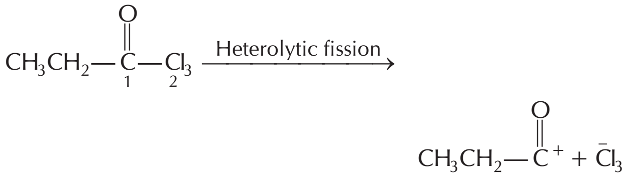


19. —NO_2 group shows –*M* effect while CH_3O— group shows + *M* effect. (–*M* effect stabilises the anion).
Hence, the order of stability is

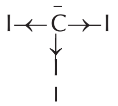


20. The correct order is I > III > II > IV

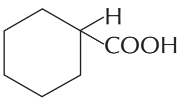
	+ *M* effect, hyperconjugation (6Hs) and + *I* effect (2–Me groups)
	+ *M* effect, hyperconjugation (3Hs) and +*I* effect (1–Me group)
 (2° carbocation)	Hyperconjugation (5Hs) and + *I* effect
 (1° carbocation)	Hyperconjugation (2Hs) and + *I* effect

21. 

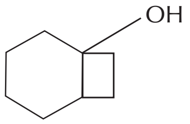
$$CH_3CH_2-\overset{\overset{O}{\|}}{\underset{1}{C}}-\underset{2}{C}I_3 \xrightarrow{\text{Heterolytic fission}} CH_3CH_2-\overset{\overset{O}{\|}}{C}{}^{+} + \bar{C}I_3$$

$\bar{C}I_3$ is the most stable carbanion because of –*I* effect of I which disperses negative charge on $\bar{C}$ of  $I \leftarrow \underset{\underset{I}{\downarrow}}{\bar{C}} \rightarrow I$

22. (A) $CH_3-CH(CH_3)-CH_2-CH(CH_3)-CH(CH_3)-CH_3$
2,3,5-trimethyl hexane

(B) 

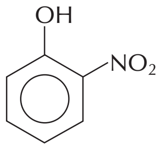
cyclohexane carboxylic acid

(C) 

bicyclo [4.2.0] octan-1-ol

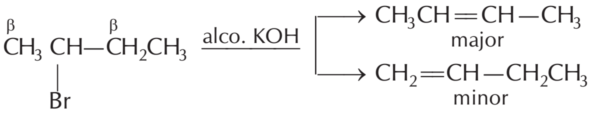
(D) $(CH_3)_3Bi$
trimethyl bismuthane

23. *Ortho* nitrophenol is the most acidic because electron withdrawing group increases acidic character due to –*I* effect of NO_2 group.



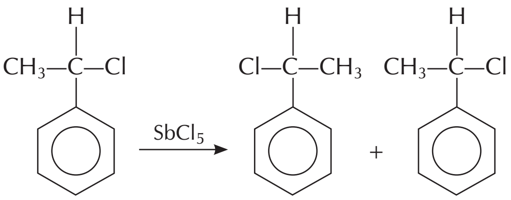
o-nitrophenol

24. An organic reaction intermediate (neutral species) having divalent carbon atom with six valence electrons, out of which two are present in same orbital with opposite spin is called singlet carbene.

25. 

$$\overset{\beta}{C}H_3\,\underset{\underset{Br}{|}}{C}H-\overset{\beta}{C}H_2CH_3 \xrightarrow{\text{alco. KOH}} \begin{cases} \underset{\text{major}}{CH_3CH=CH-CH_3} \\ \underset{\text{minor}}{CH_2=CH-CH_2CH_3} \end{cases}$$

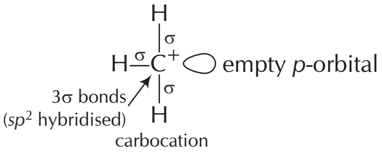
This reaction is governed by Saytzeff's rule. According to this rule, the elimination of β-hydrogen atom take place from the carbon having the lesser number of H-atoms or in other words a stable alkene is formed. (More substituted alkene is more stable.)

26. 

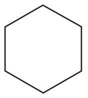
The solution of D(+)-2-chloro-2-phenyl ethane in toluene racemises slowly in the presence of $SbCl_5$ due to the formation of carbocation.

27. S_N2 reaction does not involve ion formation, these infact involve formation of transition state.

28. *R*COOH does not form oxime with H_2NOH as —OH group reduces the polarity of $>C=O$ bond or reduces the positive charge on carbonyl carbon.

29. 

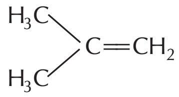
Nucleophile being electron rich can supply a pair of electrons whereas electrophile being electron deficient can receive a pair of electrons. Hyperconjugation is found when C—H bonds are in conjugation with carbon having empty *p* orbital.

 and $CH_3CH_2CH_2CH_2CH=CH_2$

Both have C_6H_{12} formula but different structures, so these are isomers.

$\overset{sp}{C}H\equiv\overset{sp}{C}H$ (Ethyne) exhibits *sp* hybridisation.

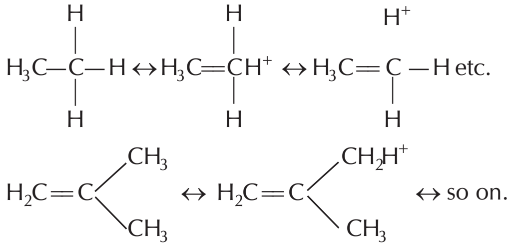
30. Only *iso*-butylene is not a cyclic compound.



31. Electron dificient species like

$AlCl_3, SO_3, NO_2^+, CH_3^+, CH_3-\overset{+}{C}=O$ are called electrophiles.

32. Conditions for hyperconjugation.



$$H_3C-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H \leftrightarrow H_3C=\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}H^+ \leftrightarrow H_3C=\underset{\underset{H}{|}}{\overset{H^+}{C}}-H \text{ etc.}$$

6(hyperconjugative structures)

33. The low reactivity of a halogen bonded to an unsaturated carbon is due to the +*M* effect of the halogen. The C—Br bond in vinyl bromide has a partial double bond character due to the + *M* effect of bromine, resulting in low reactivity.

34. Singlet carbene and nitromethyl carbanion are planar species since the central carbon atom in each of them is sp^2-hybridised.

Triphenylmethyl carbocation is also in sp^2 hybrid state but it is propeller-shaped due to the repulsion between *ortho* hydrogens of the rings. However, in *iso*-propyl carbanion, C is sp^3-hybridised.

35. Charge separation structures are less important than those in which the charge is delocalised, because there is electrostatic attraction between unlike charges.

36. —COOH is the principal functional group while —CN is the substituent group.

37. In this molecule, the central C atom is *sp* hybridised.

$$H_2C\overset{\sigma}{=}C\overset{\sigma}{=}CH_2$$

2σ bonds (*sp* hybridised)

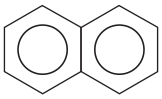
38. The stability of carbocation is explained on the basis of hyperconjugation and inductive effect hence, the stability order of carbocation is $3° > 2° > 1° >$ methyl carbocation.

39. Both the structures are resonating structures of formic acid. In $H—\overset{O^{\ominus}}{\overset{|}{C}}=\overset{+}{O}H$ negative charge is on oxygen (which is more electronegative) but in $H—\underset{\ominus}{\overset{O^{\oplus}}{\overset{|}{C}}}—\ddot{\underset{\cdot\cdot}{O}}—H$ negative charge is on carbon (which is less electronegative) therefore (I) will be more stable than the (II).

40. Energy of resonance hybrid is less than that of the canonical forms. It cannot be represented by a single structure.

41. Toluene shows resonance due to delocalisation of π-electrons.

42. Compounds containing two or more fused benzene rings are called polynuclear aromatic hydrocarbons. *e.g.*, naphthalene



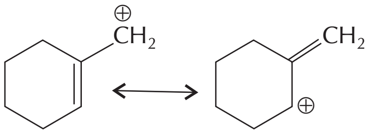
43. Due to resonance, all C—C bond distances in benzene are equal.

44. Possible structure for the given ion are

$$\underset{\text{I}}{CH_3—O—\overset{\oplus}{C}H_2} \quad \underset{\text{II}}{CH_3—\underset{\cdot\cdot}{\overset{\oplus}{O}}=CH_2}$$

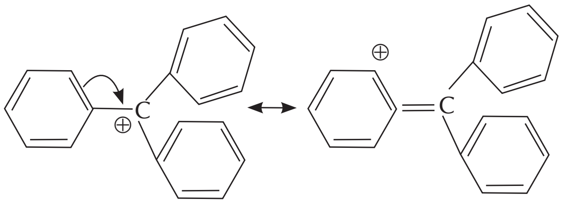
Structure II is more stable because every atom has complete octet.

45. Structure I is more stable due to resonance. (See resonance structure '*A*' and '*B*'). No resonance is possible in structure II.



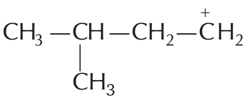
(*A*) (*B*)

46. Stabilised due to nine possible canonical structures.



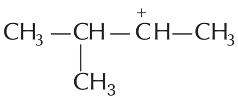
⟷ Other canonical structures

47. Four possible carbocations are



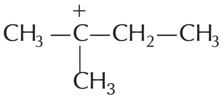
$CH_3—\underset{CH_3}{\underset{|}{CH}}—CH_2—\overset{+}{C}H_2$

(I)



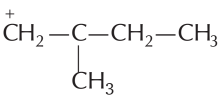
$CH_3—\underset{CH_3}{\underset{|}{CH}}—\overset{+}{C}H—CH_3$

(II)



$CH_3—\underset{CH_3}{\underset{|}{\overset{+}{C}}}—CH_2—CH_3$

(III)



$\overset{+}{C}H_2—\underset{CH_3}{\underset{|}{C}}—CH_2—CH_3$

(IV)

Order of increasing stability I < IV < II < III

48. Strong –*I* group if present on α-carbon stabilises the transition state of the S_N2 reaction. Thus, substrate having carbonyl group on β-carbon is the excellant substrate for S_N2 reaction.

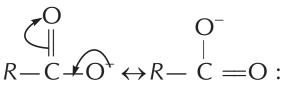
49. Rate of nucleophilic substitution reaction is directly proportional to the basicity. Thus, rate is maximum when Nu^- is RO^-.

50. Nucleophilic strength increases down a column of the Periodic Table (in solvents that can have hydrogen bonds, such as water, alcohols, thio alcohols).

Nucleophilic strength $RO^- < RS^-$

Base strength $RO^{\ominus} > RS^-$

Thus, $RS^{\ominus}$ is more nucleophilic but less basic than RO^-.

51. 

$R—\overset{O}{\overset{\|}{C}}—O^- \leftrightarrow R—\overset{O^-}{\overset{|}{C}}=O$: In carboxylate ion, the negative charge is present on oxygen, a more electronegative element here, thus it is resonance stabilised.

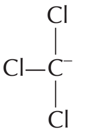
$HC\equiv C^-$: Carbon is *sp* hybridised so its electronegativity is increased and is higher relative to the nitrogen.

$\overset{-}{N}H_2$: Nitrogen is more electronegative than sp^3 hybridised C-atom. From the above discussion, it is clear that the order of the stability of conjugated bases is as

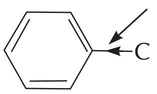
$RCOO^- > HC\equiv C^- > \overset{-}{N}H_2 > R^-$

and higher is the stability of conjugated bases, lower will be basic character. Hence, the order of basic character is as

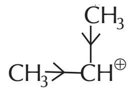
$RCOO^- < HC\equiv C^- < \overset{-}{N}H_2 < R^-$

52. 

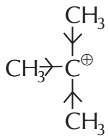
it involves $p\pi$-$d\pi$ back bonding



– *M* effect and
– *I* effect of Ph group

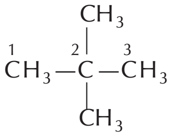


+I effect is exerted by two —CH_3 groups



+I effect is exerted by three —CH_3 groups

53. The structure *neo*-pentane is



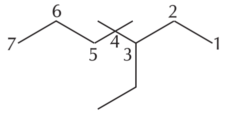
$$\overset{1}{C}H_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{\overset{2}{C}}}-\overset{3}{C}H_3$$

IUPAC name : 2,2-dimethyl propane

54. The correct decreasing order of priority for the functional groups of organic compounds in the IUPAC system is

$$—COOH > —SO_3H > —COOR > COCl > —CONH_2 > —CN > —CHO$$

55.

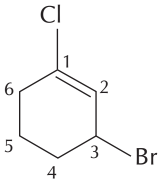


3-ethyl-4, 4-dimethylheptane

56. S_N2 reactions are greatly controlled by steric factor. $\underset{1°}{R—CH_2—X}, \underset{2°}{R_2CH—X}, \underset{3°}{R_3C—X}$,

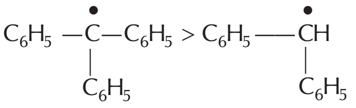
S_N2 reactivity decreases as bulkyness of alkyl group increases.

57.



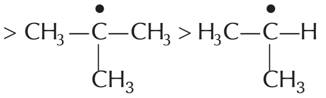
Unsaturation (double bond) is given priority over halogen. So, the correct IUPAC name is 3-bromo-1-chlorocyclohexene.

58. Order of stability of given free radicals is



$$C_6H_5-\underset{\underset{C_6H_5}{|}}{\dot{C}}-C_6H_5 > C_6H_5-\underset{\underset{C_6H_5}{|}}{\dot{C}H}$$

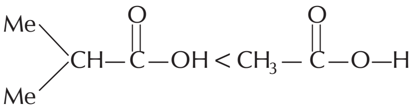
Highly stable by delocalisation



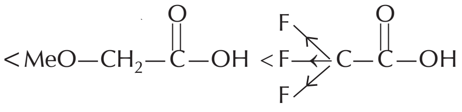
$$> CH_3-\underset{\underset{CH_3}{|}}{\dot{C}}-CH_3 > H_3C-\underset{\underset{CH_3}{|}}{\dot{C}}-H$$

9-hyperconjugative hydrogens and + I effect

59.



$$\begin{matrix}Me\\Me\end{matrix}>CH-\overset{\overset{O}{\|}}{C}-OH < CH_3-\overset{\overset{O}{\|}}{C}-O-H$$



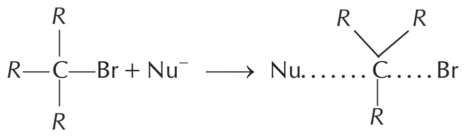
$$< MeO-CH_2-\overset{\overset{O}{\|}}{C}-OH < F_3C-\overset{\overset{O}{\|}}{C}-OH$$

–I effect increases acidity.
+ I effect decreases acidity.
–CF_3 exerting more –I effect than MeO—
Me_2CH— exerting more +I effect than —CH_3.

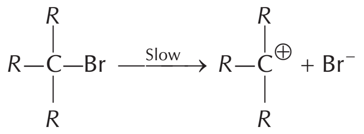
60. Free radicals have unpaired electrons, so are neutral and reactive.

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3-CH_3,$$

61. In S_N2 reaction, nucleophile and alkyl halide react in one step.



Thus, tertiary carbon is under steric hindrance, hence reaction does not take place until (C—Br) bond breaks.



which is an S_N1 reaction.

62. Out of the given acids, strongest is HCOOH. (highest K_a value)

Since, $pK_a = -\log K_a$

Thus, lowest pK_a is of HCOOH.

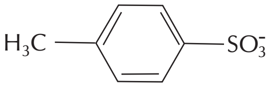
63. If acid is weak, its conjugate base (nucleophile) is strong and *vice-versa*.

(A) $CH_3-\overset{\overset{O}{\|}}{C}-O^-$ is a conjugate base of $CH_3-\overset{\overset{O}{\|}}{C}OH$ (I)

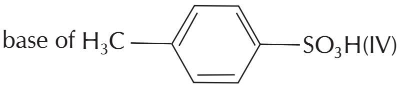
(B) CH_3O^- is conjugate base of CH_3OH (II)

(C) CN^- is a conjugate base of HCN (III)

(D)



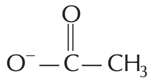
$H_3C-C_6H_4-SO_3^-$ is a conjugate base of



$H_3C-C_6H_4-SO_3H$ (IV)

Thus, order of acidic nature is D > A > C > B and of nucleophilicity is B > C > A > D.

64. Cl^- is the best leaving group as it is the weakest nucleophile out of NH_2^-, Cl^-, $O^-—C_2H_5$ and

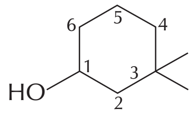


$O^- - \overset{\overset{O}{\|}}{C} - CH_3$

Note If acid HX is weak, its conjugate base X^- is strong and *vice-versa*.

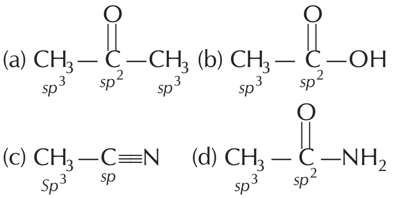
$$NH_3 < C_2H_5OH < CH_3COOH < HCl$$
$$\xrightarrow{\text{Acidic strength increases}}$$
$$NH_2^- > C_2H_5O^- > CH_3COO^- > Cl^-$$
$$\xleftarrow[\text{Basic strength of conjugate base increases}]{}$$

65.



Carbon with —OH group is given C_1, thus it is 3,3-dimethyl-1-cyclohexanol.

66.

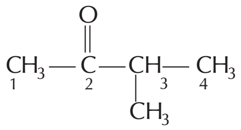


(a) $\underset{sp^3}{CH_3}-\underset{sp^2}{\overset{O}{\overset{||}{C}}}-\underset{sp^3}{CH_3}$ (b) $\underset{sp^3}{CH_3}-\underset{sp^2}{\overset{O}{\overset{||}{C}}}-OH$

(c) $\underset{Sp^3}{CH_3}-\underset{sp}{C}\equiv N$ (d) $\underset{sp^3}{CH_3}-\underset{sp^2}{\overset{O}{\overset{||}{C}}}-NH_2$

Acetonitrile does not contain sp^2-hybridised carbon.

67.

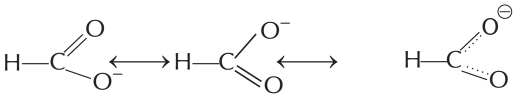


$\underset{1}{CH_3}-\underset{2}{\overset{O}{\overset{||}{C}}}-\underset{\underset{CH_3}{|}}{\overset{}{CH}}_{3}-\underset{4}{CH_3}$

3-methyl butan-2-one
or 3-methyl-2-butanone

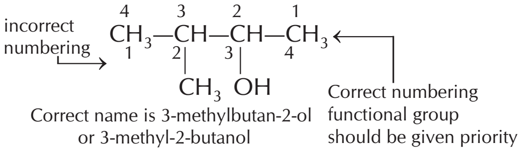
keto ($-\overset{O}{\overset{||}{C}}-$) functional group is given priority.

68.



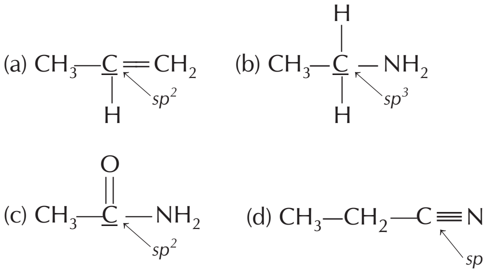
Resonating (canonical) structures of formate ion

69.



Correct name is 3-methylbutan-2-ol or 3-methyl-2-butanol

70.



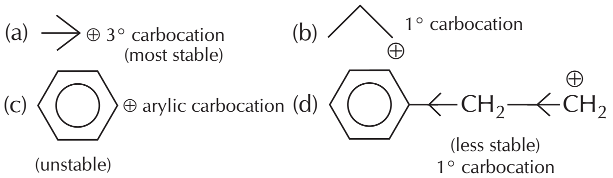
(a) $CH_3-\underset{\underset{H}{|}}{\underline{C}}=CH_2$ sp^2 (b) $CH_3-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{\underline{C}}}-NH_2$ sp^3

(c) $CH_3-\overset{\overset{O}{||}}{\underline{C}}-NH_2$ sp^2 (d) $CH_3-CH_2-C\equiv N$ sp

71. When R is attached to vinylic (≈ arylic) system, positive inductive effect occurs in the following order

$-O^{-} > -COO^{-} > (CH_3)_3C- > (CH_3)_2CH- > CH_3CH_2- > CH_3-$

72. S_N1 (unimolecular nucleophilic substitution) reaction is favoured with stability of carbocation.



14 Isomerism in Organic Compounds

JEE Main MILESTONE

- Isomerism
- Chain or Nuclear Isomerism
- Position Isomerism
- Functional Isomerism
- Metamerism
- Ring Chain Isomerism
- Geometrical Isomerism
- Optical Isomerism
- Conformations or Conformers

14.1 Isomerism

Compounds having the same molecular formula but differ in structural formula, properties and spatial arrangement are called **isomers** and the phenomenon is called **isomerism.**

Types of Isomerism

Isomerism can be of the following two types

(i) Structural isomerism (ii) Stereo isomerism

The isomers differ in properties due to different modes of combinations or arrangement of atoms within a molecule.

The relevance of isomerism may be described by assuming that atoms are arranged in a specific manner in a molecule and there is a different arrangement of each isomer.

Structural Isomerism

When the isomerism is due to difference in the sequence (connectivity) of atoms within the molecules (without any reference to space), the phenomenon is called **structural isomerism.** In other words, the structural isomers are the compounds which have same molecular formula but different structural formulae, hence different properties. The structural isomerism is also called **constitutional isomerism** and categorised to

(i) Chain isomerism
(ii) Position isomerism
(iii) Functional isomerism
(iv) Metamerism
(v) Tautomerism
(vi) Ring-chain isomerism
(vii) Isotopic isomerism.

Tautomerism and ring-chain isomerism are considered as the specialised sub-types of functional isomerism.

Stereo Isomerism

When the isomerism is caused by different arrangement of atoms or groups in space, *i.e.,* 3D-arrangement, the phenomenon is called **stereo isomerism.** In other words, the stereo isomerism is shown by those compounds which have the same structural formula (alongwith same molecular formula) but differ in configuration (the term configuration refers to three dimensional arrangement of atoms that characterise a particular compound). That's why this isomerism is also called **configurational isomerism** and can be categorised to

(i) Geometrical or *cis-trans* isomerism,

(ii) Optical isomerism

Caution Point *Neither resonance forms nor conformations constitute isomers.*

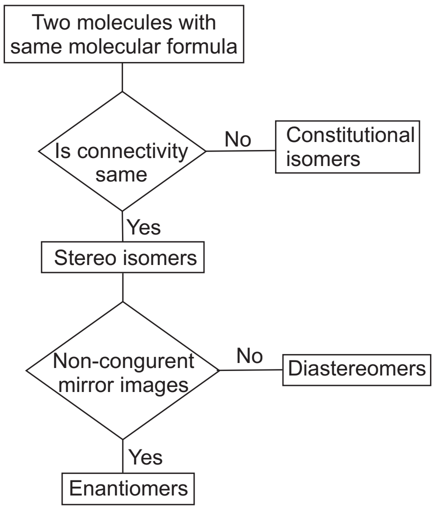


Fig 14.1 Simple flow chart representing the classification of isomers

14.2 Chain or Nuclear Isomerism

The **chain isomers** have the same molecular formula but differ in order in which the carbon atoms are bonded to each other, *e.g.*, *n*-pentane (normal chain), 2-methyl butane (*iso*-chain) and 2,2-dimethyl propane (*neo*-chain). This isomerism is also called **nuclear** or **skeletal isomerism** as different isomers differ in carbon skeleton.

Important Points Related to Chain Isomerism

1. This isomerism is seen mainly in hydrocarbons. In aliphatic hydrocarbons except alkynes a member with minimum 4 C-atoms can show this isomerism.
2. It is also possible in members of a homologous series.
3. Chain isomers may show similar or different chemical properties but definitely differ in physical properties.

Sample **Problem 1** *Which of the following are chain isomers?*

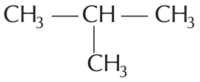
(*a*) CH_3CHCl_2 *and* CH_2ClCH_2Cl

(*b*) $CH_3(CH_2)_2CH_3$ *and* $(CH_3)_2CHCH_3$

(*c*) $CH_3(CH_2)_2OH$ *and* CH_3CH_2OH

(*d*) $CH_3CH_2CH_3$ *and* $CH_3(CH_2)_2CH_3$

Interpret (*b*) $CH_3CH_2CH_2CH_3$ and


$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

both have same number of carbon atoms, *i.e.*, 4 but their parent chain is different, *i.e.*, former chain has 4 carbon atoms while later has only 3 carbon atoms. Thus, these are the examples of chain isomerism.

Sample **Problem 2** *How many chain isomers are possible for the compound* $C_5H_{11}OH$?

(*a*) 7	(*b*) 5
(*c*) 9	(*d*) 4

Interpret (*d*) The possible chain isomers for the compound are as

(i) $CH_3(CH_2)_3CH_2OH$

(ii) $CH_3CH_2CH(CH_3)CH_2OH$

(iii) $CH_3CH(CH_3)CH_2CH_2OH$

(iv) $CH_3C(CH_3)_2CH_2OH$

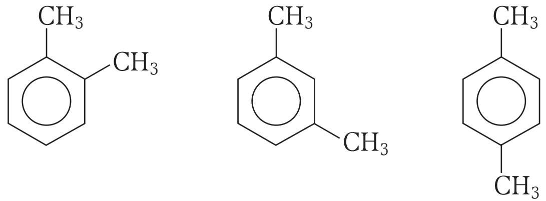
Thus, four chain isomers are possible for this compound.

14.3 Position Isomerism

In position isomerism, the difference lies in the position of substituent group or atom in the same chain, *e.g.*,

1. $\underset{\text{but-1-ene}}{CH_3-CH_2-CH=CH_2}$ $\underset{\text{but-2-ene}}{CH_3-CH=CH-CH_3}$

   Carbon chain length is same but position of double bond is different.

2. 

   1,2-dimethyl benzene   1,3-dimethyl benzene   1,4-dimethyl benzene

   Position of one $-CH_3$ group is differing with respect to other in the benzene ring.

Important Points Related to Position Isomerism

1. The cyanides, aldehydes, carboxylic acids and their derivatives do not exhibit position isomerism when present singly.
2. Chain and position isomerism cannot exist together *i.e.*, if two compounds are chain isomers then these will not be considered as position isomers and *vice-versa*.

3. Due to difference in the position of groups or atoms, these isomers show difference in physical as well as chemical properties.
4. Monosubstituted alicyclic compounds and aromatic compounds do not exhibit positional isomerism.

Sample **Problem 3** *Which of the following compounds, do not exhibit position isomerism?*

(a) *o-xylene* (b) *Butadiene*
(c) *Butanal* (d) *Propene*

Interpret (c) Butanal, $CH_3CH_2CH_2CHO$ do not exhibit position isomerism, as —CHO is the principal functional group and if present singly, as in this case, numbering is always started from it.

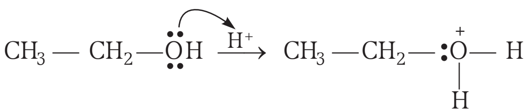
14.4 Functional Isomerism

When different functional groups are attached to the same carbon chain *i.e.,* those compounds which have same molecular formula but different structures due to difference in functional groups attached, are called **functional isomers,** *e.g.*,

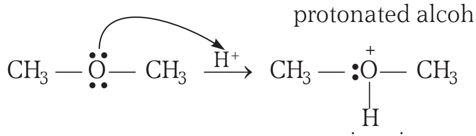
1. C_2H_6O have two functional isomers *i.e.,*
   C_2H_5OH (ethyl alcohol) and CH_3OCH_3 (dimethyl ether) Similarly
2. Similarly, $C_2H_4O_2$ have
   CH_3COOH (acetic acid) and $HCOOCH_3$ (methyl formate)

Important Facts Related to Functional Isomerism

1. If two molecules contain different functional groups, never write chain or positional isomerism, there will always be functional isomerism.
2. Functional isomers show similar approach towards a reagent as distribution of electron cloud (due to the presence of similar atoms) remains more or less same in the molecule. *e.g.*,
   CH_3CH_2OH and CH_3OCH_3 have similar approach towards H^+ as both have oxygen with high electron density around itself as central atom. *i.e.*,



protonated alcohol



oxonium ion

Similarly, just like aldehydes and ketones, oxiranes also show nucleophilic additions reactions.

3. Generally compounds having the same general formula exhibit functional isomerism *e.g.,*

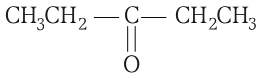
Table 14.1 **General Formula for Different Functional Groups**

S.No.	General formula	Functional isomers
1.	C_nH_{2n}	Alkene and cycloalkane
2.	C_nH_{2n-2}	Alkyne, cycloalkene and alkadiene
3.	$C_nH_{2n+2}O$	Alcohol and ether
4.	$C_nH_{2n}O$	Aldehydes, ketones and epoxides
5.	$C_nH_{2n}O_2$	Acids, ester, hydroxy aldehyde and hydroxy ketone.

14.5 Metamerism

In **metamerism** (*meta* = middle), the difference lies in nature of alkyl groups attached to the same polyvalent functional group. These isomers are called **metamers.** *e.g.,*

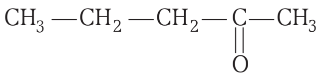
1. $>C=O$ group (carbonyl group)



$CH_3CH_2-\underset{\underset{O}{\|}}{C}-CH_2CH_3$

pentan-3-one

and



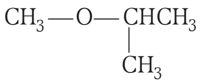
$CH_3-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-CH_3$

pentan-2-one

2. —O— (ether group)

$CH_3CH_2-O-CH_2CH_3$ (diethyl ether) with $CH_3CH_2CH_2-O-CH_3$ (methyl propyl ether)

and

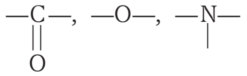


$CH_3-O-\underset{\underset{CH_3}{|}}{C}HCH_3$

methyl *iso*-propyl ether

Important Points Related to Metamerism

1. Polyvalent functional groups are those functional groups which have more than one free valency. *e.g.*,

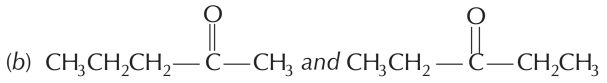


$-\underset{\underset{O}{\|}}{C}-,\ -O-,\ -\underset{|}{N}-$

2. Metamers include same class of compounds.
3. If two molecules contain same functional group (polyvalent) never write chain or position isomerism, it will always be metamerism.
4. Metamerism is never shown by alkenes or alkynes.

Sample Problem 4 *Which of the following pairs are metamers?*

(*a*) $CH_3-CH_2-CH_2-S-CH_3$ *and* $CH_3CH_2-S-CH_2CH_3$



(*b*) $CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-CH_3$ *and* $CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_2CH_3$

(*c*) $CH_3CH_2CH_2-O-CH(CH_3)_2$ *and* $CH_3CH_2CH_2-O-CH_2CH_2CH_3$

(*d*) *All of the above*

Interpret (*d*) In each pair of compounds same functional group is present and different alkyl groups are attached to the same functional group. Thus, each pair includes metamers.

Hot Spot 1

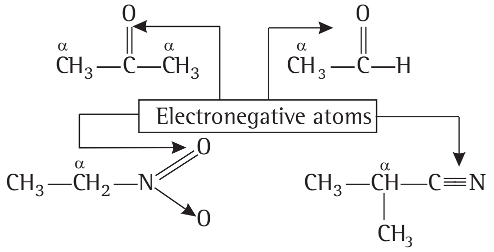
TAUTOMERISM

It is an important topic for JEE Main examination. The level of question is easy to moderate. The questions based on this topic are generally reasoning type like "Which compound exhibit tautomerism or which does not"

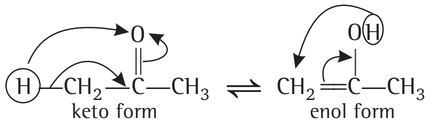
Tautomerism is a special type of functional isomerism. "When the molecules have same molecular formulae but different structural formulae due to wandering nature of hydrogen atom in between two polyvalent atoms, the isomers are called **tautomers** and their property as **tautomerism.**" The tautomerism is also called **kryptomerism** or **allelotropism** or **desmotropism** or **dynamic isomerism.**

The structural requirements for tautomerism include

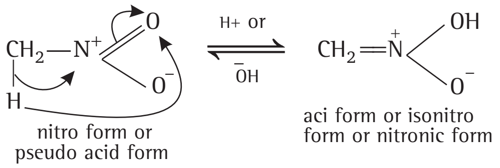
1. The compound must have at least one highly electronegative atom (*e.g.*, F, O and N) bonded with a multiple bond.
2. Compound must have at least one acidic hydrogen present on α-carbon atom of the molecule. *e.g.*,



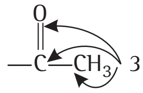
The basic cause of tautomerism is the migration of acidic hydrogen from carbon to multiple bonded electronegative atom, *e.g.*, in acetone tautomerism will be seen as



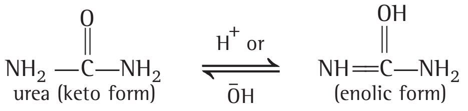
Similarly, nitroalkanes containing α-hydrogen show tautomerism as

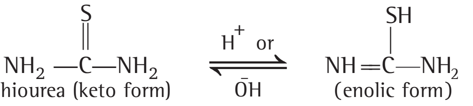


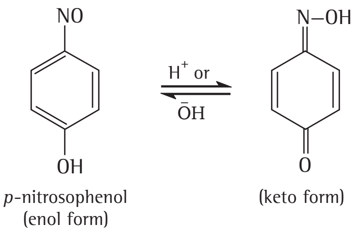
The above examples of tautomerism comes under **TRIAD system** as these involve three molecules in tautomeric system, *i.e.*,



Other examples of such triad system are

(i) 

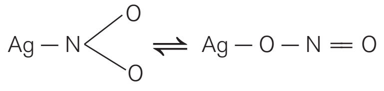
(ii) 

(iii) 

The other system of tautomers in tautomerism is **DYAD system** which involves only two atoms alongwith acidic hydrogen, *i.e.*,

$$\underset{\text{hydrocyanic acid}}{H-C\equiv N} \rightleftharpoons \underset{\text{isohydrocyanic acid}}{H-N\overset{\rightarrow}{=}C}$$

Caution Point *Silver nitrate or silver nitrite is the only compound in which tautomerism is shown by the migration of silver instead of hydrogen.*

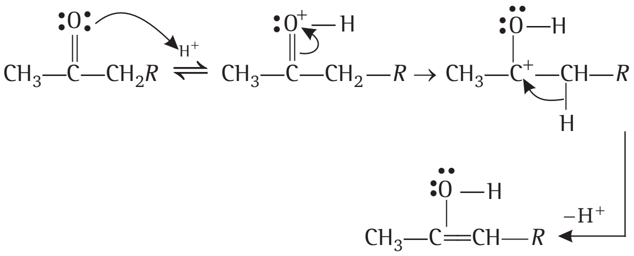


1,2-tautomerism

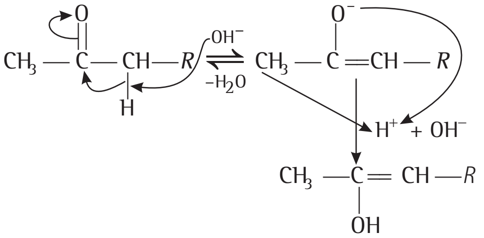
Important Facts Related to Tautomerism

1. Tautomers always exist in **dynamic equillibrium.**
2. Number of sigma bonds, pi bonds and lone pair of electrons are always same in both the tautomers.
3. It is a chemical phenomenon which takes place only in liquids and gaseous phase. It never takes place in solid state.
4. The process can be catalysed by the acid as well as bases.

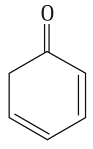
   (a) **Acid catalysed conversion**



   (b) **Base catalysed conversion**



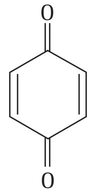
5. In most of the cases, the content of keto form is always greater than the enol form *i.e.,* keto form is more stable than the enol form. Percentage of enolic contents of some common compounds in decreasing order will be



$> C_6H_5COCH_2COCH_3 > CH_3COCH_2COCH_3$

$> CH_3COCH_2COOC_2H_5 > CH_3COCH_2CHO > CH_3COCH_3$

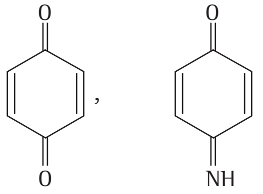
$> CH_3CHO >$



6. **Enol content** is also affected by solvents. It **increases in non-polar aprotic solvent and decreases in polar protic or polar aprotic solvent.** Enol content order in different solvents is Hexane > benzene > acetone > methanol > H_2O

   [Enol content being more volatile is separated by careful distillation of the mixture in a fused quartz apparatus.]

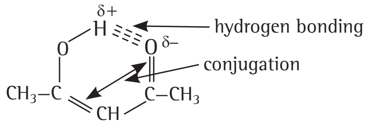
7. Compound having quinonoid structure does not show tautomerism because of the absence of free α –H atoms. For example,



8. The conversion of keto form into enol form is called **enolisation** and depends upon various factors such as structure (especially from resonance and hydrogen bonding point of view), temperature and the nature of solvent. Among these the most important aspect is the structural aspect, *e.g.*,

   (i) Ketonic form predominates in simple monocarbonyl compounds like CH_3CHO, CH_3COCH_3 etc., (due to greater bond strength of $>C{=}O$ bond in comparison to $>C{=}C<$ bond).

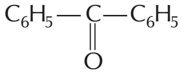
   (ii) Similarly enolic forms predominate in β-diketones due to intramolecular hydrogen bonding and resonance *i.e.,* the $CH_3COCH_2COCH_3$ will have



9. Enol content is reduced due to steric factor *e.g.,* the enol content of α-methyl acetyl acetones (44% in gaseous state) is much lower as compared to that of acetyl acetone (92% in gaseous state) due to greater internal strain in the former case.

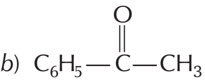
Sample Problem 5 *Keto-enol tautomerism is observed in*

(*a*)



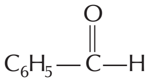
$C_6H_5-\underset{\underset{O}{\|}}{C}-C_6H_5$

(*b*)



$C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3$

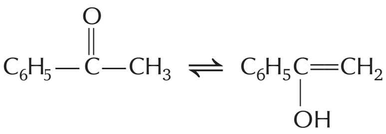
(c)



$C_6H_5-\overset{\overset{O}{\|}}{C}-H$

(*d*) *None of these*

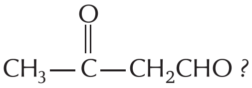
Interpret (*b*) In order to solve such problem, first find the compound which contains free α –H atoms (H atoms bonded by single bonded C atom). Among the given only $C_6H_5CO\overset{\overset{\alpha\text{-c}}{\downarrow}}{C}H_3$ contains three α –H atoms, so it will show keto-enol tautomerism.



$$C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3 \rightleftharpoons C_6H_5\underset{\underset{OH}{|}}{C}{=}CH_2$$

In rest of the given compounds, migration of H-atom is not possible, due to the absence of free α-H atom.

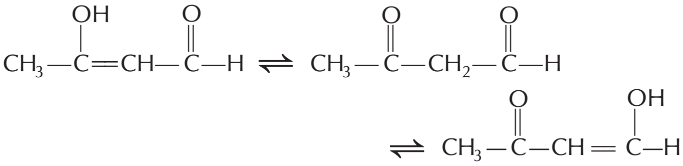
Sample Problem 6 *How many tautomeric structures are possible for the compound*



$CH_3-\overset{\overset{O}{\|}}{C}-CH_2CHO$?

(*a*) 3 (*b*) 4 (*c*) 5 (*d*) 7

Interpret (*a*) To find the number of tautomeric structures, first find the carbonyl groups attached directly to the carbons that bears α-H atoms. Now draw the tautomeric forms *e.g.*, Three tautomeric structures are possible for the given compound as



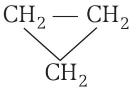
$$CH_3-\overset{\overset{OH}{|}}{C}=CH-\overset{\overset{O}{\|}}{C}-H \rightleftharpoons CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-H \rightleftharpoons CH_3-\overset{\overset{O}{\|}}{C}-CH=\overset{\overset{OH}{|}}{C}-H$$

14.6 Ring Chain Isomerism

If one isomer has open chain structure and the other has cyclic structure then isomers are known as **ring chain isomers** and isomerism is called **ring chain isomerism,** *e.g.,*

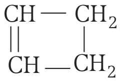
(i) Alkene and cycloalkane

C_3H_6, *i.e.*, $CH_3-CH=CH_2$ and



(ii) Cycloalkene and alkyne

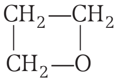
C_4H_6, *i.e.*,



and $CH_3-CH_2-C\equiv CH$

(iii) Alkenol and cyclic ether

C_3H_6O, *i.e.*, $CH_2=CH-CH_2OH$ and



Ring chain isomers are always functional isomers.

Caution Point *Alkanes and their derivatives can't show ring chain isomerism because they do not have an element of unsaturation.*

The isomerism arised due to the presence of different isotopes of an element in the compound is called **isotopic isomerism.** *e.g.,*

$$H_2O \text{ and } D_2O;\ {}^{12}CH_4 \text{ and } {}^{14}CH_4$$

Check Point 1

1. Why do aldehydes or carboxylic acids not exhibit position isomerism, when present singly?
2. Why do functional isomers show a similar approach towards the same reagent?
3. For exhibiting metamerism, presence of which type of functional groups is necessary and why?
4. In acetaldehyde, CH_3CHO keto form predominates while in $CH_3COCH_2COCH_3$ enol form predominates. Explain why?
5. Why alkanes do not exhibit ring chain isomerism?

14.7 Geometrical Isomerism

When a π-bond is present between two atoms, it restricts the free rotation of atoms around its axis. This gives rise to two different structural formulae (properties of these forms differ due to different arrangement of atoms about double bonds in alkenes or about single bonds in cyclic compounds). This isomerism which arises due to difference in spatial arrangement of groups about the

1. doubly bonded C-atoms in **alkenes,**
2. single bonded C-atoms in **cyclic compounds,**
3. doubly bonded C and N-atoms in **oximes,**
4. doubly bonded N-atoms in **diazo compounds,** is called **geometrical isomerism.**

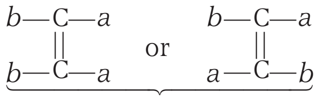
Conditions for Exhibiting Geometrical Isomerism

The conditions for exhibiting geometrical isomerism include

1. There should be frozen rotation about two atoms in the molecules *e.g.*,.
   (i) $>C=C<$, frozen rotation about C—C double bond in alkenes.
   (ii) , frozen rotation about carbon-carbon single bond in cycloalkanes.
   (iii) $>C=N$, frozen rotation about carbon-nitrogen double bond in oximes and imines.
   (iv) $-N=N-$, frozen rotation about nitrogen-nitrogen double bond in azo compounds.
2. Both the atoms of above written bonds should contain different substituents.

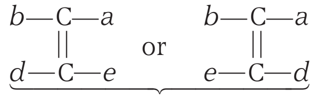
Geometrical Isomerism in Alkenes

The forms in which similar groups are present on the same side of double bond are called ***cis* forms** [Latin *cis* = same side] and the forms, in which similar groups are present on the different sides are called ***trans* forms** [Latin *trans* = across]. *e.g.,*



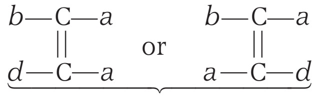
$$\underbrace{\begin{array}{c} b-\text{C}-a \\ \| \\ b-\text{C}-a \end{array} \quad \text{or} \quad \begin{array}{c} b-\text{C}-a \\ \| \\ a-\text{C}-b \end{array}}$$

(I)
non-identical



$$\underbrace{\begin{array}{c} b-\text{C}-a \\ \| \\ d-\text{C}-e \end{array} \quad \text{or} \quad \begin{array}{c} b-\text{C}-a \\ \| \\ e-\text{C}-d \end{array}}$$

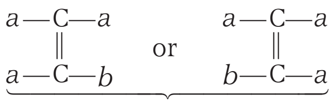
(II)
non-identical



$$\underbrace{\begin{array}{c} b-\text{C}-a \\ \| \\ d-\text{C}-a \end{array} \quad \text{or} \quad \begin{array}{c} b-\text{C}-a \\ \| \\ a-\text{C}-d \end{array}}$$

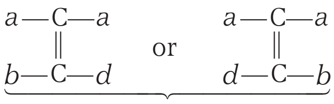
(III)
non-identical

These forms show usually similar chemical but different physical properties. However some forms may show difference in chemical properties as well. *Geometrical isomerism is not seen in those forms in which the double bonded carbon atom have same groups attached to it. e.g.,*



$$\underbrace{\begin{array}{c} a-\text{C}-a \\ \| \\ a-\text{C}-b \end{array} \quad \text{or} \quad \begin{array}{c} a-\text{C}-a \\ \| \\ b-\text{C}-a \end{array}}$$

(IV)
both the structures are identical



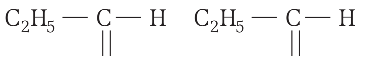
$$\underbrace{\begin{array}{c} a-\text{C}-a \\ \| \\ b-\text{C}-d \end{array} \quad \text{or} \quad \begin{array}{c} a-\text{C}-a \\ \| \\ d-\text{C}-b \end{array}}$$

(V)
both the structures are identical

Geometrical figures in (IV) and (V) will be identical, hence, no geometrical isomers are possible.

The conversion of *cis* isomer into *trans* isomer or *vice-versa* is possible only if either of the isomer is heated to a high temperature or absorbs light. The heat supplies the energy to break the π-bond. Some examples of geometrical isomers are as

1. Two geometrical isomers are possible for **hex-3-ene** ($CH_3CH_2CH{=}CHCH_2CH_3$). This is because each double bonded carbon atom is attached to two different groups, *i.e.,*—CH_2CH_3 and H. The *cis* and *trans* isomers of hex-3-ene are shown below



$$\begin{array}{c} C_2H_5-\text{C}-\text{H} \\ \| \\ C_2H_5-\text{C}-\text{H} \end{array} \quad \begin{array}{c} C_2H_5-\text{C}-\text{H} \\ \| \\ \text{H}-\text{C}-C_2H_5 \end{array}$$

cis hex-3-ene *trans* hex-3-ene

2. Both **fumaric** and **maleic acids** have the same molecular formula, $C_4H_4O_4$. They differ in most of their physical properties and in some of their chemical properties. Originally they were thought as structural isomers and assigned different names. Later on van't Hoff suggested them as geometrical isomers. Maleic acid, which gives anhydride at lower temperatures, is considered as *cis* acid, while fumaric acid is the *trans* variety.

$$\begin{array}{c} \text{H}-\text{C}-\text{COOH} \\ \| \\ \text{H}-\text{C}-\text{COOH} \end{array} \quad \begin{array}{c} \text{COOH}-\text{C}-\text{H} \\ \| \\ \text{H}-\text{C}-\text{COOH} \end{array}$$

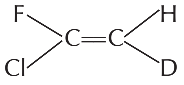
maleic acid [*cis*] fumaric acid [*trans*]

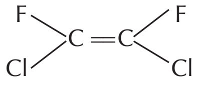
These isomers

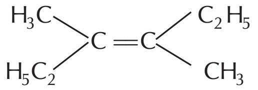
(i) differ in physical properties such as melting point, dipole moment and acidities. The *trans* isomer has no dipole moment since it is symmetrical, unlike the *cis* isomer. The *cis* isomer is stronger acid than the *trans* isomer.

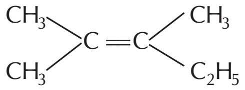
(ii) differ even in chemical properties *e.g., cis* acid undergo dehydration at 100°C and form an anhydride. However the *trans* acid does not form an anhydride until heated to 240°C. At that temperature there is sufficient thermal energy to break the double bond, so that the *cis* acid changes to *trans* and then anhydride are formed in sucession. They can be separated by conventional techniques like fractional distillations, gas chromatography etc.

Sample Problem 7 *Which of the following will not show geometrical isomerism ?* **[NCERT Exemplar]**

(*a*)


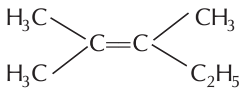
(*b*)


(*c*)


(*d*)


Interpret (*d*) To find whether a compound exhibit geometrical isomerism or not, first see is it a double bonded compound or cyclic compound. Now check the two groups attached to double bonded carbon are different or same. If a double bond or cycle is present and different groups are present at the C forming such centre, the compound exhibits geometrical isomerism.

Among the given, all have double bonds but the group present on double bonded carbon in case of (d) are same. That's why it does not exhibit geometrical isomerism.

Same group


Caution Points

(*i*) *Geometrical isomers may be considered as diastereomers as they have different physical properties.*

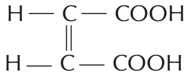
(*ii*) *Stereoisomers that are not the mirror images of each other are also called diastereomers.*

Sample **Problem 8** *Which of the following will show geometrical isomerism?*

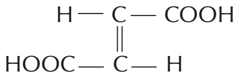
(*a*) C_2H_5Br (*b*) $CH_2(COOH)_2$

(*c*) $(CHCOOH)_2$ (*d*) C_2H_6

Interpret (*c*) Presence of at least one double bond and different groups at double bonded carbon atoms are two essential conditions for exhibiting geometrical isomerism. $(CHCOOH)_2$ fulfils both the conditions thus, exists in *cis* and *trans* forms as


$\begin{array}{c}H-C-COOH\\ \|\\ H-C-COOH\end{array}$

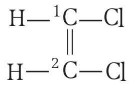
cis-form
(maleic acid)


$\begin{array}{c}H-C-COOH\\ \|\\ HOOC-C-H\end{array}$

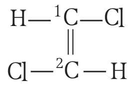
trans–form
(fumaric acid)

Distinction Between *cis* and *trans* Isomers

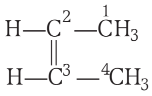
1. The *trans* forms are more stable than the corresponding *cis* isomer. This is because, in the *cis* isomer, the bulky groups are on the same side of double bond. The steric repulsion of the groups makes the *cis* isomer less stable than the *trans* isomer in which the bulky groups are far apart (they are on the opposite sides of the double bond).
2. Melting point of *trans* form is higher than the melting point of *cis* form because of symmetrical packing of *trans*-compounds in its crystal lattice.
3. Boiling point of *cis* form is higher than that of the *trans* form because of steric hindrance in *cis*- compound and high polarity of *cis*- compound.
4. Solubility of *cis*-isomer is higher as compared to *trans*-isomer, as molecules of *trans*- isomer are more tightly held in the crystal lattice than the corresponding *cis*-isomer and hence, it is easier to break the crystal lattice of *cis*- isomer as compared to *trans*- isomer.
5. Generally, a *cis*-isomer (*e.g.*, maleic acid) cyclises on heating to form the corresponding anhydride, while a *trans*-isomer does not form its anhydride at all.
6. The *cis*-isomer of a symmetrical alkene (alkene in which both the carbon atoms have similar groups) has a definite dipole moment, while the *trans*- isomer has zero dipole moment. *e.g.*,


$\begin{array}{c}H-{}^1C-Cl\\ \|\\ H-{}^2C-Cl\end{array}$

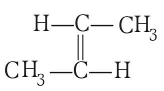
cis–dichloroethene
(μ = 1.9D)


$\begin{array}{c}H-{}^1C-Cl\\ \|\\ Cl-{}^2C-H\end{array}$

trans–dichloroethene
(μ = 0.0D)


$\begin{array}{c}H-C^2-\overset{1}{C}H_3\\ \|\\ H-C^3-{}^4CH_3\end{array}$

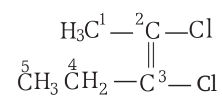
cis–but–2–ene
$\mu \neq 0$

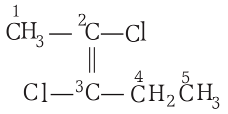

$\begin{array}{c}H-C-CH_3\\ \|\\ CH_3-C-H\end{array}$

trans-but–2–ene
μ=0.0D

In *trans*-isomers of symmetrical alkenes, the effect produced in one half of the molecule is cancelled by that in the other half of the molecule.

In case of unsymmetrical alkenes, the *cis*- isomer has higher dipole moment than the corresponding *trans*-isomer. *e.g.*,


$\begin{array}{c}H_3C^1-{}^2C-Cl\\ \|\\ \overset{5}{C}H_3\,\overset{4}{C}H_2-C^3-Cl\end{array}$


$\begin{array}{c}\overset{1}{C}H_3-\overset{2}{C}-Cl\\ \|\\ Cl-{}^3C-\overset{4}{C}H_2\overset{5}{C}H_3\end{array}$

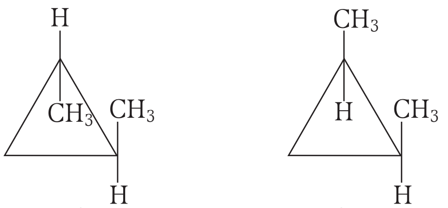
cis–2,3–dichloropent–2–ene
(high dipole moment)

trans–2,3 dichloropent–2 –ene(less dipole moment)

Geometrical Isomerism in Cyclic Compounds

Geometrical isomerism is also possible in cyclic compounds as no free rotation is possible about carbon-carbon single bonds in such compounds. Thus, for rotation, bond breaking is required which results in the ring cleavage. *e.g.*,

1,2-dimethyl cyclopropane exists in the following two isomeric forms

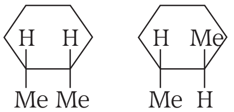


trans form *cis* form

1,2-dimethyl cyclopropane

Other examples of cyclic compounds exhibiting geometrical (*cis-trans*) isomerism are as

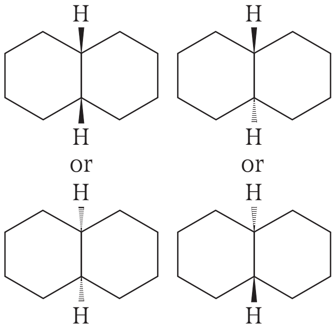
I.



cis *trans*

1,2-dimethyl cyclohexane

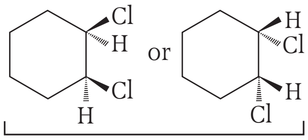
II.



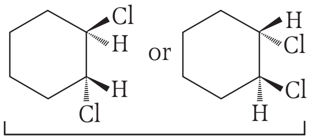
cis *trans*

decalin or bicyclo (4. 4. 0) decane or decahydro naphthalene

III.

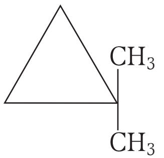


cis-1,2-dichloro cyclohexane



trans-1,2-dichloro cyclohexane

A requirement for geometrical isomerism in cyclic compounds is that there must be at least two other groups besides hydrogen on the ring and these must be on different C-atoms of the ring. For example no geometrical isomers are possible for 1, 1-dimethylcyclopropane.



1,1-dimethyl cyclopropane (no isomers possible)

Geometrical Isomerism in Nitrogen Compounds

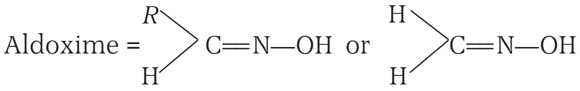
Geometrical isomerism is also seen in oximes, imines and azo compounds (all of them are nitrogen compounds). The oximes are formed by the reaction of carbonyl compounds ($>C{=}O$ compounds *i.e.,* aldehydes and ketones) with NH_2OH (hydroxyl amine) as :

$$>C{=}\boxed{O + H_2}N{-}OH \longrightarrow \underset{\text{oxime}}{>C{=}N{-}OH} + H_2O$$

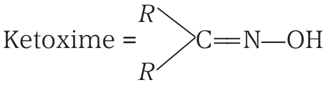
If $>C{=}O$ is aldehyde then oxime is aldoxime.

If $>C{=}O$ is ketone then oxime is ketoxime.

Hence,



$$\text{Aldoxime} = \begin{matrix} R \\ H \end{matrix}\!\!>C{=}N{-}OH \text{ or } \begin{matrix} H \\ H \end{matrix}\!\!>C{=}N{-}OH$$

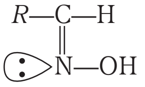


$$\text{Ketoxime} = \begin{matrix} R \\ R \end{matrix}\!\!>C{=}N{-}OH$$

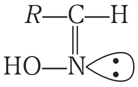
In nitrogen compounds, the steric repulsion occurs between the lone pair of nitrogen with bond pair of larger group (*i.e.,* in oximes and imines) or between the two lone pairs of two nitrogens (*i.e.,* in azo compounds) resulting to *syn* (corresponding to *cis*) and *anti* (corresponding to *trans*) forms, *e.g.*,

(a) **In oximes**

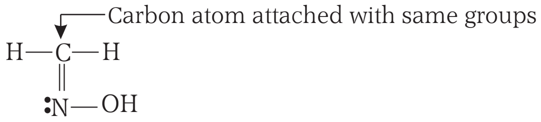
(i) In aldoximes



syn oxime

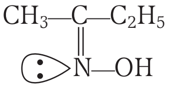


anti oxime



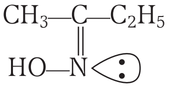
Thus, the first member of aldoximes does not show any geometrical isomer.

(ii) **In ketoximes**



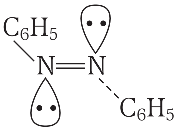
This compound is *syn* for ethyl group and *anti* for methyl group or this can be called *anti* compound.

Similarly,



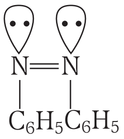
This compound is *anti* for ethyl group and *syn* for methyl group or this can be called *syn* compound.

(b) **In azo compounds**



anti oxime

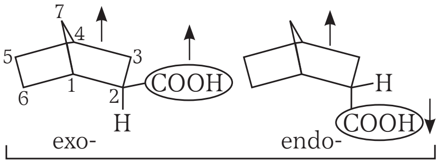
and



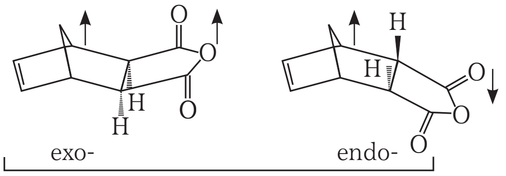
syn oxime

Exo and Endo in Bicyclic Compounds

exo and endo terms are used in case of bicyclic compounds. When two rings or a ring and a group are in *cis*-position, it is called exo-stereoisomer, when two rings or a ring and a group are in *trans*-position, it is called endo-stereoisomer; *e.g.,*

I.


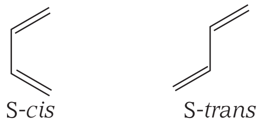
bycyclo (2. 2. 1) heptane-2-carboxylic acid

II.


endo-stereoisomer is more stable than exo-stereoisomer

Geometrical Isomerism Across a Single Bond

Cis-and *trans*-isomerism is also possible across a single bond. *e.g.,* in buta-1,3-diene.



S-*cis* form of butadiene undergoes Diels Alder reaction with dienophile while S-*trans* does not.

Calculation of Number of Geometrical Isomers

The number of geometrical isomers of a compound can be calculated with the help of following formulae.

(i) In compounds with n number of π bonds and different ends, number of geometrical isomers = 2^n.

(ii) In compounds with n number of π bonds and same ends.

Case I When n = even number

Then, number of geometrical isomers $= 2^{(n-1)} + 2^{\left(\frac{n}{2}-1\right)}$

Case II When n = odd number

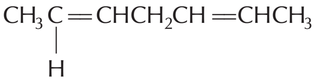
Then, number of geometrical isomers

$$= 2^{(n-1)} + 2^{\left(\frac{n+1}{2}-1\right)}$$

Sample **Problem 9** *The number of geometrical isomers possible for 2, 5- heptadiene is*

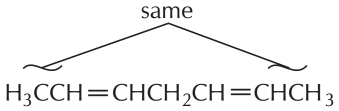
(*a*) 2 (*b*) 3 (*c*) 4 (*d*) 5

Interpret (*b*) To solve such problem, first draw the structure of given compound, if not given,



$\mathrm{CH_3\underset{|\atop H}{C}{=}CHCH_2CH{=}CHCH_3}$

Now find whether the two ends (terminals) are same or different.



$$\overset{\text{same}}{\mathrm{H_3CCH{=}CHCH_2CH{=}CHCH_3}}$$

Now n = no. of double bone = 2 *i.e.,* even.

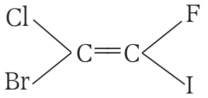
So, no. of geometrical isomers $= 2^{2-1} + 2^{\left(\frac{2}{2}-1\right)}$

$= 2 + 2^0$

$= 2 + 1 = 3$

E, Z-System of Geometrical Isomers

Cis and *trans* system of geometrical isomerism cannot work in compounds which do not have identical groups on the sides of double bond, *e.g.*,

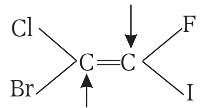


1-bromo-1-chloro-2-fluoro-2-iodoethene

The configuration of these compounds can be specified by using the notations *E* (from German *Entgegen* = opposite) and *Z* (from German *Zusammen* = together). For determining *E* and *Z* configurations, we have to assign priority to the groups attached to the doubly bonded C-atoms. The rules for assigning the priority are as follows

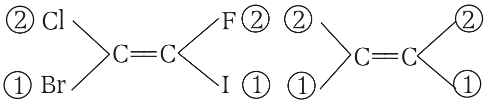
1. The priority can be assigned on the basis of the atomic number of the group attached (in fact the atomic number of that atom of the group is considered which is attached directly to the atom). *The group with higher atomic number will get the first priority*, *e.g.*,

Second C-atom according to IUPAC nomenclature



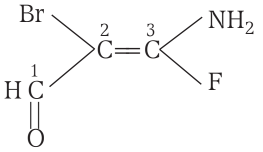
First C-atom according to IUPAC nomenclature

Out of chlorine and bromine attached to first C-atom, the atomic number of Br is higher, thus, Br gets priority over Cl. Similarly out of fluorine and iodine attached, the atomic number of iodine is greater thus iodine will get priority over F. Thus, the compound looks like



Now as it is very clear that the bulky groups are at the same side of double bond, hence the form is ***Z* form** (analogous to *cis* form)

2. Similarly, in the compound



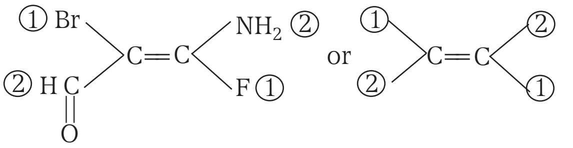
3-amino-2-bromo-3-fluoroprop-2-en-1-al

The priorities are given as

(i) Out of two groups *i.e.,* Br and — CHO attached to the C-atom number 2, the atomic number of Br is greater than the C-atom of — CHO group (as written earlier that if the functional group contains more than one atom then the atomic number of that atom is considered which is attached directly to the doubly bonded C-atom). Hence, in this case Br gets priority over — CHO group.

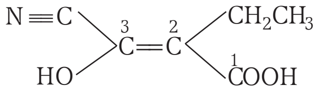
(ii) Out of the two groups attached to the C-atom number 3 *i.e.,* F and —NH_2, the atomic number of F is greater than that of the N of —NH_2 group, thus F gets priority over —NH_2.

Hence, the compound looks like



Now, as it is very clear that the bulky groups are at the opposite side of double bond, hence the form is called ***E* form** (it is analogous to *trans* form).

3. Now, if two or more atoms are attached to doubly bonded C-atoms with the same atomic number, then the priority is given according to the atomic number of next atom as in the compound written below

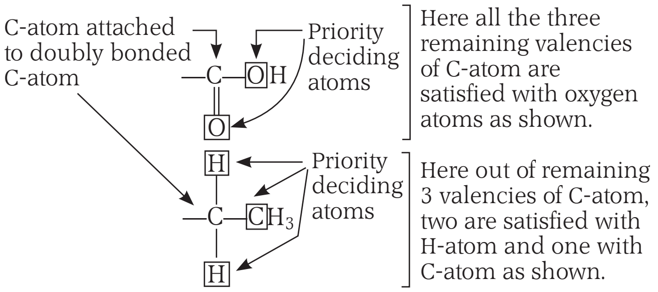


2-ethyl-3-cyano-3-hydroxy prop-2-en-1-oic acid

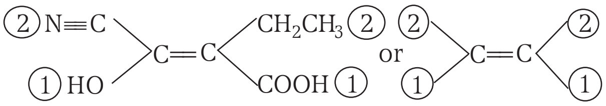
Here,

(i) out of the — OH and — CN groups attached to the 3rd C-atom, the atomic number of oxygen of — OH group is greater than the atomic number of C-atom of — CN group. Hence, — OH gets priority over —C≡N.

(ii) On the other hand, out of the two groups attached to C-atom number 2, each one begins with C-atom. Here, the — COOH group is given priority over —CH_2CH_3 group due to following reason.



Thus, oxygen of first case is preferred over C or H of second case and the compound looks like



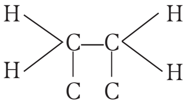
i.e., the compound is in ***Z*-form.**

From the above point (3) *the two things are clear*

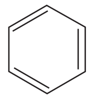
(i) If atoms attached to doubly bonded C-atoms are same, the priority is determined by going next away to such atoms.

(ii) Multiple bonds are treated as each atom of the multiple bond is attached to multiple atoms.

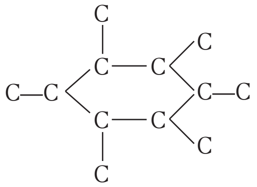
e.g., $H_2C{=}CH_2$ will be treated as



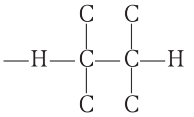
or



will be as

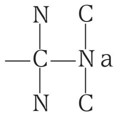


or HC≡CH will be as



$$-H-\underset{\substack{|\\C}}{\overset{\substack{C\\|}}{C}}-\underset{\substack{|\\C}}{\overset{\substack{C\\|}}{C}}-H$$

Similarly, —C≡N as

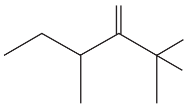


$$-\underset{\substack{|\\N}}{\overset{\substack{N\\|}}{C}}-\underset{\substack{|\\C}}{\overset{\substack{C\\|}}{N}}$$

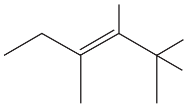
and so on.

Sample Problem 10 *Which of the following alkenes shown below has the Z-configuration of its double bond?*

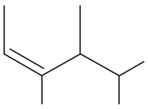
(*a*)



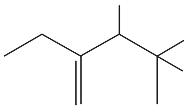
(*b*)



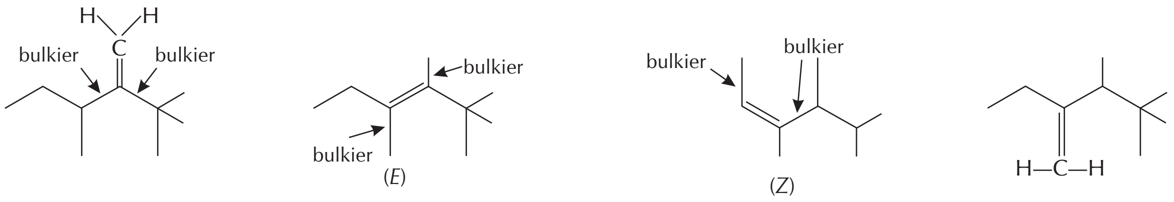
(*c*)



(*d*)



Interpret (c) *Z*-configuration shows the presence of bulkier groups at the same side of double bond.



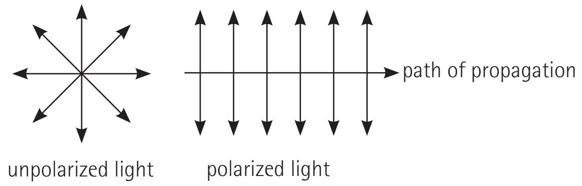
14.8 Optical Isomerism

Compounds with similar physical as well as chemical properties and with difference only in their behaviour towards plane polarized light are called *optical isomers* and this property is called *optical isomerism*.

Important Terms Related to Optical Isomerism

Before going in detail it is better to understand some terms related to this isomerism.

(a) **Plane polarized light** According to wave theory, an ordinary ray of light is considered to have particulate vibrations in all possible planes perpendicular to its path of propagation. However, in polarized light the particulate vibrations occur in one plane only.



(b) **Optical activity** The property of a compound by virtu of which it can rotate the plane of polarized light, is called optical activity.

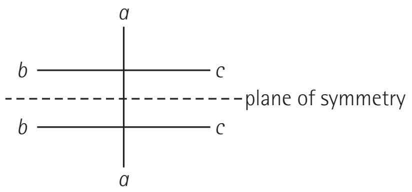
(c) **Asymmetric C-atom** C-atom having 4 different groups or atoms attached separately to its four valencies is called asymmetric carbon atom or stereocentre.

(d) **Chiral molecule** A molecule completely lacking plane of symmetry is called chiral molecule. In other words, it can also be defined as the one which is not superimposable on its mirror reflection or the one in which line of symmetrisation is lacking. An asymmetric C-atom will generally be considered as chiral and we can say that

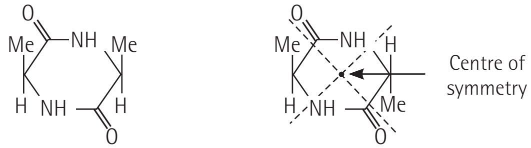
(1) A chiral molecule mostly possess at least 1-chiral carbon atom.

(2) A chiral molecule does not possess any element of symmetry like.

(i) **Plane of symmetry**



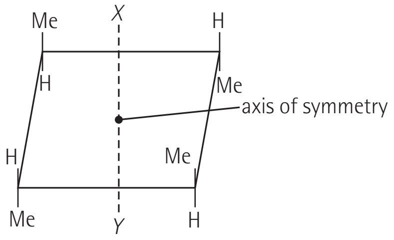
(ii) **Centre of symmetry**



no centre of symmetry (*cis* form)

trans form (has centre of symmetry)

(iii) **Axis of symmetry**



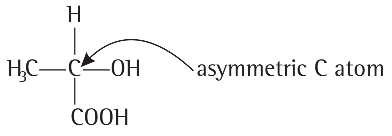
(e) **Achiral molecule** A molecule which is superimposable on its mirror image is called achiral.

Hot Spot 2

OPTICAL Isomers of Different Types

It is an important topic for JEE Main point of view. Most of the times, questions belong to this topic. A small practice of the topic can help you to solve the problem.

Usually the compounds having atleast one asymmetric C-atom (the C atom all the four valencies of which are satisfied by four different groups or atoms) are capable to exhibit optical isomerism.*e.g.*, Lactic acid.



$H_3C—C(H)(COOH)—OH$

optically active

The optical isomers can be categorised into the following two types

(a) Optically Active Compounds

Those compounds which have the ability to rotate the plane of polarised light are called **optically active compounds.** These compounds are infact chiral *i.e.*, have absence of elements of symmetry.

Among the optically active compounds following types are included

1. **Dextrorotatory** or ***d*-or (+) forms** which rotate the plane of polarised light to the right (clockwise).
2. **Laevorotatory** or ***l* or (–) forms** which rotate the plane of polarised light to the left (anticlockwise).

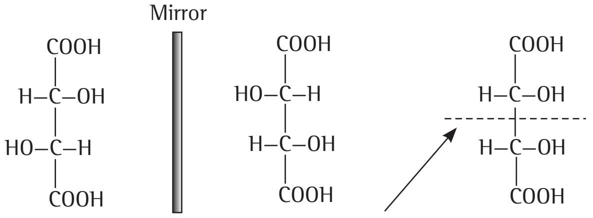
(b) Optically Inactive Compounds

Those compounds which do not have such an ability *i.e.*, which do not rotate the plane of polarised light are called **optically inactive compounds.** The reasons for the inactivity of these compounds are

(i) presence of element of symmetry
(ii) presence of *d* and *l*-forms in equal amounts.

On the basis of above reasons, optically inactive compounds can be of two types

1. ***Meso* form** It has the plane of symmetry within the molecule *i.e.*, **the one half of the molecule is dextrorotatory and rest half is laevorotatory.** Thus, within the molecule both halves show equal and opposite optical activity. As a result, the molecule becomes optically inactive. **This phenomenon of optical inactivation in which the rotation produced by one half of the molecule is cancelled by its another half is called internal compensation** *i.e.*, *meso* **forms are said to be optically inactive due to the phenomenon of internal compensation.** *e.g.*, the optically active and inactive forms of tartaric acid are as follows



optically active forms   line of symmetrization   *meso* tartaric acid

2. **Racemic mixture** The equimolar mixture of two optically active forms (*d* and *l* forms) of a compound is called **racemic mixture.** The mixture is optically inactive as both the forms neutralizes the effect of one another. Such a neutralizing effect is called **external compensation,** thus **racemic mixtures are optically inactive due to the process of external compensation.**

   The formation of racemic mixture is called **racemisation** while separation of these forms from the mixture is called **resolution.** Resolution can be achieved by mechanical method, biological method using enzymes, chemical methods (by making their diastereomers) or by chromatographic separation (by using special adsorbents).

Sample Problem 11 *Which of the following are optically inactive compounds?*

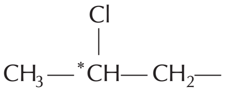
(a) Butan-1-ol (b) 2-chlorobutane
(c) Lactic acid (d) 3-chlorobutane

Interpret (*a*, *d*) In order to solve out such problems, first draw the structures of all the given compounds (in case structure are not given).

Now find the chiral or asymmetric centre and also find the presence or absence of symmetry elements. If structure contains chiral centre and have absence of symmetry elements then it will be optically active, otherwise not as

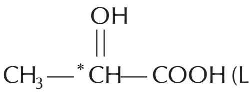
The structural formulae of the given compounds are as under

(i) $CH_3CH_2CH_2CH_2OH$ (Butan-1ol) It is not optically active since it does not contain any asymmetric carbon atom. Hence, the molecule is **achiral**.



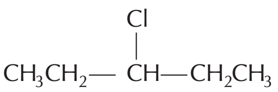
(ii) $CH_3—{}^*CH(Cl)—CH_2—CH_3$ (2-chlorobutane)

It is a chiral molecule, since it contains an asymmetric carbon atom marked with an asterisk. Hence, it is optically active.



(iii) $CH_3—{}^*CH(OH)—COOH$ (Lactic acid)

It contains one asymmetric carbon atom and its molecule is **chiral**. Thus, it shows **optical activity**.



(iv) $CH_3CH_2—CH(Cl)—CH_2CH_3$ (3-chloropentane)

It is a symmetrical molecule since it does not contain an asymmetric carbon atom. Hence, it does not show optical activity.

Enantiomers and Diastereomers

Optically active compounds which are non-superimposable mirror images of each other are called *enantiomers*. *e.g.*, in tartaric acid, first two figures written are called *enantiomers*. *Remember, an asymmetrical object can have only single mirror image, thus an optically active compound* (being asymmetrical) *can have only one enantiomer always. Secondly this mirror image is always non-superimposable.*

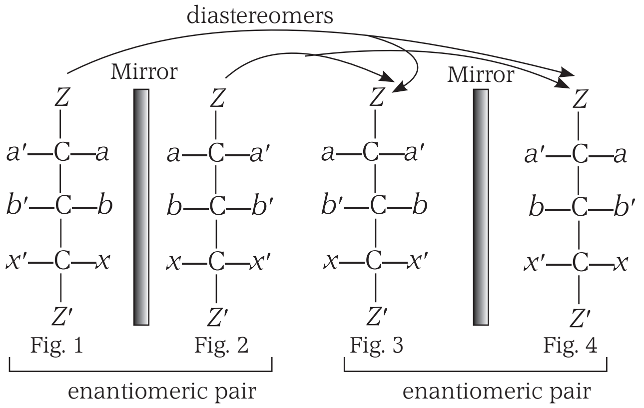
The properties of the enantiomers include

(i) These are stable compounds that differ from one another in three dimensional spatial arrangements.

(ii) These cannot be interconverted under ordinary conditions.

(iii) These have identical properties in all respects except in their interaction with plane of polarised light.

Optical isomers which are not the mirror images of each other are called **diastereomers**. *e.g.,* in the following compounds



The structure of all the four figures is same but spatial arrangement of groups differ as fig. (1) and (2) are enantiomeric, similarly fig. (3) and (4) are enantiomeric. However, Fig. (1) is diastereomeric with fig. (3) and (4) (same molecular formula, different optical behaviour and not the mirror images of each other). Similarly fig. (2) is diastereomeric with fig. (3) and (4).

Contrary to enantiomers, two diastereomers have different melting points, boiling points and solubilities. They will have different chemical reactivities towards most reagents *i.e.*, show difference in physical as well as in chemical properties.

Calculation of Number of Optical Isomers

The number of optical isomers depends upon the number of asymmetric centres and can be calculated with the help of following general relations

1. In molecules which are not divisible into two equal halves and have n number of asymmetric C-atoms
   - (i) Number of optically active forms = $2^n = a$
   - (ii) Number of enantiomeric pairs = $a/2$
   - (iii) Number of racemic mixtures = $a/2$
   - (iv) Number of *meso* forms = 0
2. In molecules which are divisible into two equal halves.

***Case* I** When n = even number,

(i) Number of optically active forms = $(a) = 2^{n-1}$

(ii) Number of enantiomeric forms = $a/2$

(iii) Number of racemic mixtures = $a/2$

(iv) Number of *meso* forms = $(m) = 2^{\left(\frac{n}{2}-1\right)}$

(v) Total number of configurational isomers = $a + m$

***Case* II** When n = odd number,

(i) Number of optically active forms $= (a) = 2^{(n-1)} - 2^{\left(\frac{n-1}{2}\right)}$

(ii) Number of enantiomeric pairs = $a/2$

(iii) Number of racemic mixtures = $a/2$

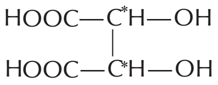
(iv) Number of *meso* forms = $(m) = 2^{\left(\frac{n-1}{2}\right)}$

(v) Total number of configurational isomers = $a + m$.

Sample **Problem 12** *The number of opitcal isomers for the compound* $(CH(OH)COOH)_2$ *is*

(a) 1
(b) 2
(c) 3
(d) 4

Interpret (c) The structure of the compound can also be written as



$$\begin{array}{c} HOOC—\overset{*}{C}H—OH \\ | \\ HOOC—\overset{*}{C}H—OH \end{array}$$

∴No. of asymmetric C atoms $(C^*) = 2$ but the two ends are similar or the molecule is divisible into equal values.

Hence, $a = 2^{n-1} = 2^{2-1} = 2$

$$m = 2^{\frac{n}{2}-1} = 2^{\frac{2}{2}-1} = 2^{\circ} = 1$$

No. of optical isomers = 2 + 1 = 3

Note Here structure is given, but if structure is not given first of all draw the structure.

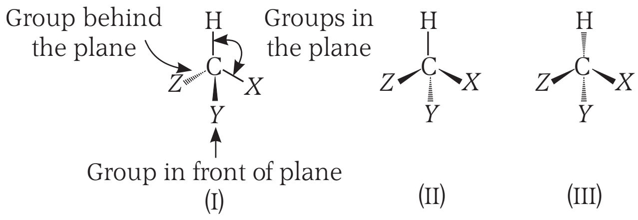
Projection Formulae

Different projection formulae have been given to define the structure a molecule completely. These can be converted into each other.

These are as follow

(a) Wedge-Dash formula

The configuration of organic molecules can be visualised by three-dimensional (3D) structures, which may be depicted by any of the following representations



Here the thick solid (solid wedge) line represents the bonds lying above the plane of paper (projecting towards the viewer), thin lines indicate the bonds lying within the plane of paper; while the dotted line indicates the bonds lying below the plane of paper. Such a representation is called Wedge-Dash formula.

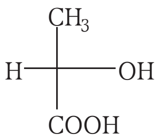
(b) Fischer Projection Formulae

A planar representation of the three dimensional structure is called **Fischer projection formulae.**

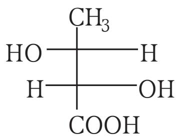
Following guidelines are used to draw it.

1. The chain of carbon atoms in arranged vertically in such a way that the most oxidised carbon occupy the top position.
2. The asymmetric carbon atom lies in the plane of paper and is represented at the interaction of crossed lines.
3. The bonds going away from you are represented by vertical lines. In other words, vertical lines represent the groups present behind the plane of paper.
4. The bonds coming towards you are represented by horizontal lines. In other words, group attached to the horizontal lines are understood to be present above the plane of the paper.

Using the above guidelines, the Fischer projection formulae for lactic acid and tartaric acid are shown as



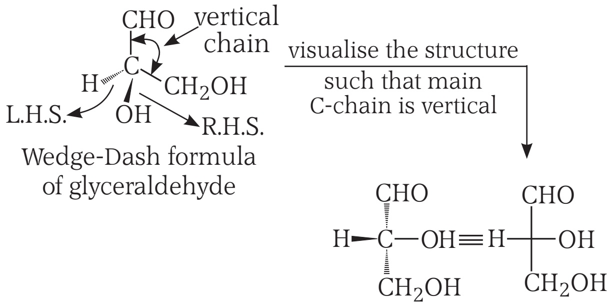
lactic acid



tartaric acid

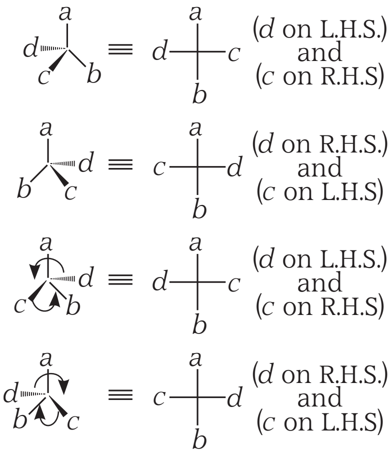
(c) Interconversion of Wedge-Dash Formula to Fischer Formula

In case of molecules having several C atoms, it is customary to orient the molecule in such a way that the C-chain is vertical. Substituents which are left and right of the viewer are written at left and right, respectively, and other two substituents which appear above and below are written at top and bottom positions, *e.g.*,

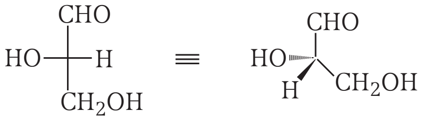


Fischer projection formula

Although the Fischer projections are planar structures, these can be rotated end-for-end on the plane of paper only in multiples of 180° but not 90° at a time. Also a Fischer projection formula may not be taken out of the plane of paper and flipped over.



(d) Interconversion of Fischer Formula to Wedge-Dash Formula



Fischer formula Wedge-Dash formula

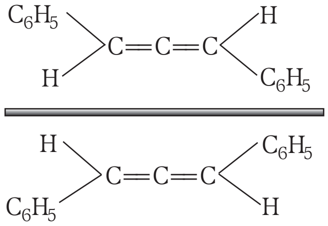
When drawing the 3D formulae from the corresponding Fischer formula, it is better to draw the group at the lower end of the vertical line towards right hand side.

Optical Isomerism in Compounds having Lack of Asymmetric C-atoms

Besides such compounds which have asymmetrical C-atoms, there are also certain compounds which are optically active but lack any asymmetric C-atom. These compounds show optical activity just because of the fact that their molecule is chiral, *e.g.*,

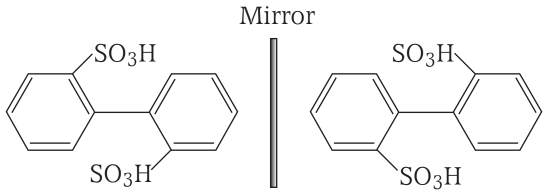
(a) Allene Derivative

Some of the allene derivatives show optical activity as 1, 3-diphenyl propadiene. In this compound the central atom forms two $sp-sp^2$ σ bonds. The central atom also has two π orbitals, which are mutually perpendicular to each other and form π bonds with the p-orbitals of other C-atoms. As a result the substituents at one end of the molecule are in a plane which is perpendicular to that of the substituents at the other end. Thus, the compound exists in two forms which are non-superimposable mirror images and are optically active.



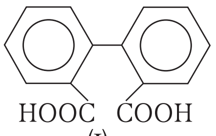
(b) Biphenyl Derivatives

Substituted biphenyls show optical isomerism, when substituent in the 2-positions are large enough to prevent rotation about the bond joining the two benzene rings, *e.g.*, biphenyl-2, 2′ -disulphonic acid exists in two forms. These two forms are non-superimposable mirror images. They do not interconvert at room temperature because the energy required to twist one ring through 180° relative to the other is too high. This is so because during the twisting process, the two $-SO_3H$ groups must come into very close proximity when the two benzene rings become coplanar and strong repulsive forces are introduced.

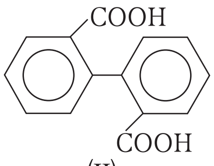


Caution Point *This type of stereoisomerism arising from restricted rotation about a single bond (and where the stereoisomers can be isolated) is called* **atrop isomerism** *and the isomers are called* **atrop isomers.**

Diphenic acid is not optically active. In configuration (I) , the molecule has a plane of symmetry and in configuration (II) , it has a centre of symmetry. Further, I is less stable than (II) because of the repulsion between two (—COOH) groups.



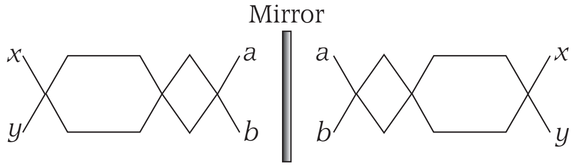
(I)



(II)

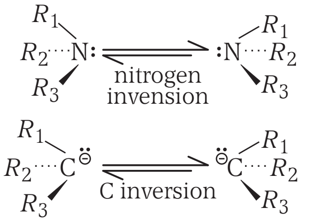
(c) Spiranes

When two double bonds in allenes are replaced by two cycloalkane rings, the resulting system also show optical isomerism.



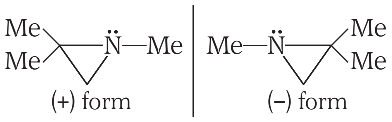
(d) *t*-amines, Amine Salts and *t*-carbanion

Amine and carbanion with a lone pair of electrons (being) considered a fourth different group) are chiral as they have pyramidal geometry, but they are optically inactive. A rapid 'Umbrella' type inversion converts either of the enantiomers to a racemic mixture.The energy required for this inversion is very low at room temperature, since this inversion does not involve bond breaking and bond formation. Thus, racemisation occurs and enantiomers cannot be isolated.



But amine salts are optically active. Nitrogen inversion is not possible *e.g.*, $[R_1R_2R_3N^{\oplus}H]Cl^{\ominus}$

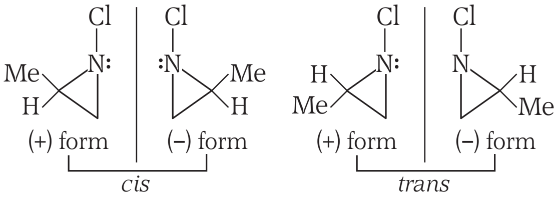
Some more examples of optically active N-containing compounds are



(+) form (–) form

1,2,2-trimethyl aziridine

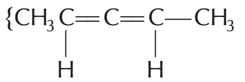
1-chloro-2-methyl aziridine shows four stereoisomers.



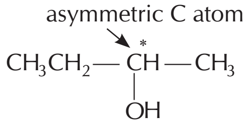
Sample Problem 13 *Which of the following does not exhibit optical isomerism?*

(a) 2,3-*pentadiene* (b) *sec-butyl alcohol*
(c) 1,2-*propadiene* (d) *All of these*

Interpret (c) The structures of the given compounds are as different groups are attached to chiral centre



$\{CH_3\underset{|}{\underset{H}{C}}=C=\underset{|}{\underset{H}{C}}-CH_3$



$CH_3CH_2-\underset{OH}{\overset{*}{C}H}-CH_3$

The attached H groups are same $\{CH_2=C=CH_2$

The mirror images of 1,2-propadiene is superimposable while those of 2,3-pentadiene and *sec*-butyl alcohol are non-superimposable. Hence, 1,2- propadiene does not exhibit enantiomerism or optical isomerism.

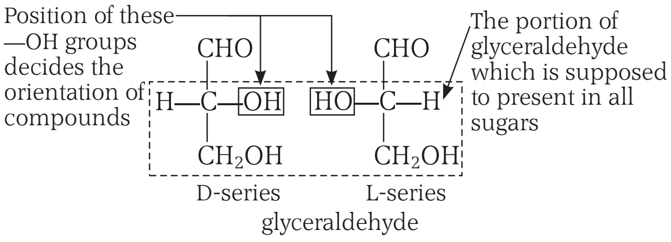
Systems of Nomenclature of Optical Isomers

The nomenclature of optical isomers canbe done in accordance with

(a) Dee-Eel (D,L) system of nomenclature
(b) *Erythro* and *threo* system of nomenclature
(c) The *R,S* (Rectus, sinister) system of nomenclature or system of absolute configuration.

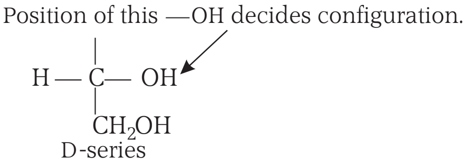
(a) D, L System of Nomenclature of Partial Configuration

The D, L system of nomenclature is used for optically active polyhydroxy carbonyl compounds (carbohydrates) mainly. This nomenclature was given by **Emil Fischer** who considered glyceraldehyde as the parental sugar.



All sugars whose Fischer projection formula shows the —OH group on the right hand side on chiral C-atom adjacent to the terminal —CH_2OH group (*i.e.*, second last C-atom) are called the sugars of D-series.

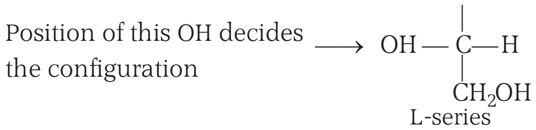
Hence, all sugars having below written structure at their terminus will belong to the **D-series.**



$H-\underset{CH_2OH}{\overset{|}{C}}-OH$

(Here D stands for dextro *i.e.*, right hand side and not dextrorotatory).

Similarly, if the —OH group is positioned left then it looks like



$OH-\underset{CH_2OH}{\overset{|}{C}}-H$

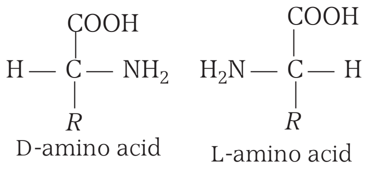
(Here, L stands for laevo *i.e.*, left hand side and not laevo rotatory).

All such sugars having this configuration are suppose to belong to the **L-series.**

As a whole we can say that any compound that can be prepared from or converted into D(+) glyceraldehyde will belong to D-series and similarly any compound that can be prepared from or converted into L(–) glyceraldehyde will belong to the L-series.

It must be noted that there is no relation between the sign of rotation (*i.e.*, +, – or *d*, *l*) and the configuration (D and L) of the enantiomer.

This nomenclature is also used for α-amino acids. *e.g.*,

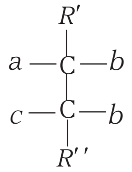


$H-\underset{R}{\overset{COOH}{C}}-NH_2 \quad H_2N-\underset{R}{\overset{COOH}{C}}-H$

(b) *Erythro* and *Threo* System

The *erythro* and *threo* system of nomenclature is used in those compounds which have

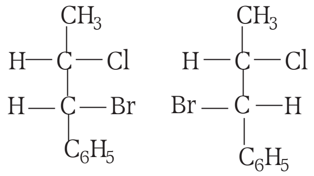
(i) only two chiral carbons and
(ii) the following structure



$a-\overset{R'}{C}-b$
$c-\underset{R''}{C}-b$

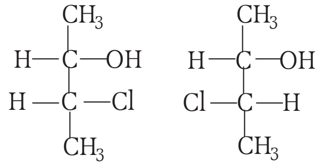
i.e., out of the 6 *substituents on two asymmetric carbons at least two should be same.*

When two like groups in Fischer projection formulae are drawn on the same side of vertical line, the isomer is called ***erythro* form** while if these are placed on the opposite sides, the isomer is said to be ***threo* form**. *e.g.*,



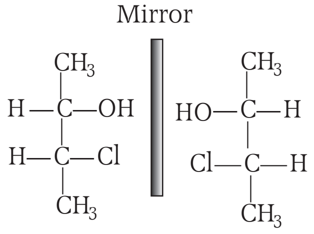
erythro form *threo* form

Similarly,

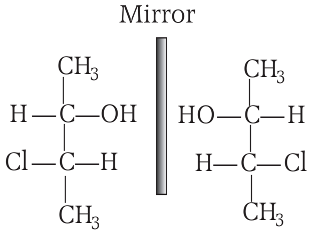


erythro form *threo* form

The *erythro* and *threo* enantiomers are also seen, *e.g.*,

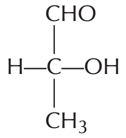


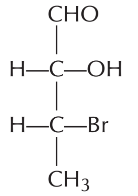
erythro enantiomers

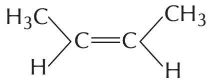


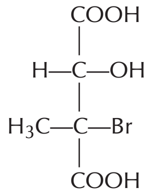
threo enantiomers

Sample **Problem 14** *Which of the following compounds is erythro form?*

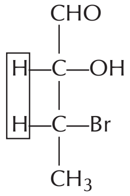
(a) 

(b) 

(c) 

(d) 

Interpret (*b*) When two like groups is Fischer projection formula are drawn on the same side of the vertical line, the isomer is called *erythro* form, *i.e.,*



erythro form

Hot Spot 3

R'S SYSTEM
or Absolute Configuration

It is an important topic for JEE Main examination as the question may be directly asked from the topic or may be based on the configuration of product of any reaction. The level of questions is average, but deep focus on the topic is required for solving problems. Here also remember if you have Wadge-Dash formula, convert it into Fischer projection to assign configuration (for better results)

R,S system is more important as compared to previous two. The actual three dimensional arrangement of groups in an asymmetrical molecule is called its **absolute configuration.** We can specify the configuration by using the *R,S* system *i.e.*, *rectus* and *sinister* system [Here, *rectus* = right hand side, *sinister* = left hand side].

This nomenclature was proposed by Cahn, Ingold and Prelog and involves two steps in it.

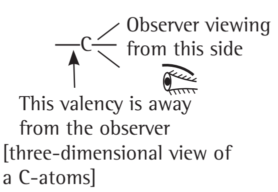
Step I Following a set of sequence rules, a sequence of priority is assigned to four different groups or atoms attached to a chiral C-atom. The most acceptable criterion of priority is based on atomic numbers *i.e.*, **atom with higher atomic number will get higher priority,** *e.g.*, in the case of bromochloroiodomethane the sequence of priority is I, Br, Cl, and H.

Step II The molecule is next visualised so oriented that the group of lowest priority is directed away from you and the arrangement of remaining groups observed. While observing you have to proceed from the group of highest priority to the group of second priority and then to the third.

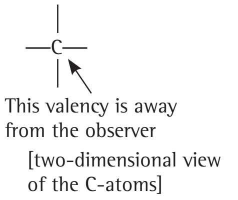
(i) If your eye travels in a clockwise direction, the configuration is called *R* [Latin *rectus* = right]

(ii) If your eye travels anticlockwise, the configuration is called *S* [Latin *sinister* = left]

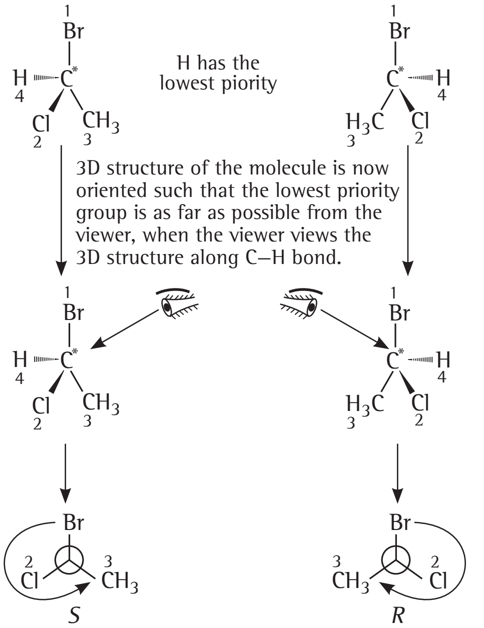
Two positioning of the lowest priority group down and away from the observer can be assumed easily in three dimensions but difficult a bit in two dimensions. *e.g.*,



You can easily position the group of lowest priority away from you if you see the C-atom three dimensionally



For positioning the group of lowest priority away from you, you have to perform pair inter changes among the groups attached to asymmetric C-atom



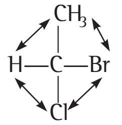
S
Highest to lowest priority is counter clockwise, hence, *S* configuration

R
Highest to lowest priority is clockwise, hence, *R* configuration

While studying, it is not possible always to keep the three dimensional view of C-atom, we perform and learn the complete exercise in accordance with two dimensional view. Thus, we have to learn the pair interchanging in detail which can be done easily if we keep following 4 points in our mind.

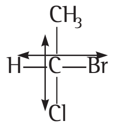
(i) Our target is to position the group with lowest priority to the valency away from the observer.

(ii) This target can be achieved by pair interchanges that will always be diagonal. That means



The interchange operations are shown by double headed arrows

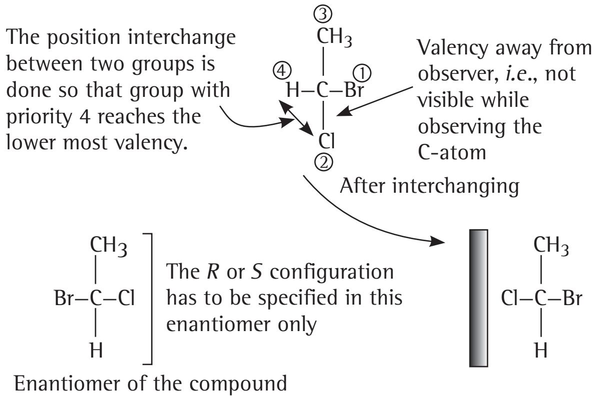
The possible ways of pair interchanging



These ways of interchanging are not possible

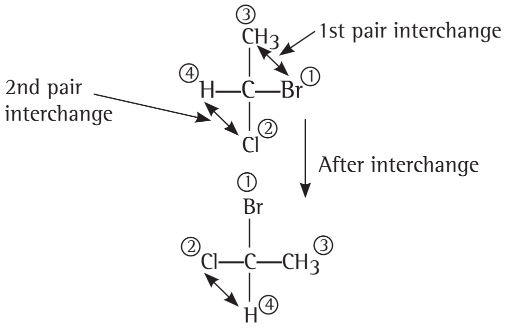
(iii) The single pair (or odd number) interchanging in Fischer projection inverts the configuration.

That means, now the enantiomer of the compound formed will give the absolute configuration of compound, *e.g.,*



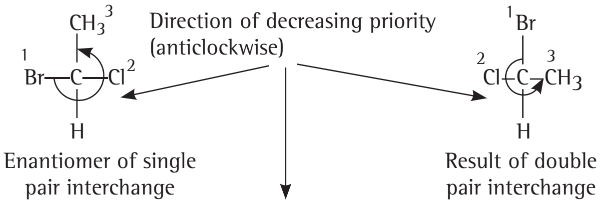
(iv) The two pair interchanges (or even number interchanges) retains the original configuration.

That is if we perform 2 pair exchanges then there is no need of enantiomer formation as seen above, *e.g.*, in the compound written above



Step III Specify the direction of decreasing priority of the three groups (1 → 2 → 3) after ignoring 4th one.

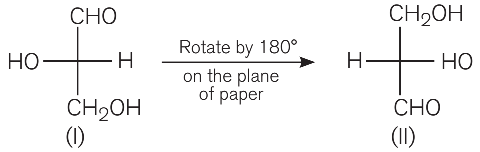
If the groups are arranged in clockwise fashion then the configuration is *R* and if these occur in anticlockwise manner, the configuration is *S*. *e.g.,* if we look at the result of single pair and double pair interchanges *i.e.,*



Hence, the configuration of the C-atom in compound is *S*.

Thus, in the above example the configuration is *S* because the groups 1, 2 and 3 are arranged in anticlockwise fashion (shown by circular arc).

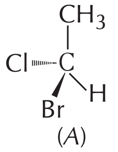
Caution Point *Rotation of Fischer projection by 180° on the plane of paper results in the equivalent Fischer projection.*



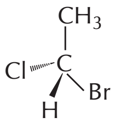
(I) and (II) are equivalent Fischer projections.

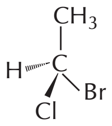
Sample Problem 15

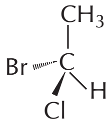
In which of the following representations given below spatial arrangement of group/atom same from that given in structure 'A'? **[NCERT Exemplar]**

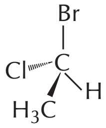


(A)

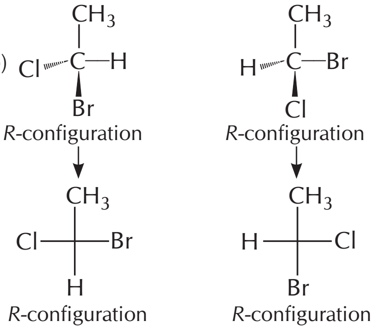
(a) 

(b) 

(c) 

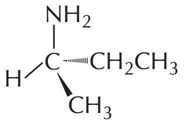
(d) 

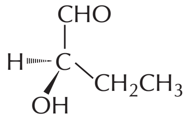
Interpret (b)



Sample Problem 16

The configuration of which of the following is not R?

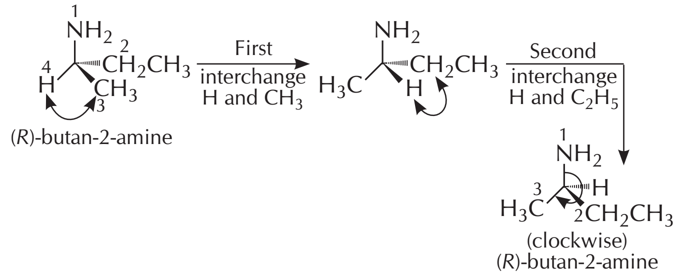
(a) 

(b) 

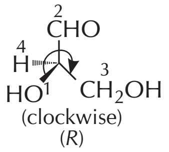
(c) 

(d) *None of these*

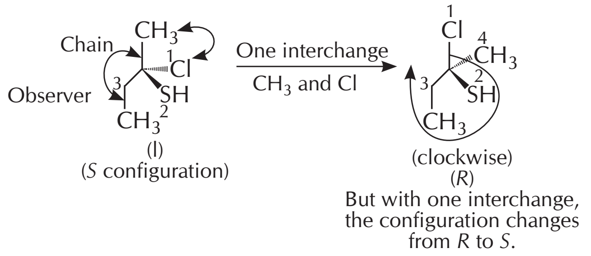
Interpret (c) The lowest priority ligand (H) is in the plane (*i.e.*, not on the dotted line) so it makes two interchanges such that H is projected away from the observer. (Priority order: —NH$_2$ > —CH$_2$CH$_3$ > — CH$_3$ > — H)



The lowest priority ligand (H) is on the dotted line. *R* and *S* can be assigned directly from the priority rule. (—OH > —CHO > — CH$_2$OH > — H)

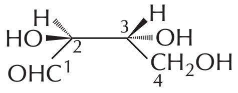


Lowest priority ligand (—CH$_3$) is in the plane (*i.e.*, not on the dotted line). So make one interchange so that (—CH$_3$) is projected away from the observer.
(Priority order.—Cl > —SH > — CH$_2$CH$_3$ > — CH$_3$



Sample Problem 17

Assign R-S configuration to the following compound



(a) C – 2 (*R*), C – 3(*S*)
(b) C – 2 (*S*), C – 3(*R*)
(c) C – 2 (*S*), C – 3(*S*)
(d) C – 2 (*R*), C – 3(*R*)

Interpret (b) Priority order at C2

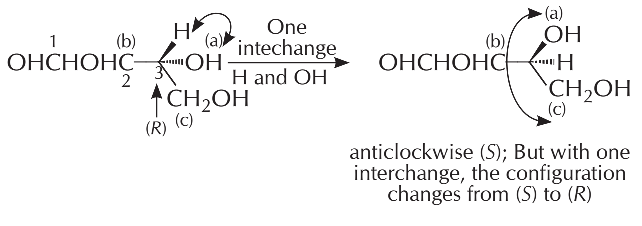
$$\underset{a}{—\text{OH}} > \underset{b}{—\text{CHO}} > \underset{c}{\text{CH(OH)CH}_2\text{OH}} > \underset{d}{—\text{H}}$$

Written as $a > b > c > d$

First assign *R/S* at C-2. Here, the lowest ligand is in the plane. (*i.e.*, on the dotted line). Priority sequence is anticlockwise hence the configuration at C-2 is *S*.

Priority order at C-3 : —OH > —CHOHCHO > CH$_2$OH > H.

Here, H is not on the dotted line, so make one interchange of H and — OH so that — OH is projected away from the observer.



So, the configuration is (2*S*, 3*R*).

Caution Point *R and S are the only configurations assigned to a particular three dimensional arrangement and these are not related to the optical rotation of the compound.*

If the absolute configuration about an asymmetric carbon is R then it is not necessary that it will rotate the plane of polarized like clockwise, it may rotate it anticlockwise also.

Measurement of Optical Activity

The optical activity of a compound can be detected and measured by means of a **polarimeter.** When a solution of a known concentration of an optically active compound is placed in a polarimeter, the beam of polarised light is rotated through a certain number of degrees either to the right (clockwise) or to the left (anticlockwise). This degree is measured and called **rotation** produced by the solution.

The degree of rotation depends upon the number of molecules of the compound encountered by light along its path. This degree of rotation, if measured, is called **specific rotation** and can be defined as the rotation produced by a solution of 10 cm length and unit concentration (1 g/mL) for the given λ of light at the given temperature. Thus, for a system in which plane of polarised light is rotated through α degrees at a temperature of t°C and using the sodium-D lines as the source, the specific rotation $[\alpha]_D^t$ is given by

$$[\alpha]_D^t = 100\,\alpha / l \times c$$

Here, l = length of the fluid filled tube in decimeters
(10 cm = 1 decimetre)
c = number of grams per 100 mL of solution

The specific rotation varies both with light wavelength and temperature.

Sample Problem 18 *The specific rotation of a pure enantiomer is +10°. Its observed rotation if it is isolated from a reaction with*

(*i*) *30% racemisation and 70% retention,*
(*ii*) *70% racemisation and 30% inversion are respectively*

(*a*) 7, 3	(*b*) 3, 7
(*c*) +7, −3	(*d*) −7, −3

Interpret (*c*) (i) $[\alpha]_{\text{obs}} = 0.70 \times +(10^\circ) = +7.0^\circ$

(ii) 30% inversion, with inversion specific rotation is (−10°)

$$\therefore \qquad [\alpha]_{\text{obs}} = 0.30 \times (-10^\circ) = -3.0^\circ$$

Sample Problem 19 *What is the percentage composition of (–) form a mixture of two enantiomers whose rotation is −10°? The specific rotation of pure enantiomers is −20°.*

(*a*) 25% (*b*) 10% (*c*) 50% (*d*) 15%

Interpret (*d*) Optical purity (OP) of sample $= \dfrac{[\alpha]_{\text{obs}}}{[\alpha]_D}$

$$= \frac{-10^\circ \times 100}{-20^\circ} = 50\%$$

So, 50% of the mixture consists of (–) enantiomer and 50% is the racemate [*i.e.*, 25% (+) and 25% (–) form].
Total percentage of (–) form = 50% + 25% = 75%
Total percentage of (+) form = 25%

Sample Problem 20 *An aqueous solution containing 10 g of optically pure fructose was diluted to 500 mL water and placed in a polarimeter tube 20 cm long. The measured rotation was −5.0°. To this solution, 500 mL of a solution containing* 10 g of racemic fructose is added. What will be the change in specific rotation?

(*a*) −62.5° (*b*) +62.5° (*c*) −12.5° (*d*) +12.5°

Interpret (*b*) As we know, 20 cm = 2 dm

$$[\alpha]_D = \frac{\theta}{l \times C} = \frac{-5.0^\circ}{2\text{ dm} \times 10\text{ g}/500\text{ mL}} = -125$$

Total volume of solution = 500 + 500 = 1000 mL

Mass per mL of pure fructose = 10 / 1000 = 0.01 g mL^{-1}

Mass per mL of mixture = (10 + 10 = 20) = 20 / 1000 = 0.02 g mL^{-1}

$$\text{OP (optical purity)} = \frac{[\alpha]_{\text{obs}}\text{ of mixture}}{[\alpha]_D\text{ of pure form}} \propto \frac{\text{Mass per mL of pure form}}{\text{Mass per mL of mixture}}$$

$$= \frac{0.01}{0.02} = 0.5 \qquad (\because l \text{ is constant})$$

New, $[\alpha]_D = -125^\circ \times 0.5 = -\,62.5^\circ$

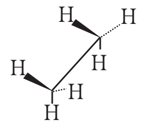
Change in specific rotation = −62.5 − (−125) = 62.5°

Check Point 2

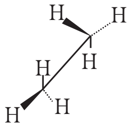
1. *Trans* form is more stable as compared to *cis* form and has zero dipole moment. Explain why?
2. Geometrical isomerism is usually exhibited by the compounds having at least one double bond between two atoms. Cyclic compounds, however, have no double bond, but exhibit geometrical isomerism. Explain.
3. Do all biphenyl derivatives are optically active? If not, mention the condition for optical activity.
4. Is presence of asymmetric carbon atom, the main condition for exhibiting optical isomerism?

14.9 Conformations or Conformers

The σ electron cloud joining the carbon atoms in alkanes is cylindrically symmetrical about a line joining the two carbon nuclei; hence bond strength should be the same for all possible arrangements. Different arrangements of atoms that can be converted into one another by rotation about single bonds are called *conformations*. Arrangement I is called the *eclipsed conformation*; arrangement II is called the *staggered conformation*. (The infinite intermediate conformations in between the above two are called **skew conformations).**



arrangement I



arrangement II

Caution Point *Conformers are also termed as rotamers and conformational isomerism as rotamerisms.*

Conformations of Ethane

In ethane molecule ($CH_3—CH_3$), the two carbon atoms are bonded by a single covalent bond. If one of the carbon atoms (methyl group) is kept fixed and the other is rotated about the C—C bond, an infinite number of arrangements of the hydrogen atoms attached to one carbon atom with respect to other are possible. These infinite number of different arrangements are called **conformations.**

To represent these conformations we can draw three dimensional pictures.

However, chemists represent conformations in two simple ways as shown below

(a) Saw Horse Representation

In it, we view carbon-carbon bond from an oblique angle and indicate spatial arrangements by showing all the C—H bonds as shown in figure 14.2.

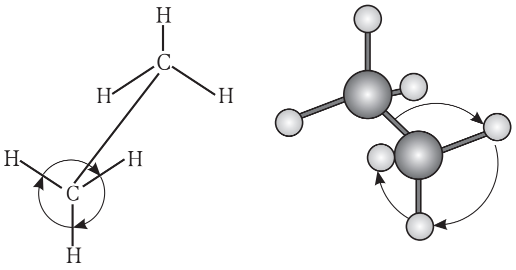


Fig. 14.2 Saw Horse representation showing rotation around C—C single bond in ethane

(b) Newmann Projection

It is a simple method to represent the conformations. In this method, the two carbon atoms forming the σ-bond are represented by two circles; one behind the other so that only the front carbon is seen. The C—H bonds of the front carbon are depicted from the centre of the circle while C—H bonds of the back carbon are drawn from the circumference of the circle.

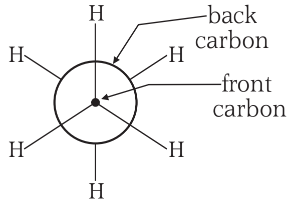


Fig. 14.3 Newmann projections of ethane

Out of all the conformations possible for ethane, only two extreme conformations are important i.e.,

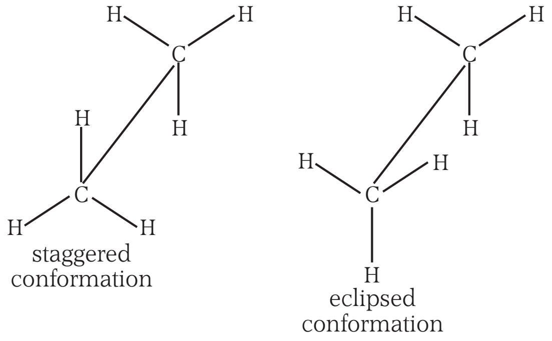
(a) Staggered Conformation

In this arrangement, the hydrogens of the two carbon atoms are staggered with respect to one another. As a result, they are at maximum distance apart and have minimum repulsion between them.

(b) Eclipsed Conformation

In this conformation, the hydrogens of one carbon atom are directly behind those of the other. Consequently, the repulsion in these atoms is maximum.

The saw horse projections of these conformations are represented in the figure below.

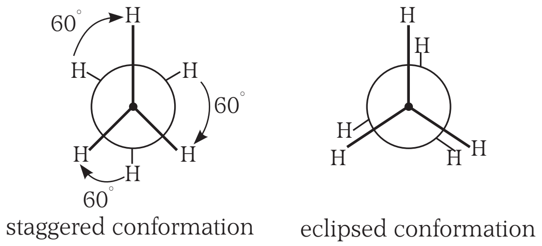


staggered conformation

eclipsed conformation

Fig. 14.4 Saw Horse representation of staggered and eclipsed conformations of ethane

The Newmann projections for staggered and eclipsed conformations of ethane are shown in figure below. It is clear that when the staggered conformation is rotated through an angle of 60°, it changes to eclipsed conformation and similarly, when eclipsed conformation is rotated through the same angle, it gives back the staggered conformation.



staggered conformation

eclipsed conformation

Fig. 14.5 Newmann projections of staggered and eclipsed conformations of ethane

Relative Stabilities of the Conformations of Ethane

The two conformations of ethane differ in their relative stabilities. The staggered conformation has minimum repulsions between the H-atoms attached tetrahedrally to the two carbon atoms. On the other hand, the eclipsed conformation has maximum force of repulsion between H-atoms. Therefore, **the staggered conformation is more stable than the eclipsed conformation.** The difference in the energy contents of the staggered and eclipsed conformations is 12.5kJ mol^{-1}. This small barrier to rotation is also called torsional barrier of the single bond. However, this energy difference is not large enough to prevent rotation Even at ordinary temperatures the molecules have thermal or kinetic energy to overcome this energy barrier. Therefore, the two conformations of ethane go on changing from one form to another thus consequently, it is not possible to isolate the different conformations of ethane.

The variation of energy *versus* rotation about the C—C bond has been shown in the following figure.

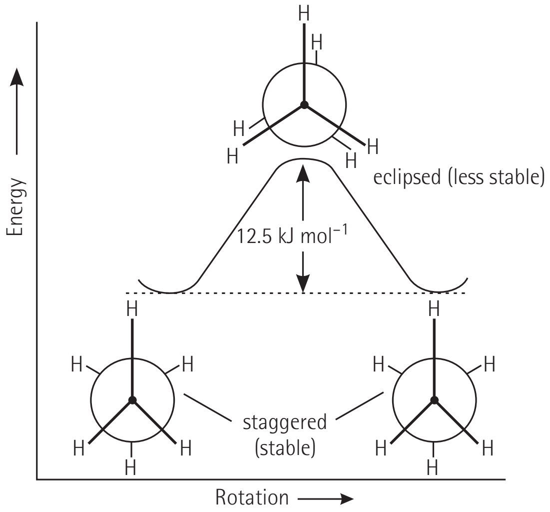


Fig. 14.6 The variation of energy *versus* rotation about C—C bond

The difference in the energy of various conformations constitutes an energy barrier in rotation. For free rotation energy barrier is 0.6 kcal/mol.

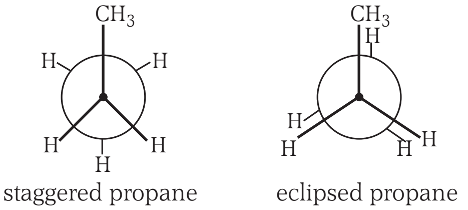
For restricted rotation, energy barrier is in between > 0.6 and < 16 kcal/mol.

For frozen rotation, energy barrier is ≥ 16 kcal/mol.

Caution Point *The dihedral angle between the* C—H *bonds on adjacent carbons in staggered and eclipsed conformations of ethane are* 180° *and* 0° *respectively whereas between the two methyl groups in the gauche and anti conformations of n-butane, these are* 60° *and* 180° *respectively.*

Conformations of Propane

The next higher member in alkane series, *i.e.,* propane ($CH_3CH_2CH_3$) also has two extreme conformations, *i.e..*, **staggered conformation** and **eclipsed conformation.** In figure only Newmann projections are shown for simplicity. However, the energy barrier in propane is 14 kJ mol^{-1}, which is slightly higher than that in ethane.



staggered propane eclipsed propane

Fig. 14.7 Newmann projections of propane

In the eclipsed conformation of propane, there are two ethane type H—H interactions and an additional interaction between C—H bond and C— C bond (of methyl group). The variation of energy *versus* rotation about C— C bond is shown in the figure.

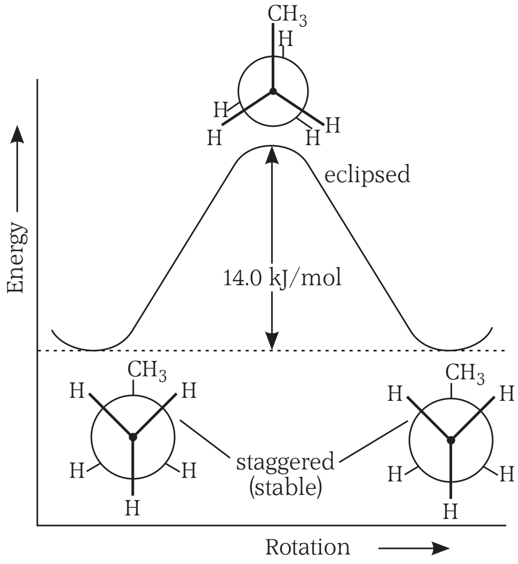
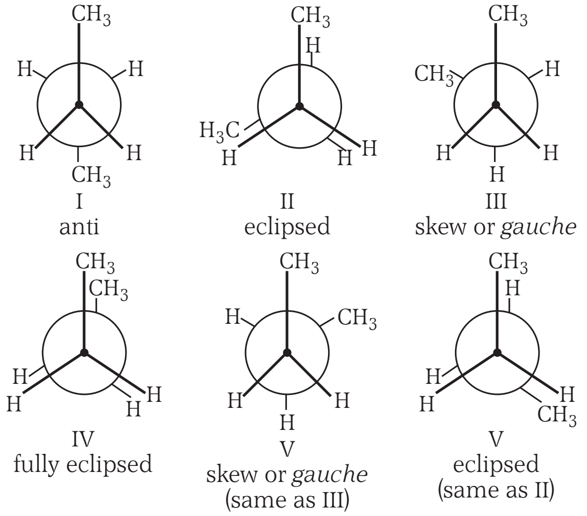


Fig. 14.8 The variation of energy *versus* rotation about C—C bond in propane

Conformations of Butane

As the alkane molecule becomes larger, the conformation situation becomes more complex. As in butane ($CH_3CH_2CH_2CH_3$), for example, the rotation about the single bond between two inner carbon atoms (C_2 and C_3) is considered. In this case, all the staggered as well as eclipsed conformations will not have same stability and energy because of different types of interaction between C—C (of methyl) and C—H bonds.

The lowest energy conformation will be the one, in which the two methyl groups are as far apart as possible *i.e.,* 180° away from each other. The conformation will be maximum staggered and is called anti conformation (marked I). Other conformations can be obtained by rotating one of the C_2 or C_3 carbon atoms roughly at an **angle of 60°** as shown below.



I
anti

II
eclipsed

III
skew or *gauche*

IV
fully eclipsed

V
skew or *gauche*
(same as III)

V
eclipsed
(same as II)

Fig. 14.9 Different conformations of butane

As is clear from the above Newmann projections, the gauche or skew conformations (II and V) are also staggered. However, in these conformations, the methyl groups are so close that they repel each other. This repulsion causes *gauche* conformations to have about 3.8 kJ mol^{-1} more energy than anti conformation. The conformations II and V are eclipsed conformations. These are unstable because of repulsions. They have 14.6 kJ mol^{-1} energy and are less stable than anti conformation. Conformation IV is also eclipsed and it is least stable having energy 18.4 kJ mol^{-1} more than anti conformation. This is because of repulsion between methyl-methyl groups which are very close together. It is called fully eclipsed conformation.

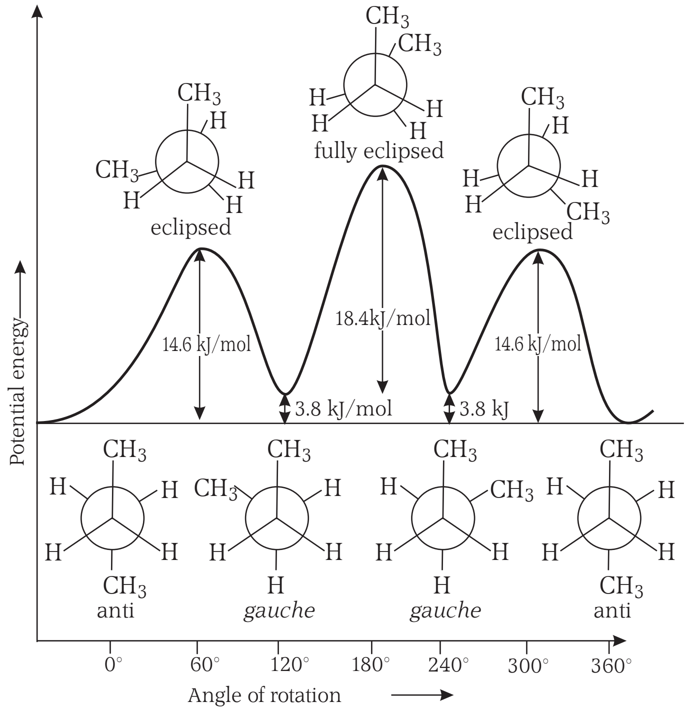


Fig. 14.10 Energy change during rotation about $C_2 - C_3$ bond of *n*-butane

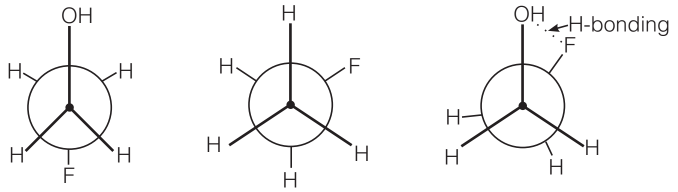
$$\overset{1}{C}H_3-\overset{2}{C}H_2-\overset{3}{C}H_2-\overset{4}{C}H_3$$

The order of stability of these conformations is

Anti > Skew or *Gauche* > Eclipsed > Fully eclipsed

The energy differences between various conformations is shown fig. 14.10.

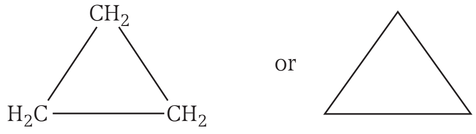
Caution Point *If there exist a possibility of H-bonding or any other such interaction then gauche form may become more stable than anti (staggered) due to H-bonding as shown below.*



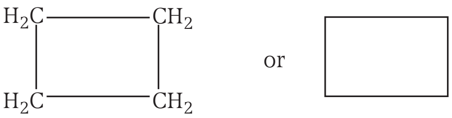
less stable
less stable
most stable

Conformations in Cycloalkanes

Conformational isomerism has also been observed in cycloalkane molecules. Cyclopropane and cyclobutane are planar molecules having bond angles of 60° and 90° respectively.



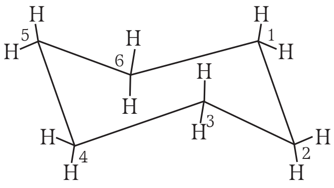
cyclopropane (bond angle = 60°)



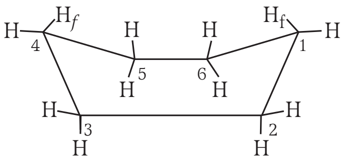
cyclobutane (bond angle = 90°)

The bond angles in these molecules are quite different from the normal tetrahedral bond angle of 109.5°, which is a normal angle for sp^3 hybridised carbon atoms. As a result of deviation from normal bond angle, there is a considerable strain in the molecules of these compounds. Therefore, these are quite reactive. Obviously, cyclopropane with a bond angle of 60° is more strained and reactive than cyclobutane (bond angle 90°).

In cyclopentane, the bond angle is 108° which is quite close to normal tetrahedral angle. Therefore, cyclopentane has very less strain and is, therefore, stable. Similarly, the bond angle in cyclohexane ring is 120° and is expected to be quite reactive and strained. However, cyclohexane is quite stable.



chair conformation

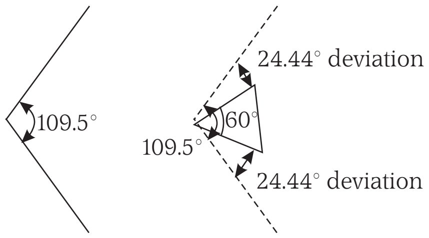


boat conformation

The stability of cyclohexane indicates that the molecule avoids strain by assuming conformation in which all the bond angles between carbon atoms are close to tetrahedral angle of 109.5°. Therefore, cyclohexane adopts a non-planar structure. *The two important conformations for cyclohexane are the chair form and the boat form as shown in the figure above.* These structures are also called **puckered ring structures**. The names of these forms are due to resemblance of their shapes with chair and boat respectively.

Baeyer's Strain Theory

The German chemist **Baeyer** was the first to suggest that the instability of small ring compounds was due to angle strain. This theory is known as **Baeyer's strain theory**. Baeyer strain theory was based upon the assumption that when an open chain organic compound having the normal bond angle 109.5° is converted into a cyclic compound, a definite distortion of this normal angle takes place leading to the development of a strain in the molecule.



Baeyer assumed that cyclic rings are planar. Assuming this, the amount of strain in various cycloalkanes can be expressed in terms of angle of deviation (d).

$$\text{Angle strain} \propto d \propto \frac{1}{\text{inner angle } (\alpha)}$$

$$\text{Stability} \propto \frac{1}{d} \propto \text{inner angle } (\alpha)$$

where, d = angle of deviation

α = inner angle in cycloalkane ring

Stabilities of the Conformations of Cyclohexane

The chair conformation of cyclohexane is more stable than the boat conformation due to the following reasons

(i) In chair conformation, the adjacent hydrogen atoms on all the neighbouring carbon atoms are quite staggered and the force of repulsion in between them is the minimum. However, in the boat conformation, the adjacent hydrogen atoms on C_2 — C_3 and C_5 — C_6 atoms are eclipsed.

(ii) The two hydrogen atoms (marked as H_f) bonded to the C_1 and C_4 atoms in boat conformation are quite close (distance = 183 pm) and repel each other. These are called **flag pole hydrogens.** Therefore, the energy of the boat conformation is more than that of chair conformation.

The energy of the boat conformation of cyclohexane is about 44 kJ mol^{-1} more than that chair conformation. Therefore, cyclohexane exists mainly in the chair form.

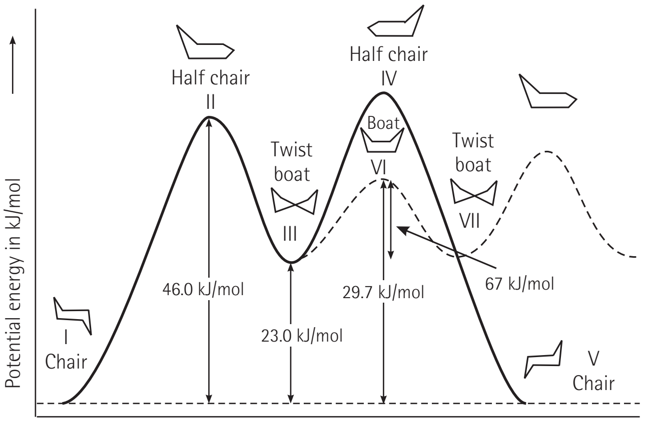


Fig. 14.11 Relative potential energies of the various conformations of cyclohexane

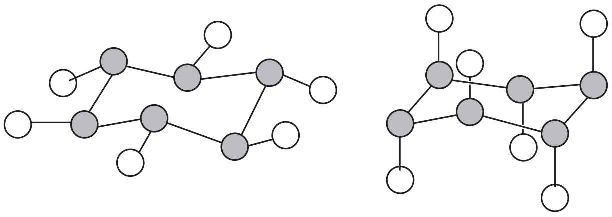
Caution Point *The two twist boat conformations are just mirror images of each other and are called enantiomeric formations.*

Sample Problem 21 *In the boat conformation of cyclohexane, the most destabilising interaction is*

(a) 1,3-*diequatorial*
(b) *eclipising*
(c) *flagpole-flagpole*
(d) 1,3-*diaxial*

Interpret (c) Boat conformation of cyclohexane has two types of destabilizing interaction, *i.e.*, eclipsing and flagpole-flagpole. Out of these flagpole-flagpole interaction is the most destabilizing.

Let us return to the model of the chair conformation of cyclohexane. Although the cyclohexane ring is not flat,

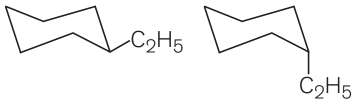


equatorial bonds axial bonds

Fig. 14.12 Chair cyclohexane : equatorial and axial bonds

we can consider that the carbon atoms lie roughly in a plane. If we look at the molecule in this way, we see that the hydrogen atoms occupy two kinds of position : six hydrogens lie in the plane, while six hydrogens lie above or below the plane. The bonds holding the hydrogens that are in the plane of the ring lie in a belt about the "equator" of the ring, and are called **equatorial bonds**. The bonds holding the hydrogen atoms that are above and below the plane are pointed along an axis perpendicular to the plane and are called **axial bonds**. In the chair conformation each carbon atom has one equatorial bond and one axial bond.

Caution Point *The structure of cyclohexane in which two or more bulkier groups ocupy equatorial positions is more stable e.g.,*



(more stable) (less stable)

Check Point 3

1. Which conformation in *n*-propane is more stable and why?
2. Draw Newmann's projection for the less stable staggered form of butane. Also give the reason for the less stability of this form.
3. Cyclohexane is expected to be quite reactive and strained but it is stable. Explain, why?
4. Why *gauche* conformation of 2-amino-3-hydroxybutane is more stable as compared to its anti form?

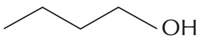
WORKED OUT Examples

Example 1 *Number of isomers represented by molecular formula* $C_4H_{10}O$ *is*

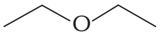
(a) 4 (b) 6
(c) 7 (d) 8

Solution (c) The following structures are possible for the molecular formula $C_4H_{10}O$.

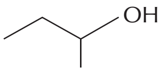
(i)



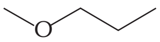
(ii)



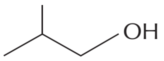
(iii)



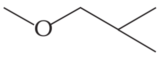
(iv)



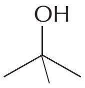
(v)



(vi)



(vii)

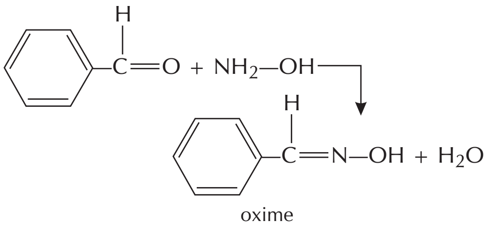


Out of these, four are alcohols and three are ethers.

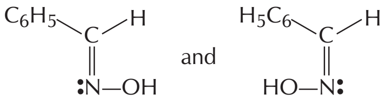
Example 2 *Types of isomerism shown by the product of the reaction between benzaldehyde and hydroxyl amine is*

(a) *syn-anti* (b) *cis-trans*
(c) *E-Z* (d) *d and l*

Solution (a)



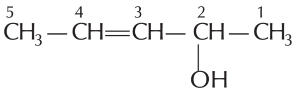
Oximes show *syn* and *anti* isomers as



Example 3 *The number of stereoisomers for pent-3-en-2-ol is*

(a) 3 (b) 4 (c) 5 (d) 2

Solution (b)



$$\overset{5}{C}H_3-\overset{4}{C}H=\overset{3}{C}H-\underset{OH}{\overset{2}{C}H}-\overset{1}{C}H_3$$

The number of stereoisomers = number of optical isomers + number of geometrical isomers

In this compound,

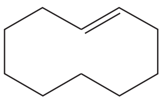
the number of optical isomers $= 2^1 = 2$

the number of geometrical isomers $= 2^1 = 2$

Thus, the number of stereoisomers $= 2 + 2 = 4$

Example 4 *Which of the following will show geometrical isomerism?*

(a) *Methyl cyclohexane* (b)



(b) $(CH_3)_2C{=}NOH$ (d) $CH_3CH{=}NOH$

Solution (d) Since, the molecules given in option (a), (b) and (c) are symmetrical, they do not exhibit geometrical isomerism.

Example 5 *The number of enantiomers and meso forms for the compound,*

$HOOC—CH(CH_3)—CHOH—CHBr—CHOHCH(CH_3)—COOH$

are respectively,

(a) 12, 2 (b) 12, 4 (c) 8, 4 (d) 8, 2

Solution (b) Since, the compound can be divided into two equal halves and has five asymmetric carbon atoms, the number of

$$\text{enantiomers} = 2^{n-1} - 2^{\left(\frac{n-1}{2}\right)}$$

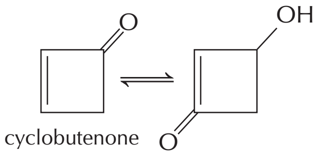
$$= 2^{5-1} - 2^2 = 2^4 - 2^2 = 16 - 4 = 12$$

$$\text{Number of } meso \text{ forms} = 2^{\left(\frac{n-1}{2}\right)} = 2^2 = 4$$

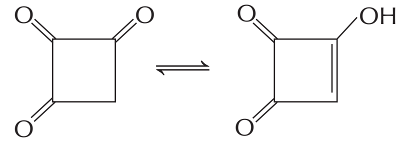
Example 6 *Which of the following is more easily enolised?*

(a) *Cyclobutenone* (b) *Triketocyclobutane*
(c) *Both are equally enolised* (d) *Nothing can be said*

Solution (b)



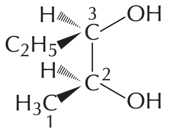
It doesn't enolise because its enol is a flat ring with $4n\pi\,\bar{e}$' s (*i.e.*, $4n\pi\,\bar{e}$'s $n = 1$) and is antiaromatic.



triketocyclobutane

It enolises because its enol has $(4n+2)\ \pi$ (*i.e.*, $2\pi\ \bar{e}'s\ n=0$) and is stabilised by aromaticity.

Example 7

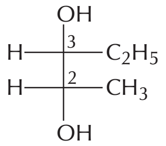


In the above compound, the configuration of C_2 and C_3 are, respectively

(*a*) *R*, *R* (*b*) *S*, *S*

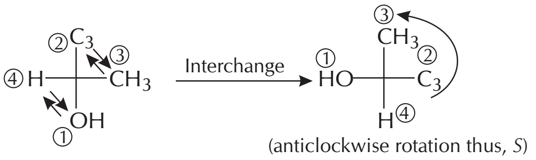
(*c*) *R*, *S* (*d*) *S*, *R*

Solution (*d*) The Fischer projection formula for the given compound is



For C_2 carbon, the order of priority is

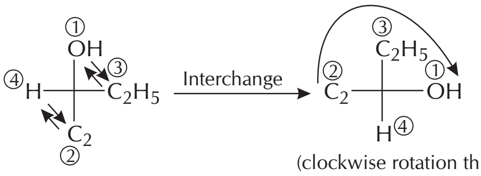
$$-OH > -C_3 > -CH_3 > -H$$



(anticlockwise rotation thus, *S*)

For C_3 carbon, the order of priority is

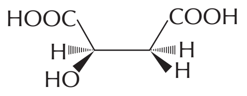
$$-OH > -C_2 > -C_2H_5 > -H$$

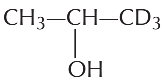


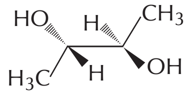
(clockwise rotation thus, *R*)

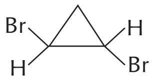
Hence, the configuration of C_2 and C_3 are respectively *S* and *R*.

Example 8 *Which of the following compounds will not show optical activity?*

(*a*)


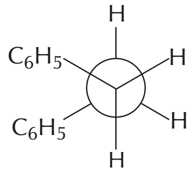
(*b*)

$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CD_3$

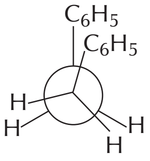
(*c*)


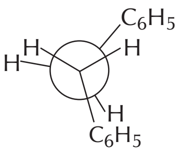
(*d*)


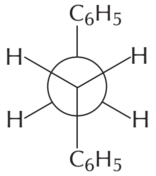
Solution (*c*) The compound given in option (*c*) is optically inactive while all others show optical activity, due to the presence of chiral carbon atom and absence of symmetry elements.

Example 9 *The most stable conformation of 1,2-diphenyl ethane is*

(*a*)


(*b*)


(*c*)


(*d*)


Solution (*d*) In conformation '*d*' the bulkier group are present as far away as possible, thus, there is minimum repulsion. Hence, this form is most stable.

Example 10 *Which of the following cycloalkanes involve maximum torsional strain?*

(*a*) *Cyclopropane* (*b*) *Cyclobutane*

(*c*) *Cyclopentane* (*d*) *Cyclohexane*

Solution (*a*) According to Baeyer's strain theory, the amount of the strain is directly proportional to the angle of deviation.

$$\text{Angle of deviation, } d = \frac{1}{2}(109°28' - \text{valency angle})$$

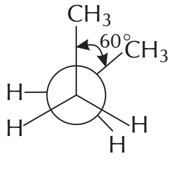
d is minimum in case of cyclohexane and maximum in case of cyclopropane, thus torsional strain is maximum in cyclopropane.

Example 11 *Dihedral angle between two methyl groups of n-butane in the gauche and anti forms are*

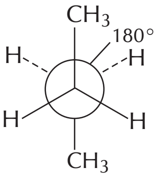
(*a*) 60°, 0° (*b*) 0°, 60°

(*c*) 60°, 180° (*d*) 180°, 60°

Solution (*c*)



gauche form



anti form

(The angle between C—C and C—H bonds on adjacent carbon atoms in any conformation is called dihedral angle.)

Hence, the dihedral angle in case of gauche is 60° and in anti form is 180°.

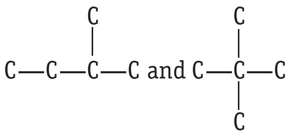
Start Practice for JEE Main

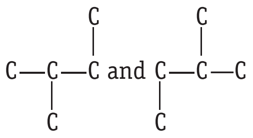
Round I (Topically Divided Problems)

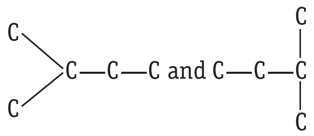
Structural Isomerism

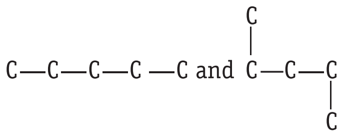
1. Compounds having the same molecular formula but different properties are called
(a) isotopes (b) isobars
(c) isomers (d) isomorphs

2. Which pair of carbon skeleton is an example of isomerism?

(a)

$$\mathrm{C-C-\overset{\overset{\displaystyle C}{|}}{C}-C \text{ and } C-\underset{\underset{\displaystyle C}{|}}{\overset{\overset{\displaystyle C}{|}}{C}}-C}$$

(b)

$$\mathrm{C-\underset{\underset{\displaystyle C}{|}}{C}-\overset{\overset{\displaystyle C}{|}}{C} \text{ and } \underset{\underset{\displaystyle C}{|}}{C}-\overset{\overset{\displaystyle C}{|}}{C}-C}$$

(c)

$$\mathrm{(C)_2C-C-C \text{ and } C-C-\underset{\underset{\displaystyle C}{|}}{\overset{\overset{\displaystyle C}{|}}{C}}}$$

(d)

$$\mathrm{C-C-C-C-C \text{ and } \overset{\overset{\displaystyle C}{|}}{C}-C-\underset{\underset{\displaystyle C}{|}}{C}}$$

3. Isomers have essentially identical
(a) structural formula (b) chemical properties
(c) physical properties (d) molecular formula

4. Which of the following is not isomeric with diethyl ether?
(a) Methyl *n*-propyl ether
(b) Butan-1-ol
(c) 2-methyl propan-2-ol
(d) Butan-2-one

5. Which of the following is not an isomer of but-1-yne ?
(a) But-2-yne (b) Buta-1,3-diene
(c) Methyl cyclopropene (d) But-2-ene

6. The compounds R—NO_2 and R—ONO are
(a) geometrical isomers (b) functional isomers
(c) metamers (d) optical isomers

7. Which among the following compounds will show metamerism?
(a) $CH_3COC_3H_7$ (b) $CH_3OC_2H_5$
(c) $CH_3SC_2H_5$ (d) CH_3OCH_3

8. The isomerism observed in alkanes is
(a) metamerism (b) chain isomerism
(c) position isomerism (d) geometrical isomerism

9. The molecular formula of a saturated compound is $C_2H_4Cl_2$. The formula permits the existence of two
(a) functional isomers (b) position isomers
(c) optical isomers (d) *cis-trans* isomers

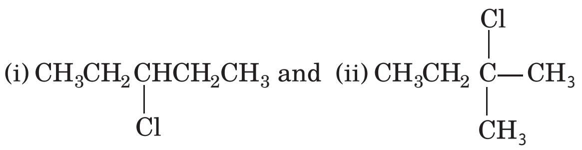
10. An alkane forms isomers if minimum number of C-atom is
(a) 1 (b) 2 (c) 3 (d) 4

11. Maximum number of open chain isomers that an alkene can have with the molecular formula C_4H_8 is
(a) 5 (b) 4 (c) 3 (d) 2

12. C_7H_8O show how many isomers?
(a) 2 (b) 3 (c) 4 (d) 5

13. Total number of isomeric alcohols with formula $C_4H_{10}O$ are
(a) 1 (b) 2
(c) 3 (d) 4

14. Compounds with following formula will show


$$\text{(i) } CH_3CH_2\underset{\underset{\displaystyle Cl}{|}}{C}HCH_2CH_3 \text{ and (ii) } CH_3CH_2\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle Cl}{|}}{C}}-CH_3$$

(a) position and functional isomerism
(b) only chain
(c) chain and functional isomerism
(d) None of the above combinations

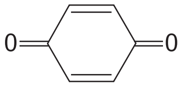
15. But-1-ene and cyclobutane exhibit
- (a) ring chain isomerism
- (b) position isomerism
- (c) tautomerism
- (d) functional isomerism

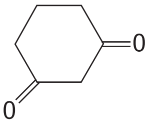
16. The type of isomerism found in urea molecule is
- (a) chain
- (b) position
- (c) tautomerism
- (d) None of these

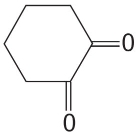
17. Which pair of isomerism is not possible together?
- (a) Chain and position
- (b) Functional and position
- (c) Tautomerism and functional
- (d) All of the above

18. Tautomerism is not exhibited by

(a) $C_6H_5-CH=CH-OH$

(b)


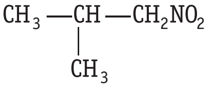
(c)


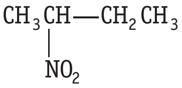
(d)


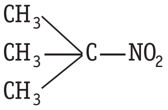
19. The type of isomerism in the molecule of compounds $CH_3CH_2COCH_2CH_3$ and $CH_3CHC(OH)CH_2CH_3$ is referred as
- (a) metamerism
- (b) chain isomerism
- (c) functional isomerism
- (d) tautomerism

20. Which of the following nitroalkane will not show tautomerism?

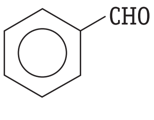
(a) $CH_3CH_2CH_2CH_2NO_2$

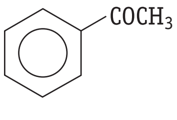
(b)

$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2NO_2$

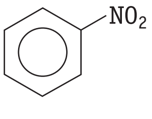
(c)

$CH_3\underset{\underset{NO_2}{|}}{CH}-CH_2CH_3$

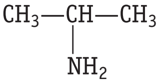
(d)

$(CH_3)_3C-NO_2$

21. Which of the following compounds can exhibit tautomerism?

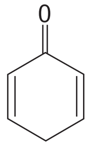
(a)


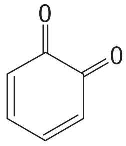
(b)


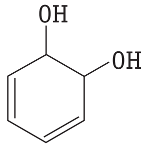
(c)


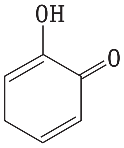
(d)

$CH_3-\underset{\underset{NH_2}{|}}{CH}-CH_3$

22. Which of the following has maximum probability of showing tautomerism?

(a)


(b)


(c)


(d)


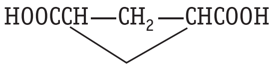
23. Enol form is more stable in
- (a) CH_3CHO
- (b) CH_3COCH_3
- (c) $CH_3COCH_2COOC_2H_5$
- (d) cyclohexanone

24. Keto form is more stable in
- (a) $CH_3COCH_2COOC_2H_5$
- (b) $CH_3COCH_2COCH_3$
- (c) CH_3COCH_3
- (d) $CH_3COCH_2COC_2H_5$

Stereoisomerism

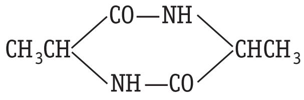
25. Stereoisomers have different
- (a) molecular formula
- (b) structural formula
- (c) configuration
- (d) molecular mass

26. Which class of compounds can exhibit geometrical isomerism?
- (a) $C_6H_5CH=NOH$
- (b) $CH_3CH=CHCH_3$
- (c)


$HOOCCH-CH_2-CHCOOH$

- (d) All of the above

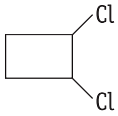
27. Which of the following shows geometrical isomerism?
- (a) 1, 2-dichloroethene
- (b) 1,2-dimethylcyclopropane
- (c)


$CH_3CH\langle{}^{CO-NH}_{NH-CO}\rangle CHCH_3$

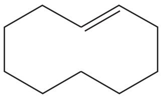
- (d) All of the above

28. The number of isomers of the compound $C_2FClBrI$ is
- (a) 3
- (b) 4
- (c) 5
- (d) 6

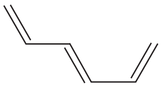
29. Which will form geometrical isomers?

(a)


(b) $CH_3CH=NOH$

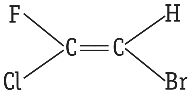
(c)


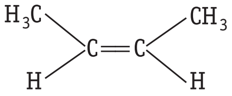
(d) All of these

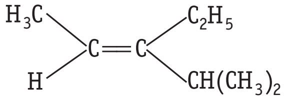
30. In  the double bonds are

(a) *cis, cis* (b) *cis, trans*
(c) *trans, cis* (d) *trans, trans*

31. The '*E*'-isomer is

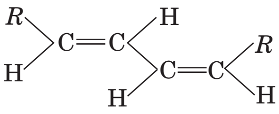
(a) 

(b) 

(c) 

(d) None of the above

32. Number of geometrical isomers for the molecule



are

(a) 2 (b) 3
(c) 6 (d) 5

33. The property by virtue of which a compound can rotate the plane of polarised light is known as

(a) polarisability (b) phosphorescense
(c) optical activity (d) polarisation

34. Chiral molecules are those which are

(a) superimposable on their mirror images
(b) non-superimposable on their mirror images
(c) unstable molecules
(d) capable of showing geometrical isomerism

35. Racemic modification can be resolved by

(a) the use of enzymes
(b) fractional crystallisation
(c) fractional distillation
(d) None of the above

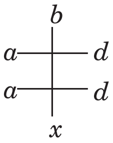
36. Racemic tartaric acid is optically inactive due to

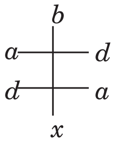
(a) external compensation
(b) internal compensation
(c) presence of plane of symmetry
(d) All of the above

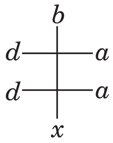
37. (+) and (–) forms of optically active compounds are different in

(a) boiling points
(b) melting points
(c) specific gravity
(d) specific rotation

38. Which of the following is/are *threo* isomers?

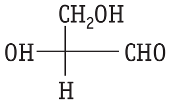

(i)

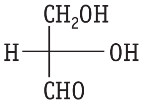

(ii)

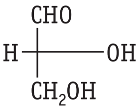

(iii)

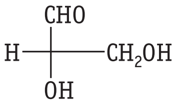
(a) Only (i) (b) Only (ii)
(c) Only (iiii) (d) All (i), (ii) and (iii)

39. Which of the following Fischer projection formula is same as D-glyceraldehyde?

(a) 

(b) 

(c) 

(d) 

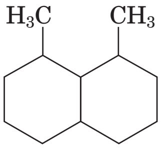
40. A compound contains 2 dissimilar asymmetric C-atoms. The number of optical isomers are

(a) 2 (b) 3 (c) 4 (d) 5

41. How many carbon atoms in the molecule HOOC—$(CHOH)_2$—COOH are asymmetric?

(a) 1 (b) 2
(c) 3 (d) None of these

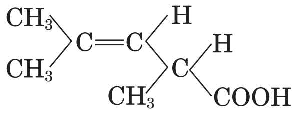
42. Number of chiral centres in



is/are

(a) 1 (b) 2 (c) 3 (d) 4

43. The following compound can exhibits



(a) tautomerism
(b) optical isomerism
(c) geometrical isomerism
(d) geometrical and optical isomerism

44. Which of the following statements is not correct ?

(a) A *meso* compound has chiral centres but exhibits no optical activity
(b) A *meso* compound has no chiral centres and thus is optically inactive
(c) A *meso* compound has molecules in which one half of molecule is superimposable on the other even through chiral centre is present in them
(d) A *meso* compound is optically inactive because the rotation caused by one half of molecule is cancelled by the rotation produced by another half

45. An enantiomerically pure acid is treated with racemic mixture of an alcohol having one chiral carbon. The ester formed will be

(a) optically active mixture
(b) pure enantiomer
(c) *meso* compound
(d) racemic mixture

46. Which of the following will exhibit geometrical isomerism?

(a) Propene
(b) Butene-2
(c) Butene-1
(d) 1,1-dichloro butane

47. During the debromination of *meso*-dibromobutane, the major compound formed will be

(a) *cis*-2-butene
(b) 1-butene
(c) *n*-butane
(d) *trans*-2-butene

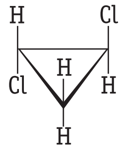
48. Which statement is true?

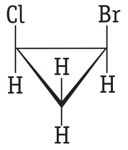
(a) A compound with *R* configuration is the (+) enantiomer
(b) If configuration changes from + to –, that essentially means inversion of configuration takes place
(c) An achiral molecule reacts always with racemic forms, to give a chiral molecule,
(d) By breaking two bonds on the chiral centre configuration changes

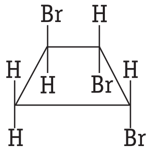
49. The terms stereoisomers, enantiomers and diastereomers will refer

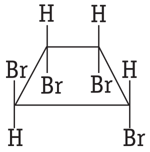
(a) only to configurational isomers including geometrical isomers
(b) only to configurational isomers
(c) to both configurational as well as conformational isomers
(d) to neither configurational nor conformational isomers

50. Which of the following compounds is not optically active?

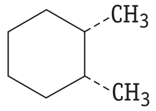
(a)


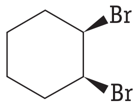
(b)


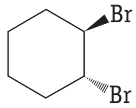
(c)


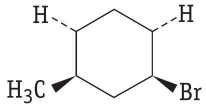
(d)


51. Mark the unidentical compound

(a)


(b)


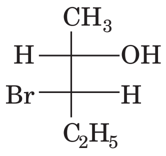
(c)


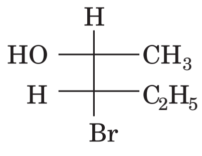
(d)


52. The functional groups —OH, —COOH, —CHO, —OCH_3 attached to a chiral carbon is in the preference order

(a) OH > COOH > CHO > OCH_3
(b) OCH_3 > OH > CHO > COOH
(c) OCH_3 > OH > COOH > CHO
(d) OCH_3 > COOH > CHO > OH

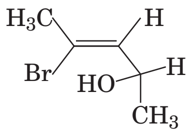
53. The molecules represented by the following two structures are





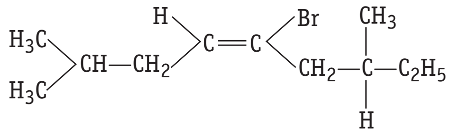
(a) epimers
(b) diastereomers
(c) enantiomers
(d) identical

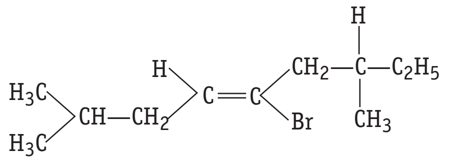
54. The compound, whose stereo chemical formula is written below, exhibits *x*-geometrical isomers and *y*-optical isomers. The value of *x* and *y* are



(a) 4 and 4
(b) 2 and 2
(c) 2 and 4
(d) 4 and 2

55. Correct structures of [*E*][*S*]-5-bromo-2,7-dimethyl, non-4-ene is

(a)


(b)


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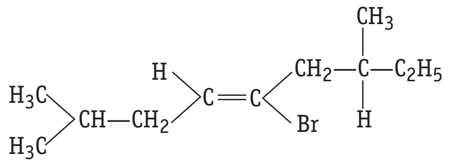
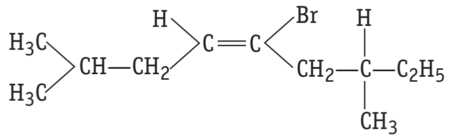


(d)


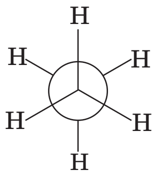
Conformations

56. Incorrect statement is
(a) ethane can have an infinite number of conformations
(b) cyclopropane molecule has considerable angle strain
(c) eclipsed form of ethane is less stable than staggered conformation
(d) staggered conformation possesses maximum energy

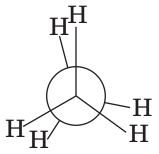
57. The dihedral angle between the two methyl groups in *gauche* conformation of *n*-butane is
(a) 120° (b) 180°
(c) 45° (d) 60°

58. The Baeyer angle strain is minimum in
(a) cyclopropane (b) cyclobutane
(c) cyclopentane (d) cyclohexane

59. Which type of conformation is shown by I and II?



(I)



(II)

(a) I is eclipsed, II is staggered
(b) II is eclipsed, I is staggered
(c) Both are eclipsed
(d) Both are staggered

60. At room temperature the eclipsed and the staggered forms of ethane cannot be isolated because
(a) both the conformers are equally stable
(b) they interconvert rapidly
(c) there is a large energy barrier of rotation about the σ-bond
(d) the energy difference between the conformers is large

61. The most unstable configuration of cyclohexane is
(a) boat (b) chair
(c) twist boat (d) half chair

62. In ethane and cyclohexane which one of the following pairs of conformations are more stable?
(a) Eclipsed and chair conformations
(b) Staggered and chair conformations
(c) Staggered and boat conformations
(d) Eclipsed and boat conformations

63. The most stable configuration of *n* butane will be
(a) skew boat (b) eclipsed
(c) *gauche* (d) staggered-anti

64. The most stable conformation of ethane chlorohydrin at room temperature is
(a) fully eclipsed
(b) partially eclipsed
(c) *gauche*
(d) staggered

65. The correct order of stability of conformations of cyclohexane is
(a) chair > twist boat > boat
(b) twist boat > chair > boat
(c) boat > chair > twist boat
(d) boat > twist boat > chair

66. Which of the following is the correct order of stability of the following four distinct conformation of *n* butane ?
(a) Staggered > *Gauche* > Partially eclipsed > Fully eclipsed
(b) *Gauche* > Staggered > Partially eclipsed > Fully eclipsed
(c) Staggered > Partially eclipsed > *Gauche* > Fully eclipsed
(d) Fully eclipsed > Staggered > Partially eclipsed > *Gauche*

Miscellaneous

67. Which of the following isomerism is shown by ethyl acetoacetate?
(a) Geometrical isomerism
(b) Keto-enol tautomerism
(c) Enantiomerism
(d) Diastereoisomerism

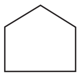
68. Molecular formula $C_5H_{12}O$ will show
(a) position isomerism (b) optical isomerism
(c) functional isomerism (d) All of these

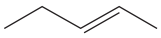
69. False statement is
(a) aprotic solvents increase the enol content in tautomerism
(b) any deviation from the normal bond angles introduces angle strain in molecule
(c) diastereomers have identical physical properties
(d) chain isomers can also be position isomers

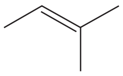
Round II (Mixed Bag)

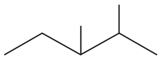
Only One Correct Option

1. Select pair of chain isomers from the following.

(I)


(II)


(III)


(IV)


(a) I and II (b) I and III
(c) I and IV (d) II and III

2. Nitroethane can exhibit one of the following kind of isomerism
(a) metamerism (b) optical activity
(c) tautomerism (d) position isomerism

3. The number of isomeric pentyl alcohols possible is
(a) two (b) four
(c) six (d) eight

4. How many enantiomer pairs are obtained by monochlorination of 2,3-dimethyl butane?
(a) Four (b) Two (c) Three (d) One

5. Consider the following statements

I. Chain and position isomerism are not possible together between two isomers.
II. Tautomerism is a chemical phenomenon which is catalysed by acid as well as base.
III. Tautomers are always metamers.
IV. Tautomers are always functional isomers.

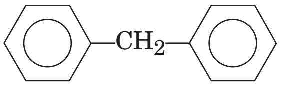
Select the correct answer by using the codes given below.
(a) only III is correct (b) III and IV are correct
(c) I, II and III are correct (d) I ,II and IV are correct

6. Increasing order of expected enol contentis
(a) $CH_3COCH_2CHO > CH_3COCH_3 > CH_3CHO > CH_3COCH_2COCH_3$
(b) $CH_3COCH_2COCH_3 > CH_3COCH_2CHO > CH_3COCH_3 > CH_3CHO$
(c) $CH_3CHO > CH_3COCH_3 > CH_3COCH_2CHO > CH_3COCH_2COCH_3$
(d) $CH_3COCH_3 > CH_3COCH_2COCH_3 > CH_3CHO > CH_3COCH_2CHO$

7. Increasing order of expected keto content
(a) $CH_3COC_2H_5 > CH_3CHO > CH_3COCH_3 > CH_3COCH_2COCH_3$
(b) $CH_3COCH_3 > CH_3CHO > CH_3COC_2H_5 > CH_3COCH_2COCH_3$
(c) $CH_3CHO > CH_3COC_2H_5 > CH_3COCH_3 > CH_3COCH_2COCH_3$
(d) $CH_3COCH_2COCH_3 > CH_3CHO > CH_3COCH_3 > CH_3COC_2H_5$

8. *Meso*-tartaric acid is optically inactive due to the presence of
(a) molecular symmetry
(b) molecular asymmetry
(c) external compensation
(d) two asymmetric C-atoms

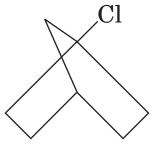
9. The molecular formula of diphenyl methane.



is $C_{13}H_{12}$.

How many structural isomers are possible when one of the hydrogen is replaced by a chlorine atom?
(a) 8 (b) 7
(c) 6 (d) 4

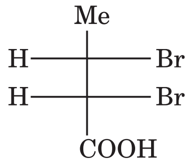
10. The number of chiral carbon atoms present in the molecule

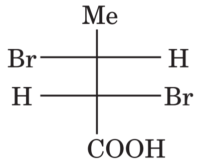


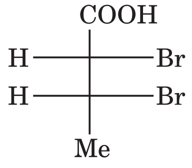
is

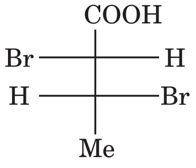
(a) 3 (b) 4
(c) 2 (d) 1

11. Which of the following are diastereomers?

I.


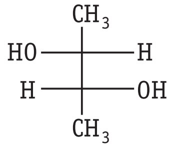
II.


III.


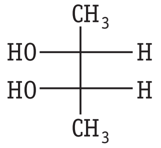
IV.


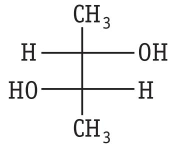
(a) (I) and (III) (b) (II) and (IV)
(c) (I) and (II) (d) None of these

12. Which of the following pairs of compounds are enantiomers?

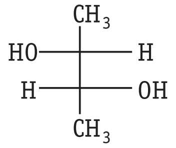
(a)


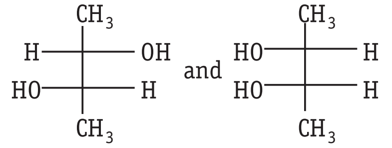
and

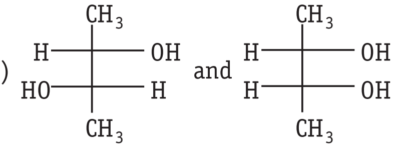


(b)


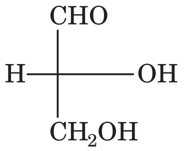
and



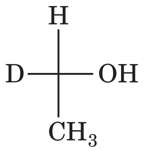
(c)


(d)


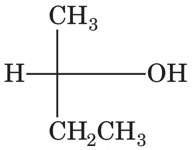
13. The *R*-isomer among the following are



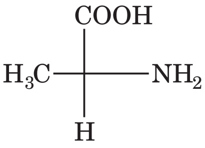
(i)



(ii)



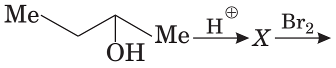
(iii)



(iv)

(a) (i) and (ii) (b) (ii) and (iii)

(c) (iii) and (iv) (d) (i) and (iii)

14. 

Five compounds with formula $C_4H_8Br_2$.

How many structures of (*X*) are possible?

(a) 2 (b) 3 (c) 4 (d) 5

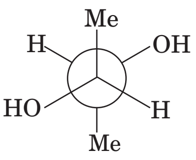
15. Which statement is true for cyclohexane?

(a) It has two possible isomers
(b) It has three conformations
(c) Boat conformation is most stable
(d) Chair and boat conformations differ in energy by 44 kJ/mol

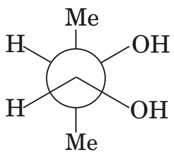
16. The number of structural and configurational isomers of a bromo compound C_5H_9Br obtained by the addition of HBr on 2-pentyne respectively are

(a) 1, 2 (b) 2, 4 (c) 4, 2 (d) 2, 1

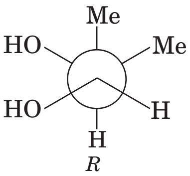
17. Among the following the Newmann projections of *meso*-2,3-butanediol are



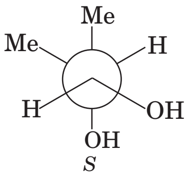
P



Q



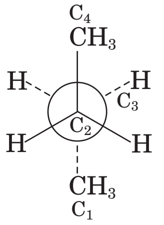
R



S

(a) *P, Q* (b) *P, R*
(c) *R, S* (d) *Q, S*

18. In the given conformation C_2 is rotated about C_2 — C_3 bond anticlockwise by an angle of 120° then the conformation obtained is



(a) fully eclipsed conformation
(b) partially eclipsed conformation
(c) *gauche* conformation
(d) staggered conformation

19. The correct order of stability of conformations of $NH_2—CH_2—CH_2—OH$ is

(a) *gauche* > eclipsed > anti
(b) *gauche* > anti > eclipsed
(c) eclipsed > *gauche* > anti
(d) anti > eclipsed > *gauche*

20. Which of the following statements is/are wrong about the more stability of chair form than boat form?

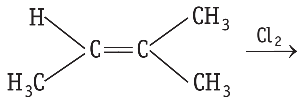
(a) In chair conformation, all the (C—H) bonds in adjacent carbons are in the skew position.
(b) In boat conformation, there are four skew interactions and two eclipsed interactions.
(c) In boat conformation, there is steric repulsion between two flag poles.
(d) In boat conformation, there are three skew interaction and three eclipsed interactions.

21. Which will give chiral molecule?

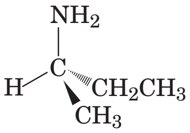
(a) $CH_3COCl \xrightarrow{LiAlH_4}$

(b) $C_2H_5CHO \xrightarrow[H^+/H_2O]{CH_3MgBr}$

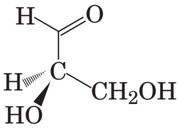
(c) $(CH_3)_2CHC_2H_5 \xrightarrow{Cu}$

(d) 

22. Consider the following structures and choose the correct statements.



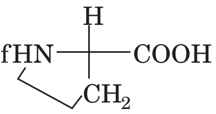
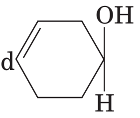
I



II

III

(a) I and II have *R*-configuration
(b) I and III have *R*-configuration
(c) Only III has *S*-configuration
(d) Both (a) and (c) are correct

23. Configuration of  and  are

(a) *R, R* (b) *R, S*
(c) *S, S* (d) *S, R*

24. The specific rotation of a pure enantiomer is + 16°. Its observed rotation if it is isolated from a reaction with 25% racemisation and 75% retention is

(a) −12° (b) +12°
(c) +16° (d) −16°

25. An organic compound contains 66% C and 13.3% H. Its vapour density is 37. The possible number of isomers of all types for the compound is

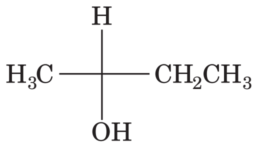
(a) 6 (b) 7
(c) 5 (d) 8

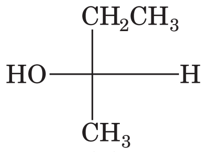
More than One Correct Option

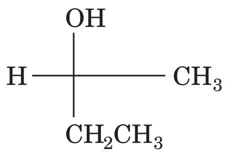
26. Which of the following statements are not correct?

(a) A *meso* compound is optically active because the rotation caused by any molecule is cancelled by an equal and opposite rotation caused by another molecules that is the mirror image of the first
(b) A *meso* compound has chiral centres but exhibits no optical activity
(c) A *meso* compound has no chiral centres and thus exhibits no optical activity
(d) A *meso* compound has molecules which are superimposable on their mirror image even though they contain chiral centres

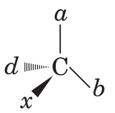
27. Consider the following compounds and choose the correct statement.

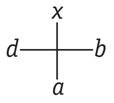
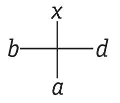

(I)

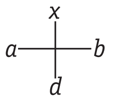
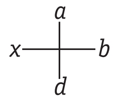

(II)


(III)

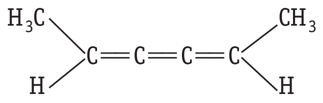
(a) structure (I) and (II) are identical
(b) all are identical
(c) structure (I) and (III) are identical
(d) structure (I) and (III) are different

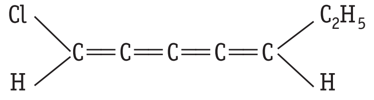
28. The Fischer-projection of the molecule as represented in the wedge formula,  is/are not

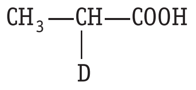
(a)  (b) 

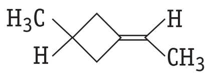
(c)  (d) 

29. Which is/are optically active?

(a) 

(b) 

(c) 
$CH_3-\underset{\underset{D}{|}}{CH}-COOH$

(d) 

Assertion and Reason

Directions (Q. Nos 30 to 34) *Each of these questions contains two statements : Statement* I (*Assertion*) *and Statement* II (*Reason*). *Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes* (*a*), (*b*), (*c*), (*d*) *given below :*

(a) Statement I is true; Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true; Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

30. **Statement I** Staggered form is less stable than the eclipsed form.

Statement II The conformation in which the bond pairs of two central atoms are very far from one another is called staggered form.

31. **Statement I** The conversion of an optically active compound into its enantiomer is called Walden inversion.

Statement II A racemic mixture is optically inactive due to internal compensation.

32. **Statement I** In keto-enol tautomerism of dicarbonyl compounds, the enol form is preferred in contrast to the keto form.

Statement II The enol form is more stable due to resonance.

33. **Statement I** A compound whose molecule has D configuration will always be dextrorotatory.

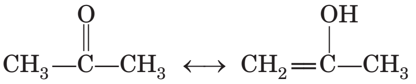
Statement II Compounds having D configuration may be dextrorotatory or levorotatory.

34. **Statement I** $CH_3—CH(Cl)OH$ is a optically active compound.

Statement II Dissymmetry arises in a chemical compound owing to the presence of chiral centre.

Comprehension Based Questions

Directions (Q. Nos 35 to 37) Tautomerism is the phenomenon in which two structural isomers differing in the relative positions of their atoms are spontaneously interconvertable and can exist in dynamic equilibrium. The two forms in tautomeric equilibrium are called tautomers of each other. The interconvertibility of tautomers is a chemical reaction which involves making and breaking of bonds. Tautomers are true isomers, and either of the individual tautomeric forms may be isolated.



$$CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—CH_3 \longleftrightarrow CH_2{=}\overset{\overset{\displaystyle OH}{|}}{C}—CH_3$$

35. In the keto-enol tautomerism of dicarbonyl compounds the enol form is preferred in contrast to the keto form, this is due to
(a) rapid chemical exchange
(b) group rearrangement
(c) presence of carbonyl group on each side of the chain
(d) resonance stabilization of enol form

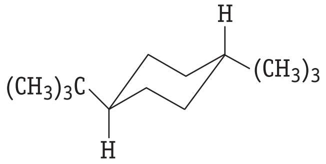
36. Keto-enol isomerism is exhibited by
(a) acetone
(b) benzaldehyde
(c) benzene
(d) formaldehyde

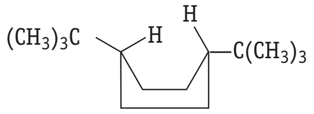
37. Acetophenone can exhibit
(a) functional isomerism
(b) chain isomerism
(c) tautomerism
(d) chain and position isomerism

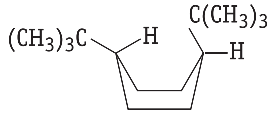
Directions (Q. Nos 38 to 40) Stability of cycloalkanes can be explained on the basis of Baeyer strain theory. This theory is applicable only for cyclopropane, cyclobutane and cyclopentane. Stability of cyclohexane and its derivative can be explained by Mohr's theory. According to this theory cyclohexane exists in two forms chair and boat. The chair form is more stable than the boat form. Every carbon of chair form has an axial and equatorial bonds. Bulky groups are generally present at equatorial position. The preferred conformation of cyclohexane ring is the chain form, but when intramolecular hydrogen bonding is possible between the group 1 and 4 positions, the molecule assume a boat form.

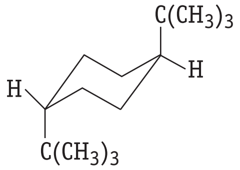
38. According to Baeyer strain theory which cycloalkane is the most stable?
(a) Cyclohexane (b) Cyclopentane
(c) Cyclopropane (d) Cyclobutane

39. Which of the following is most stable conformer of 1,4-ditert butylcyclohexane?

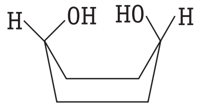
(a)


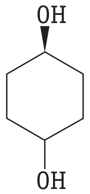
(b)


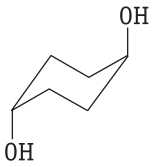
(c)


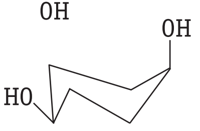
(d)


40. Which form of *trans*-1,4-cyclohexanediol is most stable?

(a)


(b)


(c)


(d)


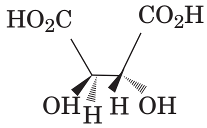
Previous Years' Questions

41. Identify the compound that exhibits tautomerism [AIEEE 2011]
(a) 2-butene (b) lactic acid
(c) 2-pentanone (d) phenol

42. Out of the following, the alkene that exhibits optical isomerism is [AIEEE 2010]
(a) 3-methyl-2-pentene (b) 4-methyl-1-pentene
(c) 3-methyl-1-pentene (d) 2-methyl-2-pentene

43. The alkene that exhibits geometrical isomerism is [AIEEE 2009]
(a) propene (b) 2-methyl propene
(c) 2-butene (d) 2-methyl-2-butene

44. The absolute configuration of

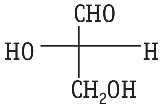


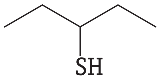
is

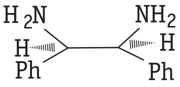
[AIEEE 2008]
(a) *S, S* (b) *R, R* (c) *R, S* (d) *S, R*

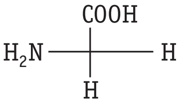
45. Which one of the following conformations of cyclohexane is chiral? [AIEEE 2007]
(a) Twist boat (b) Rigid (c) Chair (d) Boat

46. Which of the following molecules is expected to rotate the plane of polarised light ? [AIEEE 2007]

(a) 
$$\begin{array}{ccc} & CHO & \\ HO & \text{—} & H \\ & CH_2OH & \end{array}$$

(b) 

(c) 

(d) 
$$\begin{array}{ccc} & COOH & \\ H_2N & \text{—} & H \\ & H & \end{array}$$

47. Increasing order of stability among the three main conformations (*i.e.*, Eclipse, Anti, *Gauche*) of 2-flouro ethanol is [AIEEE 2006]
(a) eclipes, *gauche*, anti (b) *gauche*, eclipse, anti
(c) eclipes, anti, *gauche* (d) anti, *gauche*, eclipse

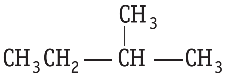
48. Which types of isomerism is shown by 2,3-dichlorobutane? [AIEEE 2005]
(a) Structural (b) Geometric
(c) Optical (d) Diastereo

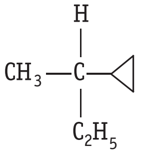
49. For which of the following parameters the structural isomers C_2H_5OH and CH_3OCH_3 would be expected to have the same values? (Assume ideal behaviour) [AIEEE 2004]
(a) Heat of vaporisation
(b) Vapour pressure at the same temperature
(c) Boiling points
(d) Gaseous densities at the same temperature and pressure

50. Which of the following compounds is not chiral? [AIEEE 2004]
(a) 1-chloropentane
(b) 2-chloropentane
(c) 1-chloro-2-methyl pentane
(d) 3-chloro-2-methyl pentane

51. Amongst the following compounds, the optically active alkane having lowest molecular mass is [AIEEE 2004]

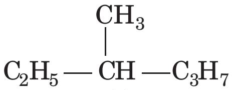
(a) $CH_3CH_2—CH_2CH_3$

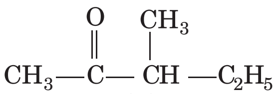
(b) 
$$CH_3CH_2—\overset{\displaystyle CH_3}{\overset{|}{CH}}—CH_3$$

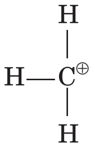
(c) 

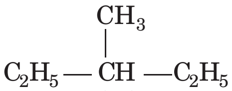
(d) $CH_3—CH_2—C\equiv CH$

52. Among the following four structures I to IV


$$C_2H_5—\overset{\displaystyle CH_3}{\overset{|}{CH}}—C_3H_7$$
(I)

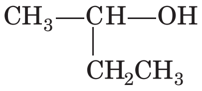

$$CH_3—\overset{\displaystyle O}{\overset{\|}{C}}—\overset{\displaystyle CH_3}{\overset{|}{CH}}—C_2H_5$$
(II)


$$H—\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle H}{\underset{|}{C^{\oplus}}}}}$$
(III)


$$C_2H_5—\overset{\displaystyle CH_3}{\overset{|}{CH}}—C_2H_5$$
(IV)

it is true that [AIEEE 2003]
(a) all four are chiral compounds
(b) only I and II are chiral compounds
(c) only III is a chiral compound
(d) only II and IV are chiral compounds

53. Following types of compounds (as I, II)

(I) $CH_3CH = CHCH_3$ (II) 
$$CH_3—\underset{\displaystyle CH_2CH_3}{\underset{|}{CH}}—OH$$

are studied in terms of isomerism in [AIEEE 2002]
(a) chain isomerism (b) position isomerism
(c) conformers (d) stereoisomerism

54. Racemic mixture is formed by mixing two [AIEEE 2002]
(a) isomeric compounds
(b) chiral compounds
(c) *meso* compounds
(d) enantiomers with chiral carbon

55. Geometrical isomerism is not shown by [AIEEE 2002]
(a) 1, 1-dichloro-1-pentene
(b) 1, 2-dichloro-1-pentene
(c) 1, 3-dichloro-2-pentene
(d) 1, 4-dichloro-2-pentene

Answers

Round I

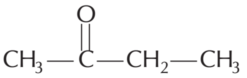
1. (c)	**2.** (a)	**3.** (d)	**4.** (d)	**5.** (d)	**6.** (b)	**7.** (a)	**8.** (b)	**9.** (b)	**10.** (d)
11. (a)	**12.** (d)	**13.** (d)	**14.** (b)	**15.** (a)	**16.** (c)	**17.** (c)	**18.** (b)	**19.** (d)	**20.** (d)
21. (b)	**22.** (d)	**23.** (c)	**24.** (c)	**25.** (c)	**26.** (d)	**27.** (d)	**28.** (d)	**29.** (d)	**30.** (c)
31. (c)	**32.** (b)	**33.** (c)	**34.** (b)	**35.** (a)	**36.** (a)	**37.** (d)	**38.** (b)	**39.** (c)	**40.** (c)
41. (b)	**42.** (b)	**43.** (b)	**44.** (b)	**45.** (a)	**46.** (b)	**47.** (d)	**48.** (d)	**49.** (a)	**50.** (d)
51. (c)	**52.** (c)	**53.** (d)	**54.** (b)	**55.** (a)	**56.** (d)	**57.** (d)	**58.** (c)	**59.** (b)	**60.** (b)
61. (d)	**62.** (b)	**63.** (d)	**64.** (c)	**65.** (a)	**66.** (a)	**67.** (b)	**68.** (d)	**69.** (c)	

Round II

1. (d)	**2.** (c)	**3.** (d)	**4.** (d)	**5.** (d)	**6.** (b)	**7.** (c)	**8.** (a)	**9.** (d)	**10.** (c)
11. (c)	**12.** (b)	**13.** (a)	**14.** (b)	**15.** (d)	**16.** (b)	**17.** (b)	**18.** (c)	**19.** (b)	**20.** (b)
21. (b)	**22.** (d)	**23.** (b)	**24.** (b)	**25.** (b)	**26.** (a,c,d)	**27.** (a,d)	**28.** (b,c)	**29.** (b,c,d)	**30.** (d)
31. (c)	**32.** (a)	**33.** (d)	**34.** (a)	**35.** (d)	**36.** (a)	**37.** (c)	**38.** (b)	**39.** (a)	**40.** (a)
41. (c)	**42.** (c)	**43.** (c)	**44.** (b)	**45.** (a)	**46.** (a)	**47.** (c)	**48.** (c)	**49.** (d)	**50.** (a)
51. (c)	**52.** (b)	**53.** (d)	**54.** (d)	**55.** (a)					

the Guidance

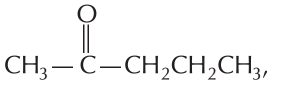
Round I

4. Butan-2-one  $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$ is not isomeric with diethyl ether $CH_3CH_2-O-CH_2-CH_3$. Because both are differing in molecular formula.

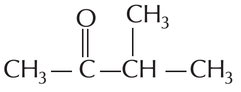
5. But-2-ene and but-1-yne do not have same molecular formula, thus are not isomers.

$CH_3-CH_2-C\equiv CH$ but-1-yne (C_4H_6) $\quad CH_3-CH=CH-CH_3$ but-2-ene (C_4H_8)

7. $CH_3COC_3H_7$ can exhibit metamerism.

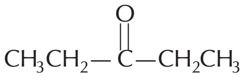


$CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_2CH_3$,



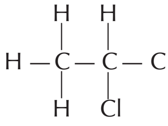
$CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{CH}-CH_3$

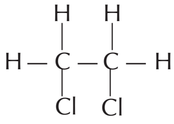
and



$CH_3CH_2-\overset{\overset{O}{\|}}{C}-CH_2CH_3$

8. Alkanes are saturated hydrocarbons without any functional group, hence can show chain isomerism only.

9. (i)  $H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}}-Cl$ (1,1-dichloro ethane)

(ii)  $H-\underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}}-H$ (1,2-dichloro ethane)

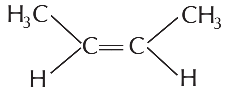
Both are position isomers.

10. Except alkynes, chain isomerism is observed when the number of carbon atoms is four or more than four.

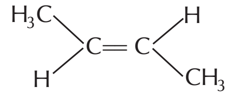
11. The following isomers the alkene have

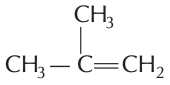
(i) $CH_3-CH_2-CH=CH_2$ (ii) $CH_3-CH=CH-CH_3$

(iii)

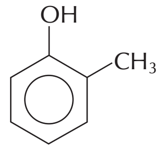


(iv)

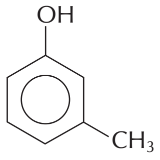


(v)  $CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2$

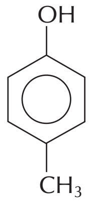
12. (i)



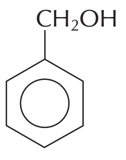
(ii)



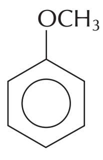
(iii)

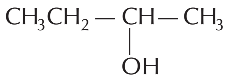


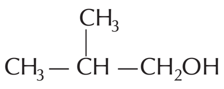
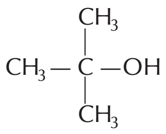
(iv)



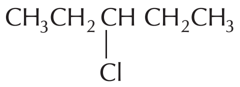
(v)



13. (i) $CH_3CH_2CH_2CH_2OH$ (ii)  $CH_3CH_2-\underset{\underset{OH}{|}}{CH}-CH_3$

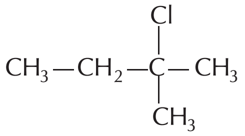
(iii)  $CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2OH$ (iv)  $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$

14. Isomeric substances that differ only in the arrangement of carbon atoms forming the base chain are known as chain isomers.



$CH_3CH_2\underset{\underset{Cl}{|}}{CH}CH_2CH_3$

and



$CH_3-CH_2-\overset{\overset{Cl}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

15. $CH_3-CH_2-CH=CH_2$ and

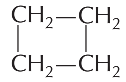
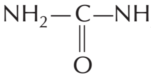
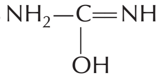


exhibit ring chain isomerism.

16. Urea,



$NH_2-\underset{\underset{O}{||}}{C}-NH_2$ shows tautomerism as



$NH_2-\underset{\underset{OH}{|}}{C}=NH$

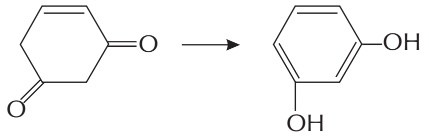
17. Tautomerism and functional isomerism is not possible together.

18. (a) shows tautomerism since aldehydes are more stable than vinyl alcohols.

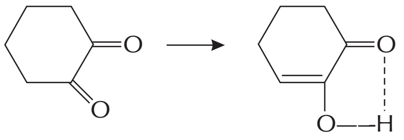
$C_6H_5-CH=CHOH \longleftrightarrow C_6H_5CH_2CH=O$

(b) does not show tautomerism because it does not have hydrogens at α-positions.

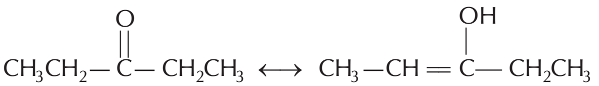
(c) shows tautomerism because enol form is stabilized by aromatic character



(d) shows tautomerism because enol form is stabilized by H-bonding.



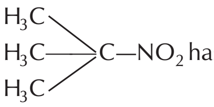
19.



$CH_3CH_2-\overset{\overset{O}{||}}{C}-CH_2CH_3 \longleftrightarrow CH_3-CH=\overset{\overset{OH}{|}}{C}-CH_2CH_3$

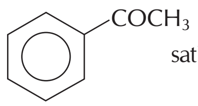
(keto form) (enol form)

20.



$(H_3C)_3C-NO_2$ has no α-hydrogen. Hence, it will not show tautomerism.

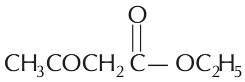
21. Presence of α –H atom along with a multi bonded functional group is an essential condition for exhibiting tautomerism.



satisfies this condition, so exhibits tautomerism.

23. The stabilising effect of enolic form is the intramolecular hydrogen bond present in enols. This provides another source of increasing bonding and hence, increased stabilisation.

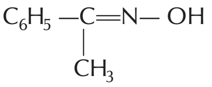
Thus,



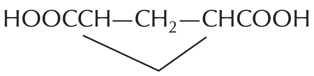
$CH_3COCH_2\overset{\overset{O}{||}}{C}-OC_2H_5$ is more stable.

24. $C=O$ double bond of a carbonyl group is a stronger bond ($>C=O$, 364 kJ/mol) than the $C=C$ bond (strength 250 kJ/mol) of the enol. Thus, CH_3COCH_3 is more stable.

26. All the compounds in which there should be restricted rotation about a bond in the molecule, show geometrical isomerism. Oximes of the type $R-CH=N-OH$,



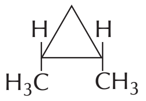
$C_6H_5-\underset{\underset{CH_3}{|}}{C}=N-OH$ and cyclic compound like



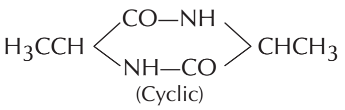
HOOCCH—CH₂—CHCOOH show geometrical isomerism.

27. Disubstituted cyclic compounds and disubstituted alkenes show geometrical isomerism.

(Non-cyclic, but have ═bond so exhibits geometrical isomerism).

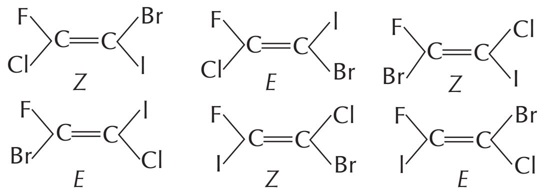


(Cyclic, two different groups at adjacent positions, so exhibits geometrical isomerism).

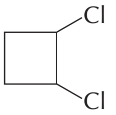


(Cyclic)

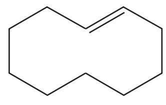
28.



29. The isomerism which arises due to restricted rotation about a bond in a molecule is known as geometrical isomerism.

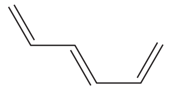


, $CH_3-CH=NOH$ and



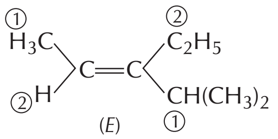
All of these form geometrical isomers.

30. In



the double bonds are *trans* and *cis*. The first and third bonds are identical

31. If the highest priority groups of two carbon atoms of the double bond are on the opposite sides, the configuration is *E*. (*Entgegen*).



(*E*)

32. When n = even number then for two identical ends, number of geometrical isomers

$$= 2^{n-1} + 2^{n/2-1}$$
$$= 2^1 + 2^0 = 3$$

35. The separation of racemic mixture back into *d* and *l* isomers is known as resolution. It can be done by

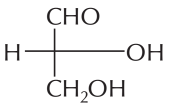
(I) mechanical method
(II) bio-chemical method using enzymes
(III) chemical method (salt formation).

36. Racemic tartaric acid is optically inactive due to external compensation. Racemic tartaric acid is an equimolar mixture of optically active *d*- and *l*- forms.

37. If a substance rotates the plane polarised light in clockwise direction, it is dextrorotatory (+). If it rotates the plane polarised light in anticlockwise direction then it is laevorotatory (–). Thus + / – form differ in specific rotation.

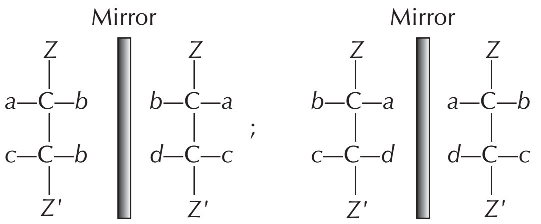
38. The prefixes *erythro* and *threo* are used in systems containing two asymmetric carbons when two of the groups are the same and the third is different. The *erythro-isomer* has identical groups on the same side when drawn in Fischer projection and *threo*-isomer has them on opposite side.

39. The configuration in the Fischer projection of which —OH group is on right hand side, H-atom is on left hand side, —CHO group is on upper side and CH_2OH is on lower side is known as D-configuration.



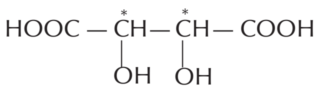
D-glyceraldehyde

40. The minimum possible isomers of compounds will be



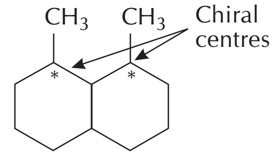
Alternative No. of optical isomers = $Z^n = 2^2 = 4$,
here n = No. of dissimilar asymmetric C-atoms.

41. A carbon atom which is attached to four different group is called an asymmetric carbon atom or chiral centre. $HOOC(CHOH)_2COOH$ has two asymmetric carbon (C^*) atoms.



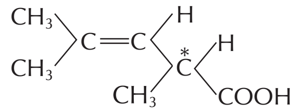
$$HOOC-\underset{OH}{\underset{|}{\overset{*}{C}H}}-\underset{OH}{\underset{|}{\overset{*}{C}H}}-COOH$$

42.



(* asymmetric C atom)

43.



The above compound has chiral centre.

Hence, it can exhibit optical isomerism while geometrical isomerism is not possible due to the presence of identical groups on double bonded carbon atoms.

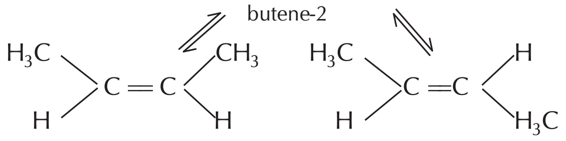
44. Compounds which do not show optical activity inspite of the presence of chiral carbon atoms are called *meso*-compounds.

45. If an enantiomerically pure acid is treated with racemic mixture of an alcohol having chiral carbon, the product formed will be optically active mixture.

46. Butene-2 exhibits geometrical (*cis*, *trans*) isomerism

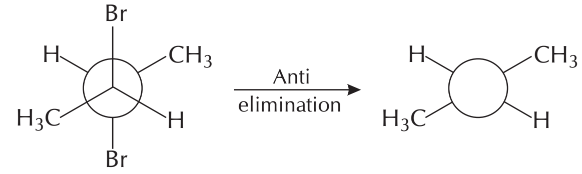
$$CH_3-CH=CH-CH_3$$

butene-2



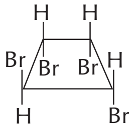
cis-isomer *trans*-isomer

47. During debromination, *meso*-dibromobutane forms *trans*-2-butene.



meso-2,3-dibromobutane *trans*-2-butene

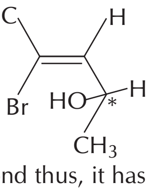
48. We know that by breaking two bond on the chiral centre configuration changes.

50. The compound  is symmetrical with respect to centre of the molecule.

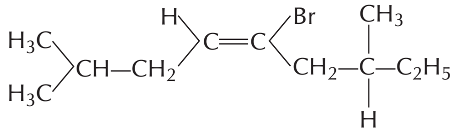
51. Compound given in option (c) is *trans* while all other have *cis* configuration.

52. If two atoms directly attached to the double bond have the same atomic number, then the relative priority of the groups is determined by a similar comparison of the atomic numbers of the next elements in the groups. Thus, the preference order of given group is

$$OCH_3 > OH > COOH > CHO$$

54. Compound  has one chiral carbon atom and one double bond thus, it has two geometrical (*cis* and *trans*) and two optical isomers.

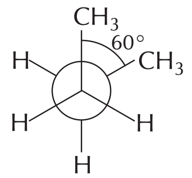
55.



[*E*][*S*]-5-bromo-2,7-dimethylnon-4-ene

56. Staggered conformation is most stable due to its minimum energy.

57. The dihedral angle is 60°.



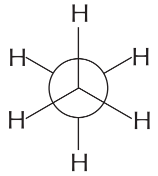
gauche conformation

58. Cyclopentane posses 0° 44′ angle strain which is minimum.

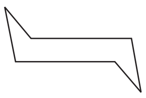
60. Staggered and eclipsed conformers cannot be physically separated because energy difference between them is so small that they most readily interconvert at room temperature.

61. Half chair is transition state conformation between the chair and boat conformations. The energy difference between the chair and half chair conformation being 44 kJ mol^{-1}. Hence, it is most unstable.

62. In ethane and cyclohexane, staggered and chair forms are more stable respectively.

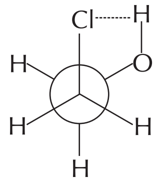


staggered form of ethane



chair form of cyclohexane

64.

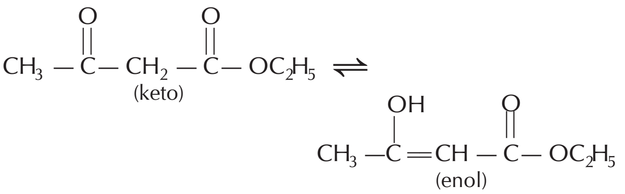


The *gauche* conformation is most stable due to the presence of H-bonding between H atom of OH and Cl.

65. The stability order of conformations of cyclohexane is

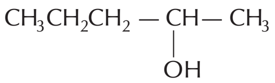
Chair > twist boat > boat

67.



$$\underset{\text{(keto)}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5} \rightleftharpoons \underset{\text{(enol)}}{CH_3-\overset{OH}{\overset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-OC_2H_5}$$

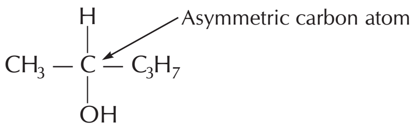
68. (i) $CH_3CH_2CH_2CH_2CH_2OH$ and



$CH_3CH_2CH_2-\underset{OH}{\underset{|}{CH}}-CH_3$

are position isomers.

(ii)



$CH_3-\underset{OH}{\underset{|}{\overset{H}{\overset{|}{C}}}}-C_3H_7$

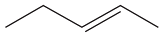
Due to the presence of asymmetric carbon atom, optical isomerism is possible.

(iii) $CH_3CH_2CH_2CH_2CH_2OH$ and $CH_3CH_2OCH_2CH_2CH_3$ are functional isomerisms.

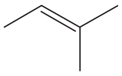
69. Diastereomers have different physical properties such as mp, bp solubilities etc.

Round II

1.

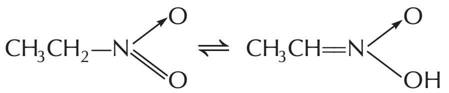


and



are chain isomers.

2. Nitroethane exhibits tautomerism.



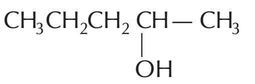
$$CH_3CH_2-N\overset{\nearrow O}{\underset{\searrow O}{}} \rightleftharpoons CH_3CH=N\overset{\nearrow O}{\underset{\searrow OH}{}}$$

nitro form aci form

3. The number of possible isomeric pentyl alcohols is eight which are as

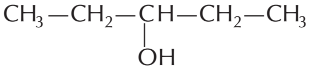
(i) $CH_3CH_2CH_2CH_2CH_2OH$ *n*-pentanol

(ii)



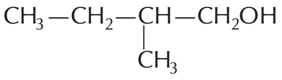
$CH_3CH_2CH_2\underset{OH}{\underset{|}{CH}}-CH_3$ 2-pentanol

(iii)



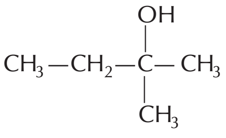
$CH_3-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-CH_3$ 3-pentanol

(iv)



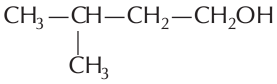
$CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2OH$ 2-methyl butanol

(v)



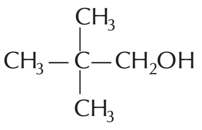
$CH_3-CH_2-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_3$ 2-methyl butan-2-ol

(vi)



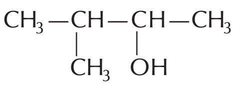
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_2OH$ 3-methyl butanol

(vii)

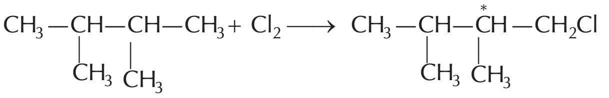


$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2OH$ 2,2-dimethyl propanol

(viii)



$CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-CH_3$ 3-methyl butan-2-ol

4. 

$$CH_3-\underset{CH_3}{CH}-\underset{CH_3}{CH}-CH_3 + Cl_2 \longrightarrow CH_3-\underset{CH_3}{CH}-\underset{CH_3}{\overset{*}{CH}}-CH_2Cl$$

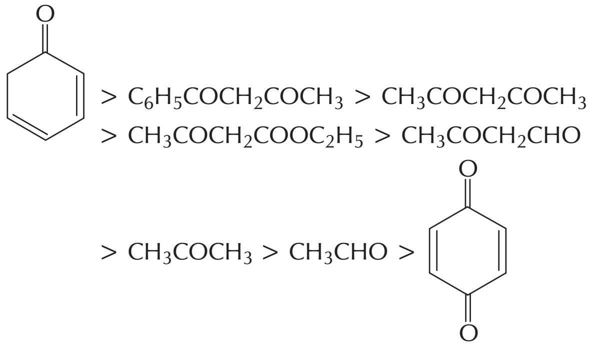
2,3-dimethyl butane 1-chloro-2,3-dimethyl butane

Due to the presence of chiral centre it shows optical activity and its mirror image are non-superimposable hence it shows one enantiomer pair.

$$CH_3-\underset{CH_3}{CH}-\underset{CH_3}{CH}-CH_2Cl \quad \Big\| \quad ClCH_2-\underset{CH_3}{CH}-\underset{CH_3}{CH}-CH_3$$

5. Tautomers may or may not be metamers. These are infact functional isomers. Tautomerism is catalysed by acid as well as base. Chain and position isomerism do not exist together.

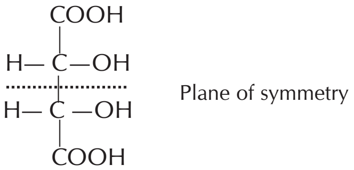
6. The percentage of enolic contents of some common compounds in decreasing order will be



$> C_6H_5COCH_2COCH_3 > CH_3COCH_2COCH_3 > CH_3COCH_2COOC_2H_5 > CH_3COCH_2CHO > CH_3COCH_3 > CH_3CHO >$

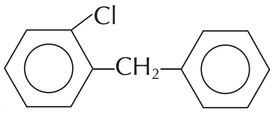
7. The reverse of enolic contents of compound is ketonic contents. Thus, the correct order of ketonic contents are

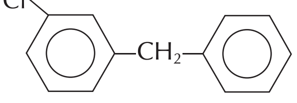
$CH_3CHO > CH_3COC_2H_5 > CH_3COCH_3 > CH_3COCH_2COCH_3$

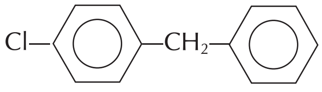
8. 

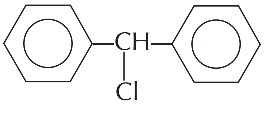
Meso tartaric acid is optically inactive due to the presence of molecular symmetry. It is optically inactive due to internal compensation, *i.e.,* the effect of one half of the molecule is neutralised by other.

9. Four structural isomers are possible for diphenyl methane when one H-atom is replaced by a Cl-atom.

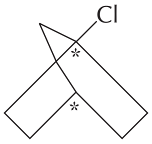
(I) 

(II) 

(III) 

(IV) 

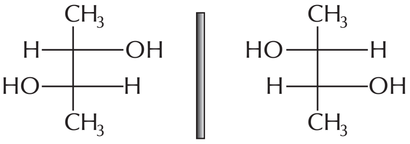
10. Carbon bonded with four different groups is known as chiral carbon atom. In case of given compound

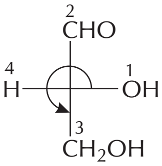


the number of chiral carbon atoms are two.

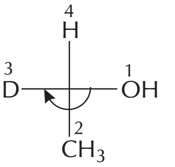
11. Superimposable compounds which are also not the mirror images of each other are called diastereomers. Thus I and II are diastereomers.

12. Optical isomers of a compound which are non-superimposable but releated to each other as an object and its mirror image are called enantiomers.

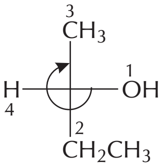


13. 

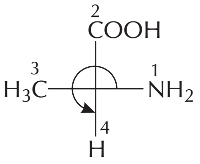
(i)
R



(ii)
R

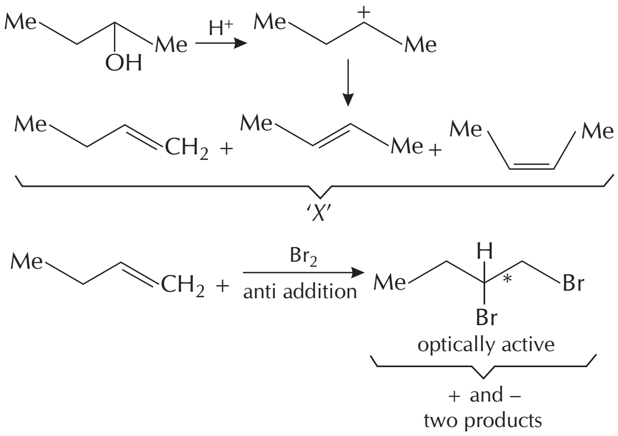


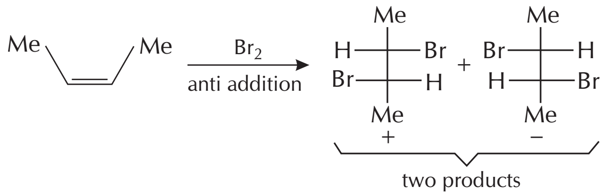
(iii)
S

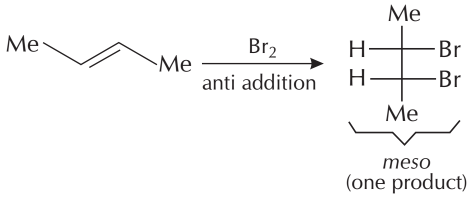


(iv)
S

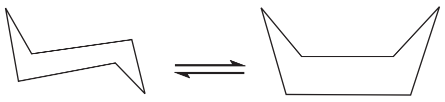
Note If H is on vertical line *R* represents clockwise and *S* represents anticlock wise rotation. Opposite is true when H or lower priority group is present on horizontal line.

14. 



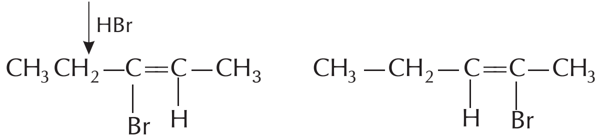


15. Chair and boat conformations of cyclohexane differ in energy by 44 kJ/mol.



chair form boat form

16. $CH_3CH_2—C\equiv C—CH_3$
2-pentyne



$CH_3CH_2—\underset{Br}{C}=\underset{H}{C}—CH_3$ $CH_3—CH_2—\underset{H}{C}=\underset{Br}{C}—CH_3$

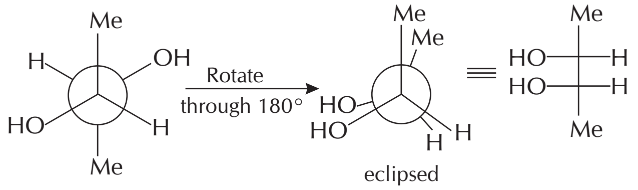
3-bromopent-2-ene
E, Z

2-bromopent-2-ene
E, Z

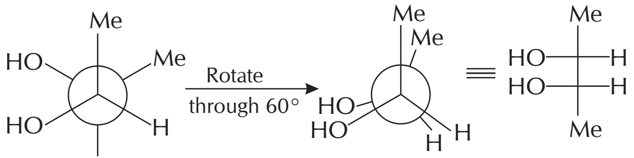
Structural isomers (position) = 2

Stereo isomers = 4

17.



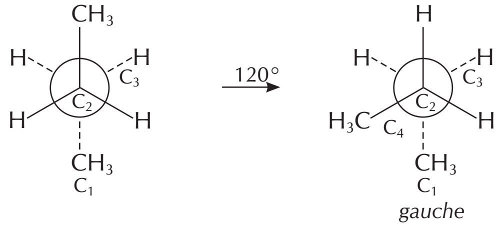
P eclipsed



R eclipsed *meso*

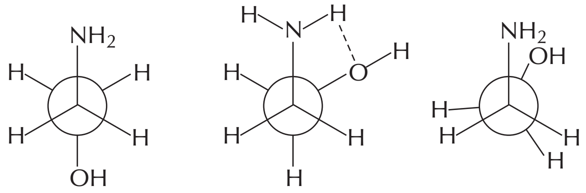
Here, *P* and *R* represent *meso*-compound.

18.



gauche conformation

19.

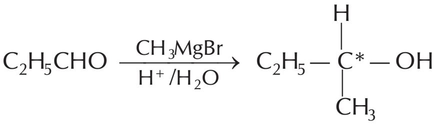


Anti *Gauche* Eclipsed

So, *gauche* form stabilized by intermolecular hydrogen bonding hence, is more stable than anti.

20. In boat conformation, there are four skew interactions and two eclipsed interactions. That's why it is less stable.

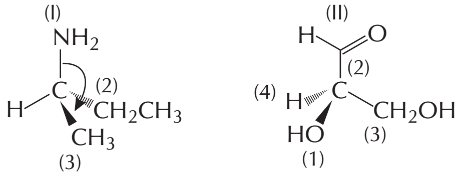
21.



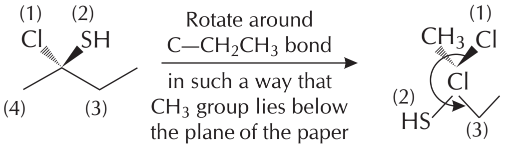
$C_2H_5CHO \xrightarrow[H^+/H_2O]{CH_3MgBr} C_2H_5—\overset{H}{\underset{CH_3}{C^*}}—OH$

(For these reactions read successive chapters.)

22.

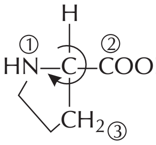


R-configuration *R*-configuration

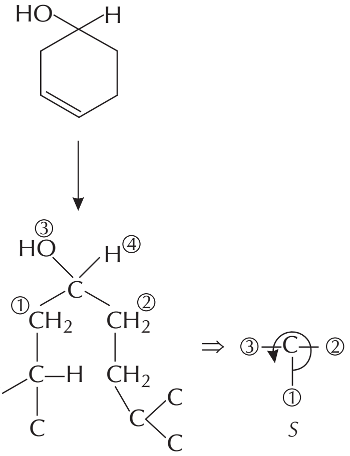


III *S*-configuration

23. Compounds in which the chiral centre is a part of the ring are handed in a analogous fashion.



R



24. % enantiomeric excess

$$= \frac{\text{observed specific rotation}}{\text{specific rotation of pure enantiomer}} \times 100$$

$$\text{Observed specific rotation} = \frac{3/4}{100} \times (+16°) \times 100$$

$$= +12°.$$

25.

Element	Percentage	At. mass	Molar ratio	Simple molar ratio
C	66%	12	$\frac{66}{12}=5.5$	4.25≈4
H	13.3%	1	$\frac{13.3}{1}=13.3$	10.3 =10
O	100–66–1 3.3 =20.7%	16	$\frac{20.7}{16}=1.29$	1 – 1

Hence, its empirical formula is $C_4H_{10}O$.

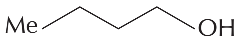
Molecular formula $=(\text{Empirical formula})_n$

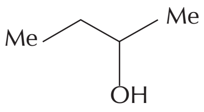
$$=(C_4H_{10}O)_n$$

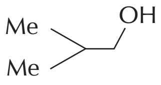
$$n=\frac{\text{emp. formula mass}}{2\times \text{VD}}=\frac{48+10+16}{2\times 37}=\frac{74}{74}=1$$

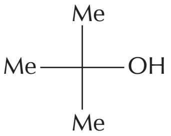
Hence, molecular formula is $C_4H_{10}O$.

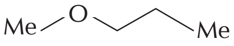
Thus, this isomers have 7 isomers, out of which four are alcohols and three are ethers.

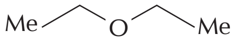
(I) 

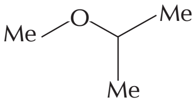
(II) 

(III) 

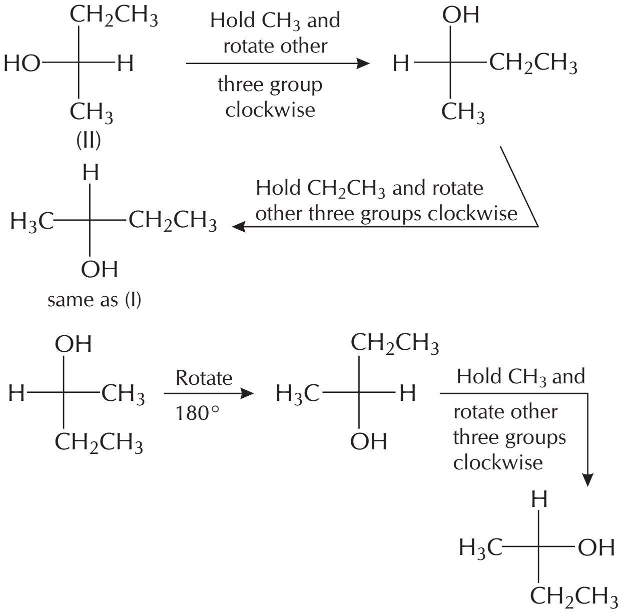
(IV) 

(v) 

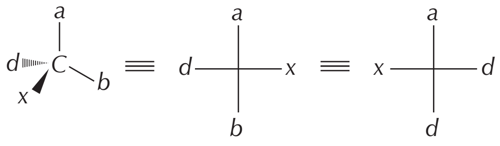
(VI) 

(VII) 

26. A *meso* compound has minimum two chiral centres, it has a plane of symmetry and it is optically inactive.

27. 

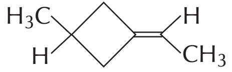
28. For Fischer's projection to be drawn bring the wedge-edge in correct visual point. The compound can also be represented as



and so on.

29. (b) Alkene with odd number of carbon atoms are non-planar so, these are optically active.

(c) $CH_3-CH(D)-COOH$ molecule contains one chiral carbon atom thus, it is optically active.

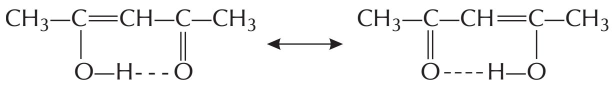
(d) 

is non-planar and does not contain any symmetry element thus, optically active.

30. The staggered form is more stable than the eclipsed form because the potential energy of staggered form, in which the bond pairs of two carbons are far away from each other, is minimum.

31. Racemic mixture is optically inactive because the two enantiomers rotate the plane polarised light equally in opposite directions and cancel each others rotation. This phenomenon is called external compensation.

32. Resonance stabilisation of enol form can be shown as

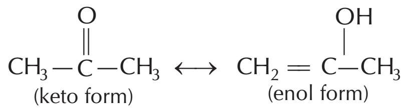


33. The configuration in a compound is independent of its physical properties like optical activity.

34. In chiral centre, chiral axis and chiral plane, if any one is present, the molecule will be optically active.

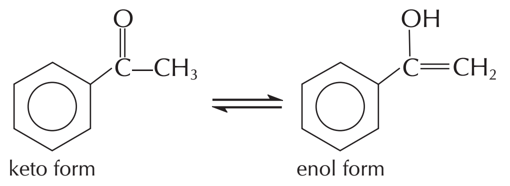
35. Due to hydrogen bonding and resonance stabilisation enol form is preferred in contrast.

36. Acetone exhibits keto-enol tautomerism.



$$\underset{\text{(keto form)}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} \longleftrightarrow \underset{\text{(enol form)}}{CH_2=\overset{\overset{OH}{|}}{C}-CH_3}$$

37. Tautomerism in acetophenone can be represented as



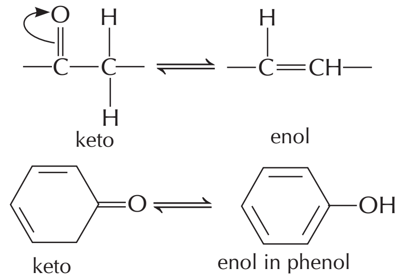
38. Baeyer predicted that a five membered ring compound would be the most stable. It has angle of deviation = 0.44°.

And we know that stability $\propto \frac{1}{d}$

39. Chair form with bulky group at equatorial position is preferred conformation when two bulky groups are present at 1,4-positions.

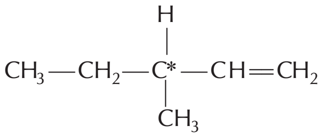
40. When intramolecular hydrogen bonding is possible between groups in 1 and 4 positions the molecule assumes a boat conformation rather than the chair conformation in which hydrogen bonding is not possible.

41. Tautomerism is due to spontaneous interconversion of two isomeric forms with different functional groups into each other. The term tautomer means constitutional isomers that undergo such rapid interconversion that can't be independently isolated.



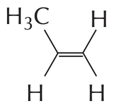
Thus, (c) 2-pentanone and (d) phenol exhibit tautomerism.

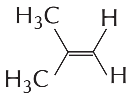
Here (c) may be considered as answer because keto form of phenol is highly unstable.

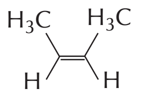
42.

$CH_3—CH_2—\overset{H}{C^*}(CH_3)—CH{=}CH_2$

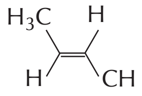
3-methyl-1-pentene

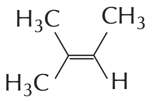
(It has one chiral centre.)

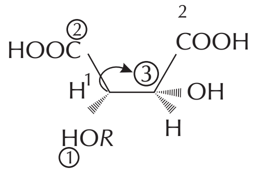
43.

propene


2-methyl propene

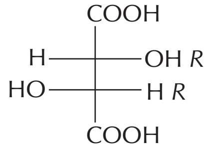

cis-2-butene

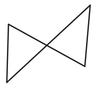

trans-2-butene


2-methyl-2-butene

44.


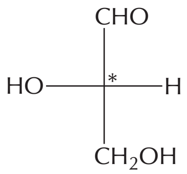
or



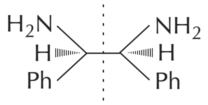
45.

twist boat

It is chiral conformation.

46. The molecule, which is optically active, has chiral centre, is expected to rotate the plane of polarised light.

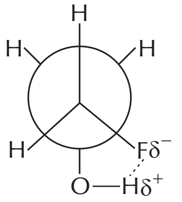


One chiral centre ⇒ optically active

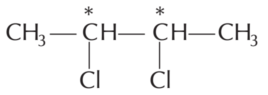


Two chiral centres, but plane of symmerty within molecule ⇒ optically inactive.

47. $HO—CH_2—CH_2—F$



Gauche conformation is comparatively more stable due to hydrogen linkage in between F and H (at O-atom), hence order is eclipse, anti (staggered), gauche.

48.

$CH_3—\overset{*}{C}H(Cl)—\overset{*}{C}H(Cl)—CH_3$

There are two chiral C-atoms (*)

Thus, optical isomerism is possible.

49. In CH_3CH_2OH, there is intermolecular H-bonding while it is absent in isomeric ether CH_3OCH_3.

Larger heat is required to vaporise CH_3CH_2OH as compared to CH_3OCH_3 thus (a) is incorrect.

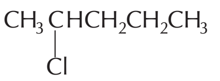
CH_3CH_2OH is less volatile than CH_3OCH_3, thus vapour pressures are different, thus (b) is incorrect.

bp of $CH_3CH_2OH > CH_3OCH_3$, thus (c) is incorrect.

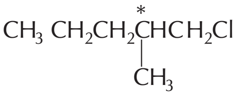
Density $= \frac{\text{mass}}{\text{volume}}$ Due to ideal behaviour at a given temperature and pressure volume and molar mass are same. Hence, they have same vapour density.

50. Chiral carbon has all the four different groups attached to it.

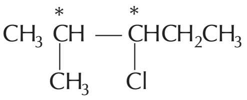
(a) $CH_3CH_2CH_2CH_2CH_2Cl$ (no chiral carbon atom)

(b) 

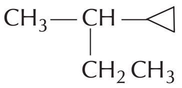
$CH_3\underset{\underset{Cl}{|}}{C}HCH_2CH_2CH_3$ (one chiral carbon atom)

(c) 

$CH_3\,CH_2CH_2\overset{*}{\underset{\underset{CH_3}{|}}{C}}HCH_2Cl$ (one chiral carbon atom)

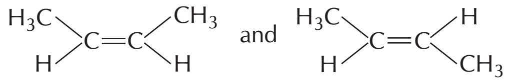
(d) 

$CH_3\,\overset{*}{\underset{\underset{CH_3}{|}}{C}}H - \overset{*}{\underset{\underset{Cl}{|}}{C}}HCH_2CH_3$ (two chiral carbon atom)

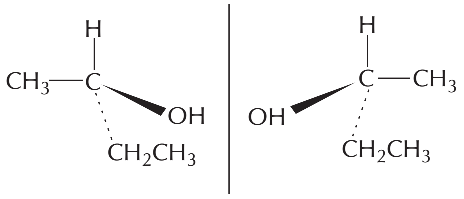
51. 

contains asymmetric carbon atom, thus optically active.

52. Chiral compounds are those which have one chiral centre *i.e.*, all four atoms or groups attached to same carbon are different.

53. 

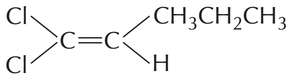
geometrical isomers
(*cis-trans*)



molecules is optically active
enantiomers

Geometrical isomers and enantiomers both are stereoisomers.

54. Racemic mixture is an equimolar mixture of enantiomers.

55. 

At least two groups or atoms attached to doubly bonded carbon atoms should be different.

15 Hydrocarbons

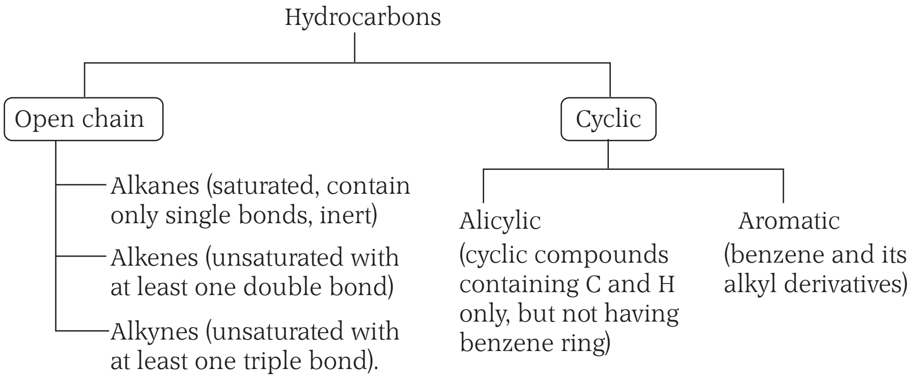
JEE Main MILESTONE

- Classification of Hydrocarbons
- Alkanes
- Alkenes
- Alkynes
- Aromaticity
- Benzene

15.1 Classification of Hydrocarbons

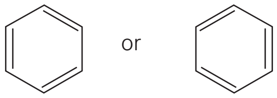
Hydrocarbons are mainly obtained from petroleum, which is the major source of commercial energy.

Hydrocarbons are classified as



*Hydrocarbons means compounds containing carbon and hydrogen only. These may contain only single bonds or double/triple bonds alongwith single bond. Only single bond containing hydrocarbons are **saturated hydrocarbons** while that have multiple bond(s) ($=$ or $\equiv$ bond) alongwith single bonds are **unsaturated compounds.***

Caution Point *Benzene ring have alternate single and double bonds.*



Such a ring is absent in alicyclic compounds.

15.2 Alkanes

Alkanes are the simplest organic compounds made up of carbon and hydrogen only. Chemically, these are almost inert that's why also called **Paraffins** (Latin, *Parum affinis* = Little affinity). The general formula for this series is C_nH_{2n+2}. Hence, the first member is CH_4 (methane).

The main sources of alkanes are **natural wax gas** and **petroleum.** The natural wax or ozokerite is found near petroleum wells and is a mixture of higher solid hydrocarbons. Bee's wax, which is mainly myricyl palmitate (an ester) also contains small quantities of $C_{27}H_{56}$ and $C_{31}H_{64}$.

Nomenclature

You have read in chapter 13 about the nomenclature of alkanes. However, names of alkanes having carbon more than 10 are tabulated below.

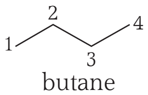
Table 14.1 **IUPAC Name of Higher Alkanes**

Molecular formula	Name	Molecular formula	Name
$C_{11}H_{24}$	Undecane	$C_{31}H_{64}$	Hentriacontanes
$C_{12}H_{26}$	Dodecane	$C_{40}H_{82}$	Tetracontanes
$C_{20}H_{42}$	Icosane (Eicosane)	$C_{50}H_{102}$	Pentacontanes
$C_{21}H_{44}$	Henicosane	$C_{90}H_{182}$	Nonacontanes
$C_{22}H_{46}$	Docosane	$C_{100}H_{202}$	Hectane
$C_{30}H_{62}$	Triacontanes		

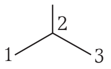
Isomerism

Alkanes exhibit mainly structural (chain) and conformational isomerism. *e.g.,*

C_4H_{10} have two chain isomers as

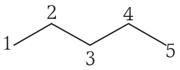
(I) 

butane

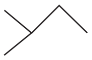
(II) 

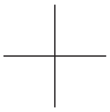
iso-butane
or 2-methyl propane

and C_5H_{12} have three chain isomers as

(I) 

pentane

(II) 
iso-pentane

(III) 
neo-pentane

(For details of isomerism see 'Chapter 14' Isomerism)

Methods of Preparation

Following methods are used for the preparation of alkanes.

1. By the Reduction of Different Compounds

Different reagents are used to reduce different compounds into alkanes, description of which is given below.

(i) **Reduction of alcohols, acids, acid derivatives and alkyl halides** is carried out by heating them with red P + HI but the yield is very less. *e.g.,*

$$CH_3COOH + 6HI \xrightarrow[425\text{ K}]{\text{Red P}} CH_3—CH_3 + 2H_2O + 3I_2$$

$$CH_3CH_2OH + 2HI \xrightarrow[425\text{ K}]{\text{Red P}} CH_3—CH_3 + H_2O + I_2$$

$$C_2H_5I + HI \xrightarrow{\text{Red P}} C_2H_6 + I_2$$

Here, red P is used to remove iodine as volatile PI_3, otherwise the reaction becomes reversible.

$$2P + 3I_2 \longrightarrow 2PI_3$$

(ii) **For reducing carbonyl compounds** (aldehydes and ketones) the reagents used are

(a) Red P + HI/Δ as

$$>C{=}O + 6HI \xrightarrow[425\text{ K}]{\text{Red P}} >CH_2 + H_2O + 3I_2$$

(b) Zn–Hg/conc HCl (Clemmensen reduction) *e.g.*,

$$>C{=}O + 4[H] \xrightarrow[\text{conc HCl}]{\text{Zn–Hg}} >CH_2 + H_2O$$

(c) Hydrazine followed by $C_2H_5O^-Na^+$ at 180°C (Wolff-Kishner reduction).

$$>C{=}O + NH_2NH_2 \xrightarrow[-H_2O]{} >C{=}N\cdot NH_2 \xrightarrow[-N_2]{C_2H_5ONa} >CH_2$$

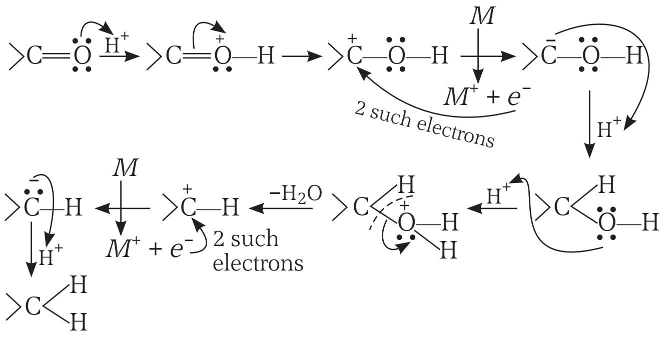
This is a specific method for reducing $>C{=}O$ *group into* $—CH_2$ *group.* N_2 *is released in the process.*

The generalised reducing agents used can be metal + proton donor and complex hydrides.

(i) Among metal + proton donor, the metal works as electron donor and the complete process looks like

$$\text{for } \boxed{>C{=}O + M \text{ with } H^+ \longrightarrow >C\begin{matrix}H\\H\end{matrix} + H_2O}$$

Here, M = metal; H^+ = any protic agent

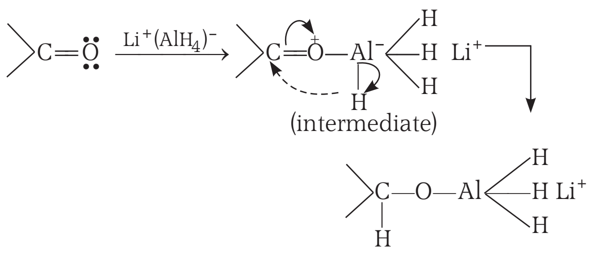


The metal used can be Na, Zn or amalgams etc., *e.g.,* Zn/HCl, Sn/HCl, Zn/CH_3COOH, Zn—Cu couple with CH_3OH, Na with ethanol etc., *e.g.,* *Alkyl halides also reduce in a similar fashion as*

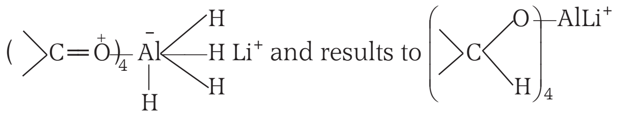
$$RX + 2\,[H] \xrightarrow[H_2O]{Zn-Cu} \underset{\text{alkane}}{R—H} + HX$$

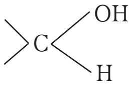
(The order of reactivity of alkyl halides is $RI > RBr > RCl > RF$).

(ii) Among the complex hydrides, LAH (Lithium aluminium hydride, $LiAlH_4$) is the best reagent and others include $NaBH_4$, $NaAlH_4$, Ph_3SnH etc. The complex hydrides function as :



LAH is a strong reducing agent because it reduces four molecules at a time, thus the intermediate formed looks like :



The latter on acid hydrolysis with HCl yields 4 molecules of  along with $AlCl_3$ and LiCl.

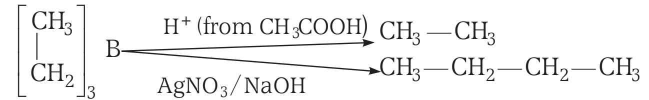
An example of such reduction is as

$$R—X \xrightarrow{LiAlH_4/NaBH_4} R—H$$

Caution Point When reducing agent is $LiAlH_4$, tertiary halides give mainly alkenes.

(iii) **Alkenes on** reduction with B_2H_6 (BH_3) in the presence of Lewis bases like THF (tetrahydrofuran), DIGLYME (diethylene glycol methyl ether) which convert dimeric B_2H_6 to BH_3 by forming acid-base complex, followed by the treatment of protic agent, form alkanes having longer chains *e.g.,*

$$3\,CH_2{=}CH_2 + BH_3 \xrightarrow[\text{DIGLYME}]{\text{THF or}}$$



trialkyl borane

Here $AgNO_3/NaOH$ is called coupling reagent that's why this reaction is also called **coupling reaction.** It also sometimes called **hydroboration reaction.**

The reaction looks like anti-Markownikoff addition but infact, it is Markownikoff addition. The difference here only is in BH_3; *the H plays the role of* (–) *ve partner while boron plays the role of* (+) *ve partner.*

2. Hydrogenation or Catalytic Reduction

The best catalyst used for hydrogenation is **Raney Ni** (an alloy containing equal amounts of Ni and Al digested with NaOH). The catalyst is very effective over normal Ni (works at 200 – 300° C) as it can work even at room temperature. Other catalysts commonly used besides Ni are Pd, Pt etc., which require a temperature between 200 – 300° C. The reduction of unsaturated hydrocarbons with Ni at temperatures between 200 – 300° C is called **Sabatier- Sanderens reaction.** The reaction looks like

$$CH\equiv CH \xrightarrow[Ni/250°C]{H_2} CH_2{=}CH_2 \xrightarrow[Ni/250°C]{H_2} CH_3{-}CH_3$$

Caution Point *Remember that* $Pd/BaSO_4$ *poisoned with S or quinoline (Lindlar's catalyst) or P-2 (Nickel boride catalyst) reduce the alkynes selectively into alkenes.*

3. Decarboxylation

Elimination of CO_2 from a carboxylic acid is called decarboxylation. Hot soda lime (NaOH/CaO) is frequently used reagent for this purpose. However, various other reagents may also be used. The reaction takes place as

$$RCOO^-Na^+ + NaOH/CaO \xrightarrow{\Delta} RH + Na_2CO_3$$

Notice that alkanes so produced, contains one less carbon atom than the original acid.

The reaction takes place by free radical mechanism and involves the formation of several byproducts like lower alkanes, hydrogen, alkenes, esters alongwith the main alkanes. The removal of these products is usually difficult. Thus, this reaction is not very useful. An example is as

$$C_2H_5COONa \xrightarrow{NaOH\ (CaO)} \underset{(44\%)}{C_2H_6} + \underset{(20\%)}{CH_4} + \underset{(33\%)}{H_2}$$
$$+ \text{ unsaturated compounds}$$

The reason of using CaO alongwith NaOH is that it keeps the NaOH (hygroscopic) dry and helps it in fusion.

Caution Point *In Kolbe's decarboxylation reaction if n is the number of carbon atoms in sodium carboxylate, the number of carbon atoms in alkane formed will be* $(n - 1)$ *while during reduction processes the number of carbon atoms in alkane formed and that in parent compound is same.*

4. Corey-House Synthesis

This method was developed in 1960 and proceed as

$$RBr + 2Li \xrightarrow{Ether} RLi + LiBr$$

$$2RLi + CuI \longrightarrow \underset{\substack{\text{lithium dialkyl}\\\text{cuperate}}}{Li(R)_2Cu} + LiI$$

$$Li(R)_2Cu + R'Br \longrightarrow R'—R + RCu + LiBr$$

This is a good method to prepare hydrocarbons (alkanes) having odd number of carbon atoms.

Caution Point *Dialkyl zinc also gives similar type of reaction but here the main product is quaternary alkane.*

$$(CH_3)_2Zn + (CH_3)_3CCl \longrightarrow (CH_3)_4C + CH_3ZnCl$$

5. From Grignard's Reagent

Grignard's reagent on treatment with compounds like H_2O, ROH, acids etc., (protic agents) forms alkane as

$$RMgX \xrightarrow{H^+} RH, \text{ i.e.,}$$

$$RMgX + HOH \longrightarrow RH + Mg(OH)X$$

$$RMgX + R'OH \longrightarrow RH + Mg(OR')X$$

$$RMgX + R'COOH \longrightarrow RH + Mg(OOCR')X$$

$$RMgX + R'C{\equiv}CH \longrightarrow RH + Mg(C{\equiv}CR')X$$

6. Kolbe's Electrolytic Method

This method is used to create a new C—C linkage and used to prepare alkenes and alkynes as well. The reaction looks like

$$\begin{array}{l}CH_3COO^-K^+\\CH_3COO^-K^+\end{array} \xrightleftharpoons{\text{Electrolysis}} \underbrace{\begin{array}{c}CH_3\\|\\CH_3\end{array} + CO_2\uparrow}_{\text{at anode}} + \underbrace{H_2\uparrow + K^+OH^-}_{\text{at cathode}}$$

Mechanism (free radical)

$$2RCOONa \xrightarrow{\text{Electrolysis}} 2RCO\ddot{O}^{\ominus} + 2Na^{\oplus}$$

At anode (oxidation)

$$2RCOO^{\ominus} \longrightarrow 2e^{\ominus} + 2RCO\dot{O} \longrightarrow 2R^{\bullet} + 2CO_2\uparrow$$
$$\longrightarrow \underset{\text{alkane}}{R—R}$$

At cathode (reduction) Reduction of H_2O takes place since reduction potential of it is greater than that of $Na^{\oplus}$.

$$2H_2O + \lambda e^{\ominus} \longrightarrow 2O^{\ominus}H + H_2\uparrow$$

Because of the generation of OH^- ions, the solution becomes alkaline.

Caution Point CH_4 *cannot be prepared by this method.*

This method is not suitable for alkanes having odd number of carbon atoms, as in such case a mixture of hydrocarbons is formed which is difficult to separate.

7. Wurtz Reaction

When alkyl halides are treated with sodium metal in dry ether, it results in the formation of an alkane having double number of carbons as that are present in parent halide. This reaction is called Wurtz reaction.

$$R\boxed{X + 2Na + X}R \xrightarrow{\text{Dry ether}} R—R + 2NaX$$

A single product is obtained as symmetrical alkane if alkyl halides are of single type but if different alkyl halides are used, the product is non-separable mixture of alkanes, so it is more suitable for the synthesis of symmetrical alkanes. *e.g.,*

$$CH_3X + 2Na + C_2H_5X \xrightarrow[-NaX]{\text{Ether}} CH_3—CH_3 + CH_3—C_2H_5$$
$$+ C_2H_5—C_2H_5$$

(A small percentage of alkene is also obtained during this reaction).

CH_4 *cannot be prepared by this reaction*

Mechanism of this reaction may be free radical or ionic but normally free radical is preferred, which takes place as

$$R—X + Na^{\bullet} \longrightarrow R^{\bullet} + NaX$$

$$R^{\bullet} + R^{\bullet} \longrightarrow R—R$$

Moreover, free radicals have a property to disproportionate as

$$R^{\bullet} + R^{\bullet} \longrightarrow \underset{\text{(saturated)}}{R} + \underset{\text{(unsaturated)}}{R}$$

This can be best understood by the following example

$$CH_3CH_2X + Na \longrightarrow CH_3\dot{C}H_2 + Na^+X^-$$

$$2CH_3\dot{C}H_2 \longrightarrow CH_3CH_2CH_2CH_3$$

$$CH_3\dot{C}H_2 + CH_3\dot{C}H_2 \xrightarrow{\text{Disproportionation}} CH_3CH_3 + CH_2{=}CH_2$$

Caution Point *This method cannot be used to convert* 3° *halides to alkanes as here alkenes are obtained instead of alkanes.*

8. Frankland Reaction

Another similar method for preparing alkanes is Frankland method in which Zn is used in the place of Na. Here, rest of the things remain absolutely same as the Wurtz reaction. The reaction looks like :

$$R\boxed{X + Zn + X}R \xrightarrow[\text{ether}]{\text{Dry}} R—R + ZnX_2$$

9. Other Methods of Preparation

(i) From Carbides

CH_4 is prepared by treated carbides, *i.e.,* Al_4C_3 and Be_2C with water. Hence, these carbides are also called **methanides.**

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$

$$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$$

(ii) Synthesis from Constituents

Lower alkanes are also prepared by synthesis, *i.e.,* build up of a chemical compound from its constituent elements as :

$$C + 2H_2 \xrightarrow[1473\ K]{\text{Electric arc}} CH_4$$

Summary of the methods described above is shown in the following flow chart.

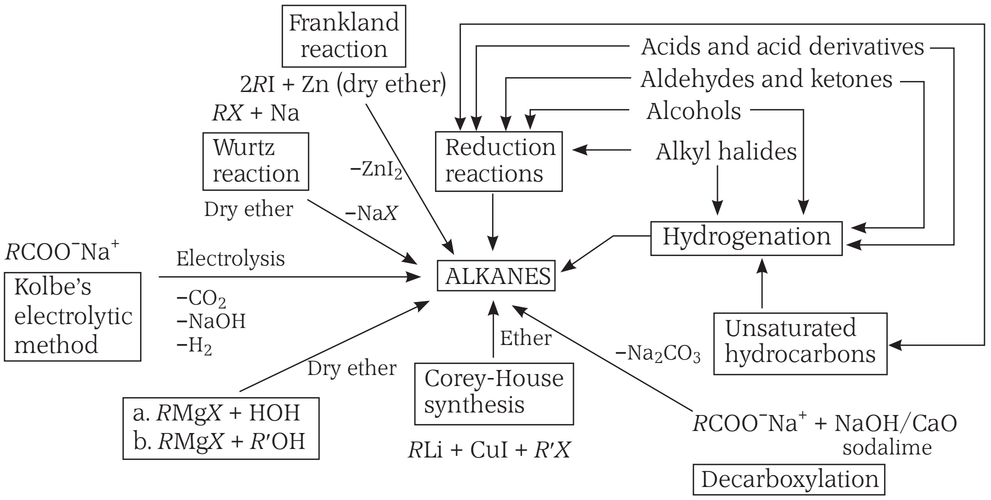


Fig. 15.1 Flow chart showing methods of preparation of alkanes

Physical Properties

Alkanes show following physical properties

1. First four alkanes are gases, next 13 are colourless liquids and all other higher ones are waxy solids.
2. These are insoluble in water but soluble in alcohol, ether, benzene etc. The solubility diminishes with increase in molecular weight.
3. As the number of carbon atoms increases, the boiling points of alkane increases because van der Waals' forces increases. However, branching results in decrease in boiling point due to decreased surface area which results in weaker van der Waals' forces.
4. The dipole moment of all alkanes, whether straight or branched chain, will be zero. However, when one H atom is replaced by another atom or group (other than alkyl group), the resultant molecule will now possess some dipole moment.
5. Melting point also increases with increase in molecular weights but alkanes with even number of carbon atoms have higher melting point than the preceding and succeeding members, due to their well packed structures.

Chemical Properties

The reaction exhibited by alkanes are as follows

1. Nitration

Higher alkanes (having more than five carbon atoms) can be nitrated when heated with fuming HNO_3. This reaction is called **liquid phase nitration,** *e.g.,*

$$C_6H_{14} + HNO_3 \longrightarrow C_6H_{13}NO_2 + H_2O$$

For nitration of lower alkanes, a technique called **vapour phase nitration** is used, in which a mixture of the lower hydrocarbons and nitric acid vapours is passed through the silica tube at highly elevated temperature (at 400–500°C). The reaction also involves cleavage of C—C linkage alongwith C—H linkage, resulting to a mixture of nitroalkanes as

$$C_2H_6 + HONO_2 \longrightarrow C_2H_5NO_2 + CH_3NO_2 + H_2O$$

Nitration (like halogenation) also follows free radical mechanism.

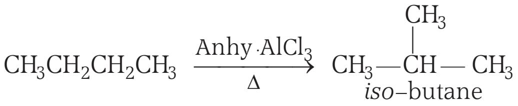
2. Sulphonation

Sulphonation is normally given by alkanes with minimum 6C-atoms onwards *i.e.,* hexane and onwards. Lower alkanes except those having tertiary hydrogen atom can't be sulphonated. Sulphonation is done by oleum (fuming H_2SO_4) *e.g.,*

$$\underset{\substack{\textit{iso}\text{-butane} \\ \text{(contains 3°C)}}}{(CH_3)_3CH} + \underset{\text{oleum}}{H_2SO_4(HSO_3OH)} \longrightarrow \underset{\substack{t\text{-butylsulphonic} \\ \text{acid}}}{(CH_3)_3CSO_3H} + H_2O$$

3. Isomerisation

This reaction is a result of molecular rearrangement involving 1,2-hydride or methyl shift. Anhydrous aluminium chloride ($AlCl_3$) is the reagent for this reaction, *e.g.,*



$$CH_3CH_2CH_2CH_3 \xrightarrow[\Delta]{\text{Anhy}\cdot AlCl_3} \underset{\textit{iso}\text{–butane}}{CH_3—\overset{\overset{\displaystyle CH_3}{|}}{C}H—CH_3}$$

This reaction does not occur unless a trace of water is present (to form HCl from $AlCl_3$) together with a trace of alkyl halide or an alkene.

Hot Spot 1

HALOGENATION

Previous years' examination paper reveals that it is an important topic for JEE Main examination. The questions are generally based on number of monochlorinated or dichlorinated products or on their yield. So, focus on these subtopics.

Halogenation is the process of replacement of one or more hydrogens of an alkane by halogen. For this reaction, order of reactivity of halogens is $I_2 < Br_2 < Cl_2 < F_2$. Reactivity decreases with decrease in the electronegativity of halogens. The reaction takes place as

$$CH_4 + Cl_2 \xrightarrow[-HCl]{h\nu \text{ or } 473-523\text{ K}} CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4$$

This reaction follows free radical mechanism and involves the following steps

Step I (Initiation step)

$$X-X \xrightarrow{\text{UV or } \Delta} \underset{\text{free radicals}}{X^\bullet + X^\bullet}$$

Step II (Propagation step)

$$R-H + X^\bullet \longrightarrow R^\bullet + HX$$

$$R^\bullet + X-X \longrightarrow RX + X^\bullet \text{ and so on}$$

Step III (Termination step)

$$X^\bullet + X^\bullet \longrightarrow X_2$$

$$R^\bullet + X^\bullet \longrightarrow RX$$

$$R^\bullet + R^\bullet \longrightarrow R-R$$

Different halogens give this reaction under different reaction conditions as

(i) Cl_2 reacts under UV light/diffused sun light/300–400°.

(ii) Br_2 reacts less vigorously and prefers site of its selection.

(iii) With I_2, reaction is reversible and carried out in the presence of oxidising agent like HIO_3, HgO, etc.

(iv) F_2 reacts with explosion.

This reaction is mainly given by those compounds which at least have one hydrogen atom present on sp^3 hybrid C-atom. Reactivity of sp^3 hybrid C-atom is as follows
tert-benzyl carbon > *sec*-benzyl carbon > *p*-benzyl carbon > *t*-allylic carbon > *s*-allylic carbon > *p*-allylic carbon > *t*-alkyl carbon > *s*-alkyl carbon > *p*-alkyl carbon > CH_4.

A chlorine free radical is so reactive that it makes primary, secondary and tertiary radicals with almost equal ease. According to reactivity selectivity principle, the greater the reactivity of a species, lesser will be selectivity. Bromine is less reactive towards alkanes than chlorine hence bromine is more selective in the site of attack when it reacts according to reactivity selectivity principle.

Since the reaction takes place by free radical mechanism, free radical inhibitors like oxygen inhibit the reaction while free radical accelerator such as benzoyl peroxide $(C_6H_5COO)_2$, tetraethyl lead $Pb(C_2H_5)_4$ etc., accelerate the reaction.

The number of monohalogenation products obtained from any alkane depends upon the number of different types of hydrogens it contains. *e.g.*, Butane contains two types of hydrogen, so it gives two monohalogenated product on mono halogenation.

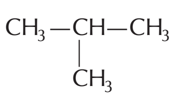
$$\underset{n\text{-butane}}{CH_3CH_2CH_2CH_3} \xrightarrow{Cl_2/h\nu} \underset{1\text{-chlorobutane}}{CH_3CH_2CH_2CH_2-Cl} + \underset{2\text{-chlorobutane}}{CH_3-CHCl-CH_2-CH_3}$$

***Sample* Problem 1** *Which of the following gives only one monohalogenated product on halogenation?*

(*a*) *Iso-propane* (*b*) *Neo-pentane*
(*c*) *Neo-hexane* (*d*) *Iso-pentane*

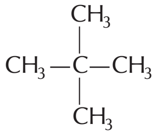
Interpret (*b*) In order to solve such problem follow the following steps

Step I Draw the structures of all the given compounds.



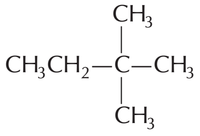
$CH_3-CH(CH_3)-CH_3$

iso-propane



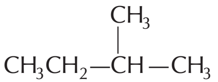
$CH_3-C(CH_3)_2-CH_3$

neo-pentane



$CH_3CH_2-C(CH_3)_2-CH_3$

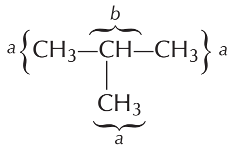
neo-hexane



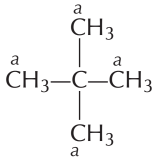
$CH_3CH_2-CH(CH_3)-CH_3$

iso-pentane

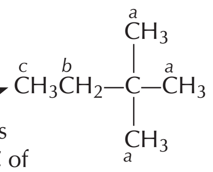
Step II Find the type of hydrogens present in each molecule.



(2 types of hydrogens)

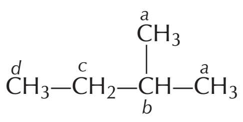


(1 type of hydrogen)



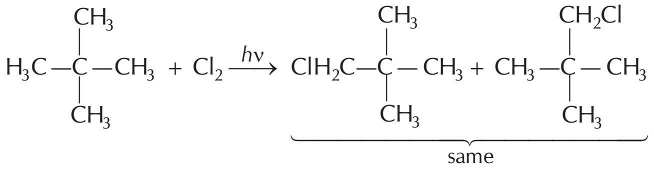
(as this C is in a different environment as compared to C of other CH_3 group)

(3 types of hydrogens)



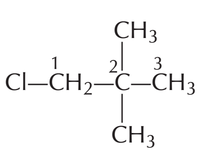
(4 types of hydrogens)

Step III The molecule having one type of H give only one monohalogenated product, so it is *neo*-pentane.



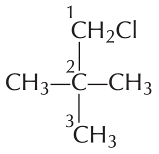
$$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 + Cl_2 \xrightarrow{h\nu} \underbrace{ClH_2C-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 + CH_3-\underset{CH_3}{\overset{CH_2Cl}{C}}-CH_3}_{\text{same}}$$

Step IV Check your answer by writing IUPAC names of products obtained, as IUPAC reveals you whether the obtained products are same or different.



$$\overset{1}{Cl-CH_2}-\overset{2}{\underset{CH_3}{\overset{CH_3}{C}}}-\overset{3}{CH_3}$$

1-chloro-2,2-dimethyl propane



$$CH_3-\underset{\overset{3}{CH_3}}{\overset{\overset{1}{CH_2Cl}}{\overset{2}{C}}}-CH_3$$

1-chloro-2,2-dimethyl propane

Yield of halogenation The yield of halogenation depends upon the reactivity of H. The order of reactivity of H for chlorination is

$$\underset{(3^\circ H)}{5} > \underset{(2^\circ H)}{3.8} > \underset{(1^\circ H)}{1}$$

For bromination the order is

$$\underset{(3^\circ H)}{1600} > \underset{(2^\circ H)}{82} > \underset{(1^\circ H)}{1}$$

From the reactivity, the yield is calculated as

$$\%\ \text{yield} = \frac{\text{Number of H atom} \times \text{relative reactivity of H} \times 100}{\text{Number of } 1^\circ \text{ H} \times \text{their reactivity} + \text{Number of } 2^\circ \text{ H} \times \text{their reactivity} + \text{Number of } 3^\circ \text{ H} \times \text{their reactivity}}$$

***Sample* Problem 2** *Find the percentage yield of 2-chlorobutane when butane is halogenated with chlorine.*

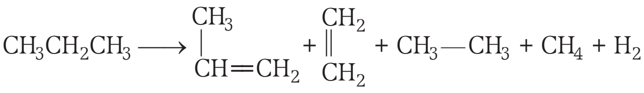
(*a*) 28.3 (*b*) 71.7 (*c*) 18.9 (*d*) 85.3

Interpret (*b*) To solve out such problems, follow the following steps.

Steps	Solution
Step I Write the structure of parent alkane	$CH_3CH_2CH_2CH_3$ butane
Step II Mark the different types of Hs as 1°, 2° or 3°	$\overset{1^\circ}{C}H_3\overset{2^\circ}{C}H_2\overset{2^\circ}{C}H_2\overset{1^\circ}{C}H_3$
Step III Count the number of 2° H as we have to find the percentage of 2-halogenated product.	Number of 2° H = 4
Step IV Calculate proportion of 2° H by multiplying their number with reactivity	$4 \times 3.8 = 15.2$
Step V Also calculate the proportions of other type of Hs.	Here only 1° H are also present. Their proportion $= 6 \times 1 = 6$
Step VI Find total proportion	$15.2 + 6 = 21.2$
Step VII Find % yield by using the formula $\% = \frac{\text{Proportion of H}}{\text{Total proportion}} \times 100$	$\% = \frac{15.2}{21.2} \times 100 = 71.7$

4. Pyrolysis

Pyrolysis (Greek, Pyro = fire, Lysis = loosening) is thermal breakage of organic molecules and when the process is applied to higher alkanes, it is called **cracking** (a word given by petroleum industry). The product is in the form of a mixture containing alkanes $(n-1)$ to CH_4, where, n = number of C atoms present in alkane undergone pyrolysis], alkenes (n to $CH_2{=}CH_2$, all possible alkenes) and H_2, *e.g.*,



$$CH_3CH_2CH_3 \longrightarrow \begin{matrix}CH_3\\ |\\ CH{=}CH_2\end{matrix} + \begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} + CH_3-CH_3 + CH_4 + H_2$$

The process generally requires temperatures in the range 500 – 800° C. Some catalysts like **finely divided silica-alumina** can also be used (catalytic cracking). A free radical mechanism is favoured.

5. Aromatisation

It is applicable to alkanes from hexane to decane, *e.g.*,

$$\text{Hexane} \xrightarrow{\text{Aromatisation}} \text{Benzene}$$

$$\text{Heptane} \xrightarrow{\text{Aromatisation}} \text{Toluene, etc.}$$

The reaction conditions for aromatisation is the presence of Al_2O_3 or Cr_2O_3 and 870 K temperature.

6. Oxidation

Oxidation can be complete or partial. Complete oxidation is called **combustion** which is shown by the generalised reaction as :

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \xrightarrow{\text{Flame}} nCO_2 + (n+1)H_2O + \text{Heat}$$

When alkanes are burnt in insufficient supply of oxygen, CO and carbon black are obtained.

$$C_nH_{2n+2} + O_2 \longrightarrow \underset{\substack{\text{carbon}\\ \text{black}}}{C} + H_2O$$

Alkanes are usually not affected by oxidising agents like $KMnO_4$ and $K_2Cr_2O_7$. However, alkanes having 3° hydrogen are oxidised by these oxidising agent to give corresponding alcohols.

$$(CH_3)_3CH + [O] \xrightarrow[\text{Alc.}]{KMnO_4} (CH_3)_3COH$$

Lower alkanes undergo restricted oxidation in the presence of metallic catalysts such as Cu at high temperature and pressure to form alcohols, aldehydes, ketones and acids *e.g.*,

$$\text{(i)}\ \underset{9\ :\ 1}{2CH_4 + 2[O]} \xrightarrow[100\ \text{atm}/200^\circ C]{\text{Cu- tube}} \underset{\text{methyl alcohol}}{2CH_3OH}$$

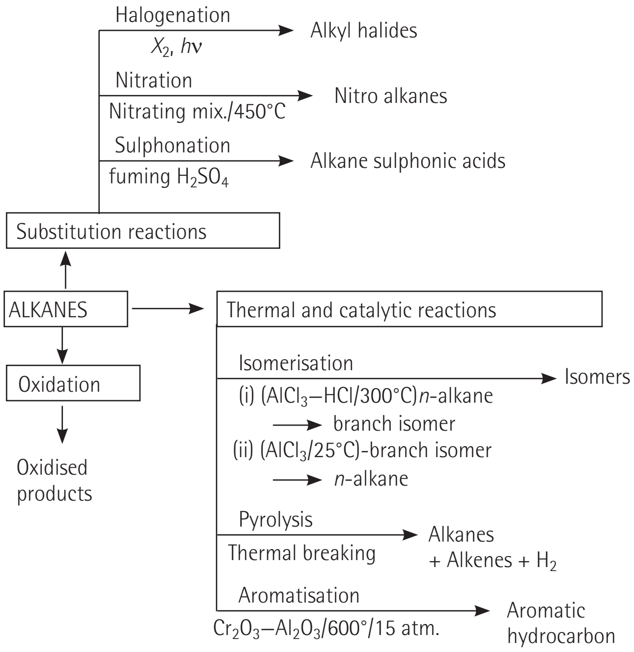
$$\text{(ii)}\ CH_4 + O_2 \xrightarrow[277^\circ C]{MoO} \underset{\text{formaldehyde}}{HCHO} + H_2O$$

$$\text{(iii)}\ HCH_3 + \frac{3}{2}O_2 \xrightarrow{(CH_3COO)_2Mn} \underset{\text{formic acid}}{HCOOH} + H_2O$$

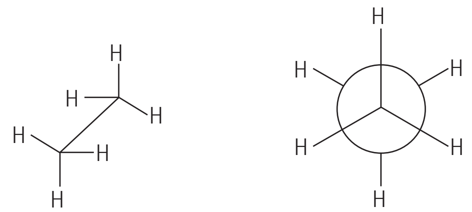
5. Methane or ethane with oxygen at high pressure and comparatively low temperatures are oxidised as

$$\begin{array}{l} CH_4 \xrightarrow{[O]} CH_3OH \xrightarrow[-H_2O]{[O]} HCHO \xrightarrow{[O]} HCOOH \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow [O] \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad H_2O + CO_2 \end{array}$$

Summary of Reactions of Alkanes



Conformations of Ethane



Saw horse projection Newmann projection

(For detail study of conformation, see chapter isomerism.)

Check Point 1

1. Alkanes are inert towards chemical reagents. Explain.
2. Why is the presence of CaO necessary during decarboxylation by NaOH?
3. Reduction with HI is usually carried out in the presence of small amounts of red P. Explain.
4. Account for the following.
   - (i) The boiling points of branched chain alkanes are lower as compared to their normal isomers.
   - (ii) Alkanes containing even number of carbon atoms have higher than expected boiling point.

15.3 Alkenes

Alkenes constitute the first series of unsaturated hydrocarbons with a π-bond proving unsaturation in them. These are characterised by the presence of a double bond between two adjacent carbons ($>C{=}C<$). Their general formula is C_nH_{2n} in comparison to C_nH_{2n+2} of alkanes. These are also called olefins (Latin, *oleum*= oil, *ficar* = to make) as their lower members form oily products on halogenation. Their main source is petroleum.

Alkenes are named by adding suffix 'ene' in the root word. These exhibit chain, position, ring-chain and geometrical isomerism. (For detail study of these topic see Chapter-13 and 14)

Methods of Preparation

Following methods are used to prepare alkenes.

1. Dehydrohalogenation

Alkyl halides when treated with alcoholic KOH/Δ gives alkenes as

$$CH_3CH_2Br \xrightarrow[\Delta]{\text{Alc. KOH}} CH_2{=}CH_2 + KBr + H_2O$$

The other reagents which can be used are high concentrations of **NaH / Δ**, **$NaNH_2$** or **KNH_2**/Δ and **sodium** or **potassium alkoxides** (for E2 reactions that occur in primary alkyl halides whose β-carbon is 1° or 2°) and **R_3N / NaOH** (for E1 reactions that occur in tertiary alkyl halides, secondary alkyl halides whose β-carbon is 3° or 4° and primary alkyl halides whose β-carbon is 3° or 4°) at room temperatures.

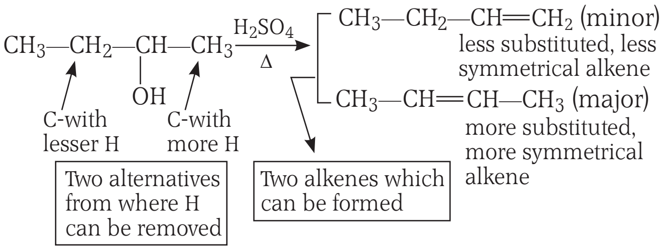
Important facts about dehydrohalogenation reaction of alkyl halides are as

1. Ease of dehydrohalogenation is 3° > 2° > 1° for alkyl halides.
2. In most of the cases **Saytzeff rule** (Zaistev rule) is followed, which was given by **A.M. Zaitsev** of university of Kazan (Russia). The rule originally was stated as "*in elimination reactions, when alternatives are available, the* H*–atom will be removed from that* C*–atom containing lesser number of hydrogens*". Two different expressions of this rule were also developed later on, which are :

   "When alternatives are available" (in elimination reactions) **:**

   (i) **More substituted alkene will be preferred.**

   (ii) **More stable** (symmetrical) **alkene will be preferred.**



2. Dehydration of Alcohols

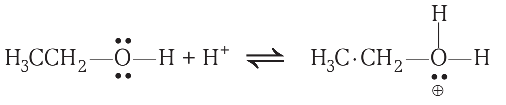
Alcohols when treated with sulphuric acid (concentrated) at 170°C, alkene is obtained.

$$CH_3CH_2OH \xrightarrow[170°C]{H_2SO_4} CH_2=CH_2 + H_2O$$

Mechanism

Step I Generation of protonated alcohol.

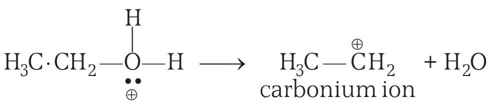
$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$



$$H_3CCH_2—\ddot{\underset{\cdot\cdot}{O}}—H + H^+ \rightleftharpoons H_3C\cdot CH_2—\overset{H}{\underset{\oplus}{\ddot{O}}}—H$$

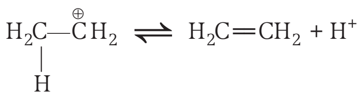
protonated alcohol

Step II Generation of carbonium ion



$$H_3C\cdot CH_2—\overset{H}{\underset{\oplus}{\ddot{O}}}—H \longrightarrow \underset{\text{carbonium ion}}{H_3C—\overset{\oplus}{C}H_2} + H_2O$$

Step III Removal of proton

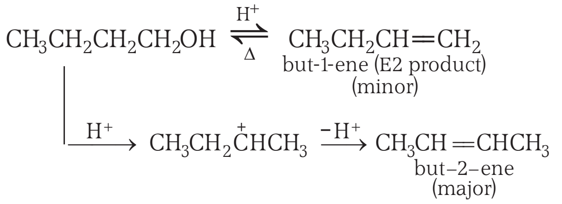


$$\underset{H}{H_2C}—\overset{\oplus}{C}H_2 \rightleftharpoons H_2C=CH_2 + H^+$$

Important facts related to dehydration are as

1. Ease of dehydration is 3° > 2° > 1° because of the involvement of carbocation intermediate.
2. The reaction can also be seen with Al_2O_3 350°C, P_2O_5, H_3PO_4, $POCl_3$ in pyridine.
3. 1° alcohols follow E2 mechanism while 3° alcohols follow E1 mechanism, 2° alcohols may follow either E2 or E1 mechanism however, E1 is preferred.

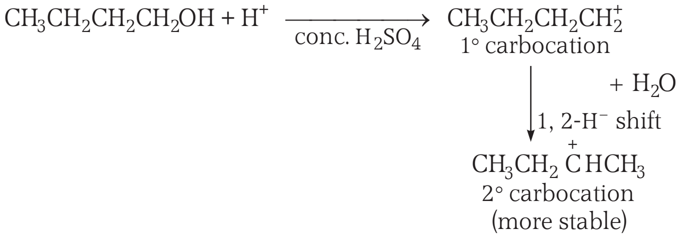
Although primary alcohols follow E2 mechanism but it is found that the yield of product is very less. The reason is the presence of H^+ ion in the reaction which works as an electrophile for alkene formed and responsible for modification or reversibility of reaction as seen in following example of butan-1-ol.



Major product (but-2-ene) formed after reaction modification due to H^+.

The rearrangement in open chain compounds in which shifting of $C_6H_5^-$ (Ph^-), CH_3^-, H^- takes place to give more stable carbocation and also the more stable product, is called *retropinacol rearrangement or Wagner rearrangement* Shifting of groups takes place in the following sequence : $C_6H_5^- > CH_3^- > H^-$

An example of such rearrangement is



This is the more stable carbocation that actually leads the formation of alkene.

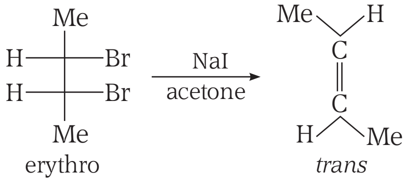
$$CH_3CH_2\overset{+}{C}HCH_3 \xrightarrow[-H^+]{} \underset{\text{2-alkene}}{CH_3CH=CHCH_3}$$

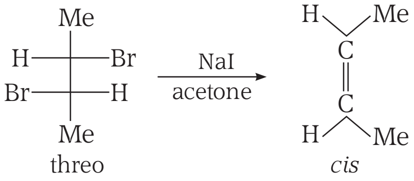
3. Dehalogenation

Only *vicinal* dihalides (in which the halogen atoms are attached to two successive C-atoms) give alkenes while *geminal* dihalides (in which the halogen atoms are attached to the same C-atoms) give alkynes when heated with a dehalogenating agent like zinc dust. The reaction takes place as

$$\underset{vic\text{-dihalide}}{BrCH_2—CH_2Br} + Zn \xrightarrow{C_2H_5OH} CH_2=CH_2 + ZnBr_2$$

Other reagents that can be used for dehalogenation are NaI in acetone and Na in dry ether (like Wurtz reaction). In the latter case elimination is associated with coupling and it is useful only for elimination from *gem* dihalides. The elimination is stereo-selective *i.e., anti* predominantly.





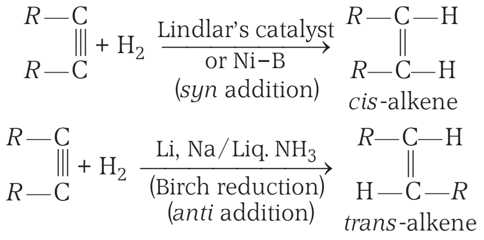
If sodium metal is used in place of zinc, the higher alkenes can be obtained.

4. Controlled Hydrogenation

Alkynes on hydrogenation with Lindlar's catalyst or nickel boride (P-2 catalyst) or with Na or Li in liquid ammonia, give alkenes.

Lindlar's catalyst is Pd poisoned with $BaSO_4$ or $CaCO_3$ in quinoline or xylene. The addition is stereo-selective and *syn* in the case of Lindlar's catalyst or nickel boride (P-2 catalyst). However, *anti*-addition is seen in the case of Na or Li in liquid NH_3. (Birch reduction)

The *syn* and *anti* additions can be seen as :

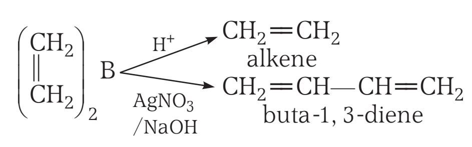


$$\begin{array}{c} R-C \\ ||| \\ R-C \end{array} + H_2 \xrightarrow[\text{or Ni–B (syn addition)}]{\text{Lindlar's catalyst}} \underset{\textit{cis}\text{-alkene}}{\begin{array}{c} R-C-H \\ \| \\ R-C-H \end{array}}$$

$$\begin{array}{c} R-C \\ ||| \\ R-C \end{array} + H_2 \xrightarrow[\text{(Birch reduction) (anti addition)}]{\text{Li, Na/Liq. }NH_3} \underset{\textit{trans}\text{-alkene}}{\begin{array}{c} R-C-H \\ \| \\ H-C-R \end{array}}$$

5. Hydroboration

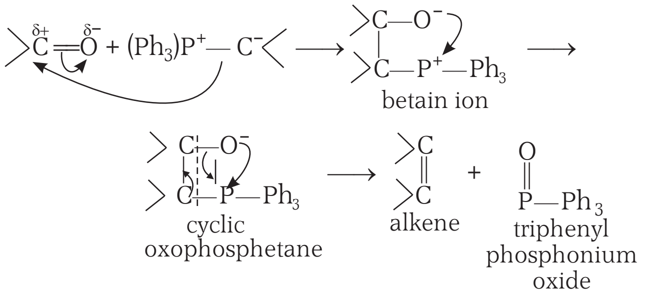
Hydroboration of alkynes can be seen as



$$3H-C\equiv C-H \xrightarrow{BH_3 \text{ in THF}} \left(\begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array}\right)_2 B \begin{cases} \xrightarrow{H^+} \underset{\text{alkene}}{CH_2=CH_2} \\ \xrightarrow{AgNO_3/NaOH} \underset{\text{buta-1, 3-diene}}{CH_2=CH-CH=CH_2} \end{cases}$$

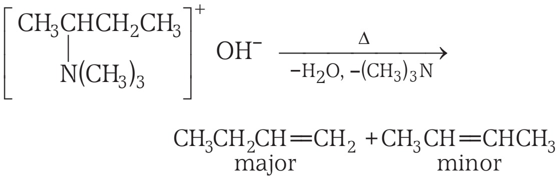
6. Wittig Reaction

In the Wittig reaction there is nucleophilic addition of triphenylphosphonium (ylide) ion which results to alkene as

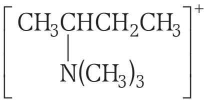


7. Pyrolysis of Quaternary Ammonium Compounds

The opposite results to Zaitsev rule were obtained by **Hofmann** while working on β-elimination in quaternary ammonium hydroxides as



$$\left[\begin{array}{c} CH_3\underset{|}{C}HCH_2CH_3 \\ N(CH_3)_3 \end{array}\right]^+ OH^- \xrightarrow[-H_2O,\ -(CH_3)_3N]{\Delta} \underset{\text{major}}{CH_3CH_2CH=CH_2} + \underset{\text{minor}}{CH_3CH=CHCH_3}$$



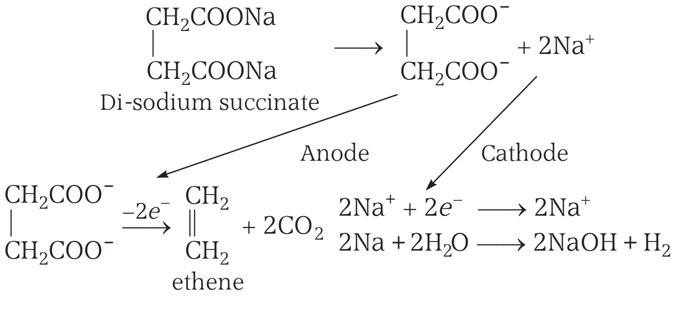
$$\left[\begin{array}{c} CH_3\underset{|}{C}HCH_2CH_3 \\ N(CH_3)_3 \end{array}\right]^+$$ X^- also gives the similar results.

He explained the difference in results on the basis of presence of bulky $N(CH_3)_3$ group in the compound, which destabilises transition state in second case. The finding of Hofmann are considered as **Hofmann rule.**

8. Kolbe's Electrolytic Method

Electrolysis of sodium or potassium salts of dicarboxylic acid, *e.g.,*

$\begin{array}{l} CH_2COO^-K^+ \\ | \\ CH_2COO^-K^+ \end{array}$ (potassium succinate) produces alkene, $\begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array}$



$$\underset{\text{Di-sodium succinate}}{\begin{array}{l} CH_2COONa \\ | \\ CH_2COONa \end{array}} \longrightarrow \begin{array}{l} CH_2COO^- \\ | \\ CH_2COO^- \end{array} + 2Na^+$$

Anode

Cathode

$$\begin{array}{l} CH_2COO^- \\ | \\ CH_2COO^- \end{array} \xrightarrow{-2e^-} \underset{\text{ethene}}{\begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array}} + 2CO_2$$

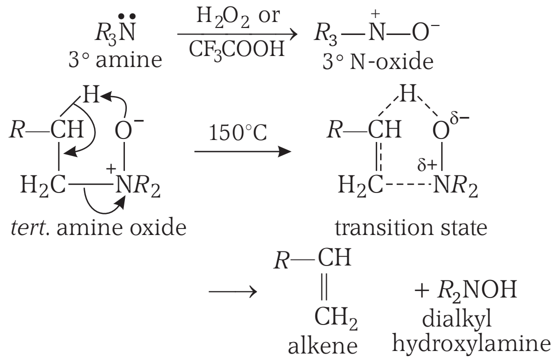
$$2Na^+ + 2e^- \longrightarrow 2Na^+$$

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

The method is an extension of **Kolbe's method** for the preparation of alkanes.

9. Cope Reaction

When a 3° amine oxide containing atleast one β-hydrogen is heated at 150°C, it decomposes to form an alkene and a derivative of hydroxylamine.



This reaction may also be carried out in dimethyl sulphoxide or THF at room temperature.

Summary of preparation methods of alkenes is given in the following flow diagram.

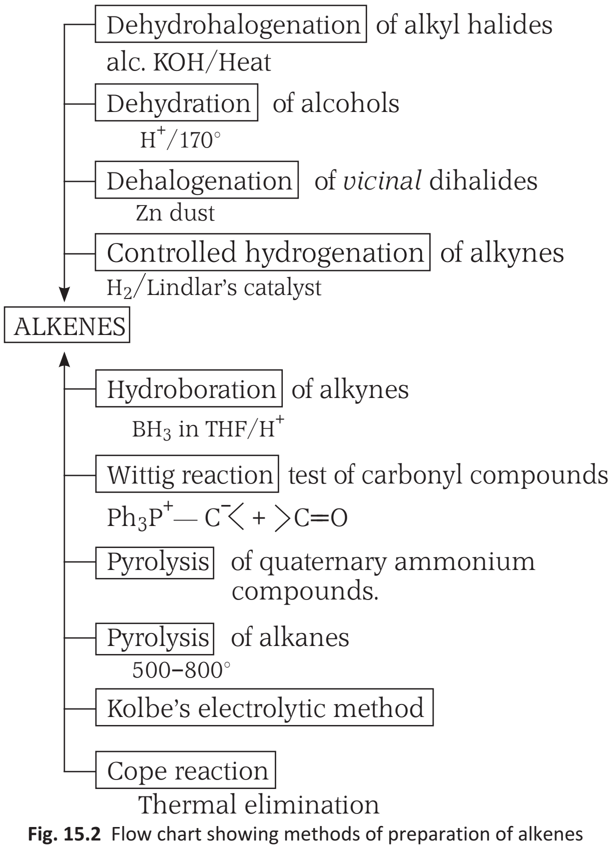


Fig. 15.2 Flow chart showing methods of preparation of alkenes

Physical Properties

1. First three alkenes are gases, next 14 are liquids and rest are solids.
2. All alkenes are colourless and odourless except ethene which has pleasent odour.
3. These are lighter than water and the density gradually increases with rise in molecular mass.
4. These also show same trend of boiling and melting points as alkanes but geometrical isomers behave differently. *cis*-alkenes have higher boiling point as compared to their *trans*-isomers. However, melting point is higher in case of *trans*-isomers.
5. In general, *trans*-form has almost zero dipole moment and thus, exhibits weaker intermolecular attractions.
6. Alkenes are insoluble in water but soluble in non-polar solvents like benzene, ether, CCl_4 etc.
7. The alkenes follows the following order of stability

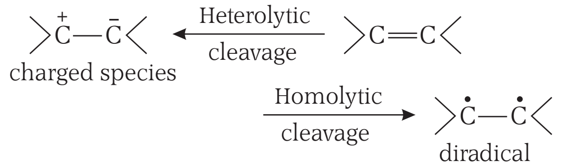
$$R_2C{=}CR_2 > R_2C{=}CHR > R_2C{=}CH_2 \approx RCH{=}CHR\ (trans > cis) > RCH{=}CH_2 > CH_2{=}CH_2$$

(On the basis of hyperconjugative structures.)

Heat of hydrogenation is also an index of stability. The *lower the heat of hydrogenation of an alkene, the more stable it is*.

Chemical Properties

Alkenes generally undergo electrophilic addition reactions because of the presence of a double bond (a strong σ and a weaker π bond), π electrons of which being loosely held are easily polarisable. These reactions involve cleavage of a π bond and formation of two new σ bonds. The cleavage may be homolytic or heterolytic.



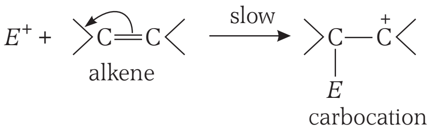
In polar solvents, addition proceeds by ionic mechanism (*i.e.,* at low temperature), whereas in the presence of light or non-polar solvents, the addition occurs by free radical mechanism (*i.e.,* at high temperature).

The steps involved in ionic mechanism are as follows

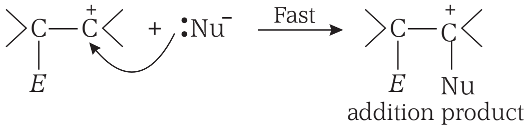
Step I Ionisation of reagent to generate electrophile and nucleophile

$$E{—}Nu \longrightarrow E^+ + :Nu^-$$

Step II Attack of electrophile on alkene



Step III Attack of nucleophile to give addition product.



Since electrophile attacks first, the reactions are called electrophilic addition reactions.

Some example of these reactions are as follows

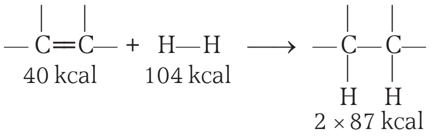
Caution Point *From the stereochemistry point of view, organic reactions can be stereoselective (i.e., one stereoisomer predominates over the other) or stereospecific (i.e., a single product is formed from both the geometrical isomers).*

While going for stereoselective reactions always remember

(i) *cis alkene + anti addition ⟶ Racemic mixture*
(ii) *trans alkene + anti addition ⟶ meso form*
(iii) *cis alkene + syn addition ⟶ meso form*
(iv) *trans alkene + syn addition ⟶ Racemic mixture*

1. Addition of Hydrogen (Hydrogenation)

Hydrogenation involves the breaking of a π-bond (about 40 kcal) and a H—H bond (104 kcal), and the formation of two C—H bonds (average value 87 kcal); the net result is the evolution of about 30 kcal of heat, which is called heat of hydrogenation.

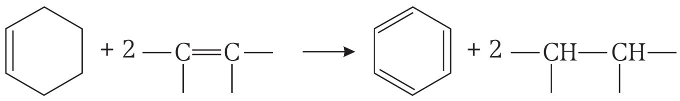


$$\underset{40\text{ kcal}}{\text{—C=C—}} + \underset{104\text{ kcal}}{\text{H—H}} \longrightarrow \underset{2\times 87\text{ kcal}}{\text{—}\underset{\text{H}}{\text{C}}\text{—}\underset{\text{H}}{\text{C}}\text{—}}$$

$$\Delta H = -30\,\text{kcal mol}^{-1}$$

For most of the alkenes, the heat of hydrogenation is approximately 30 kcal.

Wilkinson catalyst, $\mathbf{RhCl[(C_6H_5)_3P)_3]_3}$ is a good catalyst for hydrogenation (comparable with Raney Ni). Other reagents are **cyclohexene** (itself oxidises to benzene), hydrazine (itself oxidises to N_2), $NaBH_4 \cdot PtCl_2$ etc.



Birch reagent (Na in liquid NH_3 with C_2H_5OH or CH_3OH) works only on terminal double bonds in aliphatic alkenes.

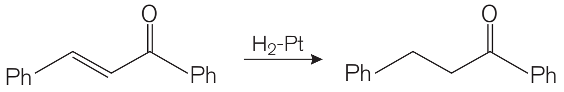
$$R\text{CH}{=}\text{CH}_2 \xrightarrow[e^-]{\text{Na}} R\text{CH}\overset{\ominus}{\ddot{\text{C}}}\text{H}_2 \xrightarrow{\text{EtOH}} R\dot{\text{C}}\text{HCH}_3$$

$$\xrightarrow[e^-]{\text{Na}} R\overset{\ominus}{\ddot{\text{C}}}\text{HCH}_3 \xrightarrow{\text{EtOH}} R\text{CH}_2\text{CH}_3$$

For hydrogenation also see alkanes (methods of preparation reaction (b).

The rate of hydrogenation of olefinic bonds (at room temperature and atmospheric pressure) is —CH$=$CH$_2$ > — CH$=$CH— or a ring double bond.

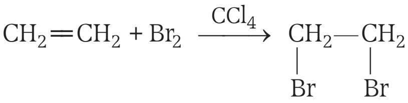
Caution Point *The C≡C bond is reduced more readily than C=C but other unsaturated groups (except nitro and acid chlorides) are reduced less readily. Catalytic hydrogenation can therefore, be used for the selective reduction of C=C in the presence of aromatic ring and carbonyl groups, whether or not the unsaturated functions are conjugated.*



Hydrogen is added in syn manner.

2. Addition of Halogens (Halogenation)

Alkenes (and also alkynes) form addition products with Cl_2 and Br_2. Br_2 water is decolourised by unsaturated hydrocarbons (hence, it is the test of unsaturation).



$$\text{CH}_2{=}\text{CH}_2 + \text{Br}_2 \xrightarrow{\text{CCl}_4} \underset{\text{Br}}{\text{CH}_2}\text{—}\underset{\text{Br}}{\text{CH}_2}$$

The reaction is stereo-selective (predominantly anti addition occurs, *i.e.,* Br atoms are on the opposite side of the plane of the molecule).

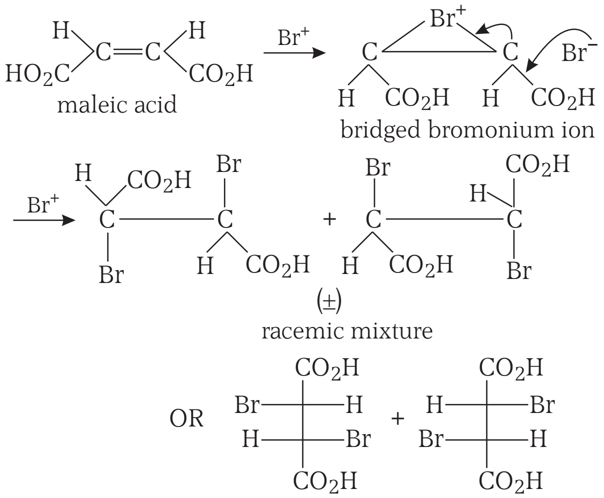
Relative rates of reaction of alkene with Br_2/CH_3OH are in order of

ethene < 1-butene < *trans*-2-butene < 2-methyl-1-butene < 2,3-dimethyl-2-butene.

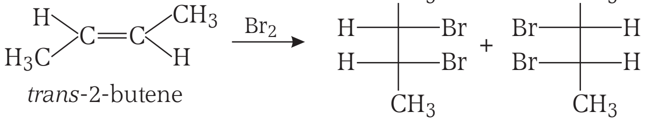
Mechanism

The reaction proceeds through the formation of a bridged bromonium ion which is more stable than carbocation followed by attack by the bromide ion.

$$\text{Br}_2 \rightleftharpoons \text{Br}^+ + \text{Br}^-$$



The attack occurs because the positively charged bromine is very electronegative and readily accepts an electron pair. With *trans*-2-butene, product of Br_2 addition is optically inactive due to the formation of symmetric *meso* compound.



identical (*meso*)

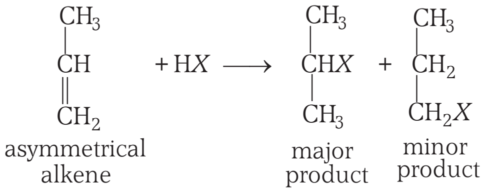
3. Reaction with Hydrogen Halides

The addition of **halogen acids** is frequently carried out by passing dry gaseous halogen acids in moderately polar solvent. In the case of asymmetric alkenes, reaction occur as per **Markownikoff rule** (given later) with exception of HBr in the presence of peroxide **(Kharasch effect)** where infact free radical mechanism is followed. The mechanism of both the reactions are seen in previous (Chapter 13).

The order of stability of carbocations is

$$3° > 2° > 1° > \overset{\oplus}{C}H_3.$$

The **Markownikoff rule** is used as a guidance for electrophilic additions in those cases where an asymmetrical reagent is added to an asymmetrical alkene or alkyne and *states that in such cases (+)ve part of the reagent goes to the* C*–atom containing more number of hydrogen or (–)ve part of the reagent goes to the* C*–atom containing lesser number of hydrogens*. If number of hydrogens are same, the (–)ve part of the reagent goes to the C-atom bearing more number of alkyl groups is also the same then addition occurs but the rule is not applicable. *e.g.,*



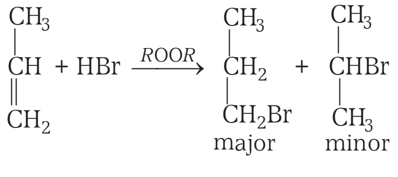
$$CH_3{-}CH{=}CH_2 + HX \longrightarrow CH_3{-}CHX{-}CH_3 + CH_3{-}CH_2{-}CH_2X$$

As the reaction is electrophilic addition thus it proceeds *via* carbonium ion formation. In the above case two carbonium ions are possible after the attack of electrophile *i.e.,*

$$(i)\ CH_3{-}CH_2{-}\overset{+}{C}H_2(1°),\quad (ii)\ CH_3\overset{+}{C}HCH_3(2°).$$

Out of these two, the latter *i.e.,* 2° carbonium ion is more stable that's why it is responsible for major product formation.

The above rule is not followed if HBr is added to an asymmetrical alkene in the presence of *ROOR* (peroxide) as :

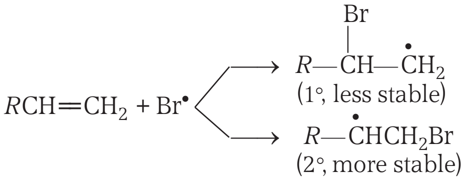


$$CH_3{-}CH{=}CH_2 + HBr \xrightarrow{ROOR} CH_3{-}CH_2{-}CH_2Br + CH_3{-}CHBr{-}CH_3$$

The main responsible factor here is organic peroxide which dissociates into free radicals and modifies the electrophilic addition to free radical addition which passes through two free radicals as their intermediates i.e.,

$$ROOR \longrightarrow 2RO^{\bullet}$$

$$RO^{\bullet} + HBr \longrightarrow R{-}OH + Br^{\bullet}$$



$$RCH{=}CH_2 + Br^{\bullet} \longrightarrow R{-}CHBr{-}\dot{C}H_2 \text{ (1°, less stable)};\quad R{-}\dot{C}HCH_2Br \text{ (2°, more stable)}$$

Now here as the 2° free radical is more stable thus it is responsible for major product formation.

$$R{-}C^{\bullet}HCH_2Br + HBr \longrightarrow RCH_2CH_2Br + Br^{\bullet}$$

The modified case of HBr in the presence of peroxide is called Kharasch effect and considered as an example of anti-Markownikoff addition as it follows an opposite course to that suggested by Markownikoff. The rule is also applicable on alkynes.

HF, HCl and HI does not give such modified reactions because

(i) The bonds between halogen and hydrogen is very strong in HF and HCl that's why $RO^{\bullet}$, free radical is unable to break them homolytically. Thus, reaction procedure is not modified.

(ii) In the case of HI, although $RO^{\bullet}$ free radical produces homolytic cleavage but $I^{\bullet}$, free radical formed has more tendency to form I_2 as compared to form free radical of carbon.

4. Reaction with Water (Hydration)

A water molecule is added when alkane it treated with dil. H_2SO_4, or subjected to hydroboration or oxymercuration-demercuration reaction.

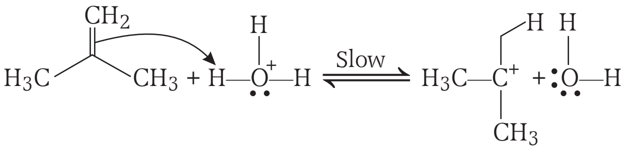
(i) **With dil. H_2SO_4** The reaction takes place as

$$CH_2{=}CH_2 \xrightarrow{\text{dil. } H_2SO_4} CH_3{-}CH_2HSO_4 \xrightarrow[\text{warm}]{H_2O} CH_3CH_2OH$$

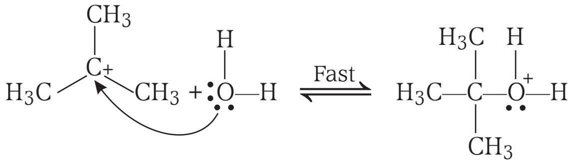
The reaction follows Markownikoff's rule.

Mechanism

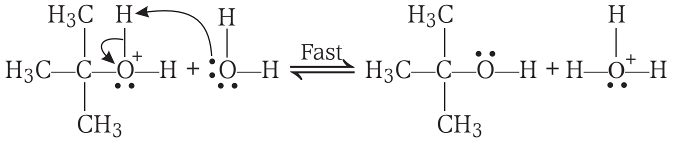
Step I The alkene accepts a proton to form more stable 3° carbocation.



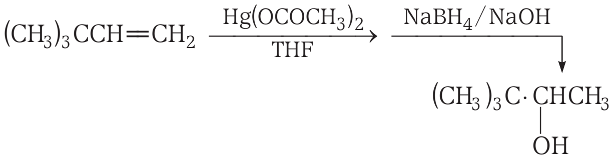
Step II The carbocation reacts with a molecule of water to form a protonated alcohol.



Step III The transfer of proton to a molecule of water leads to a product.

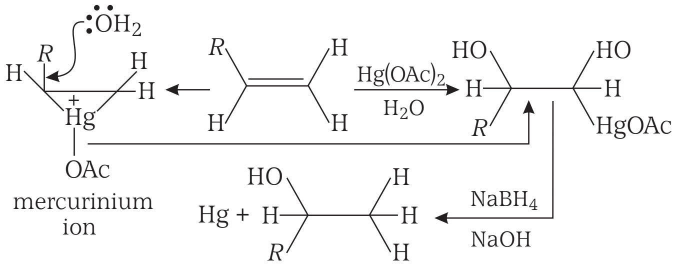


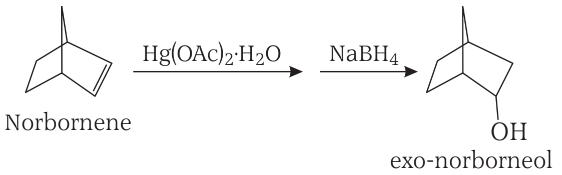
(ii) **Oxymercuration-demercuration** Mercuric acetate (in THF) followed by reduction with $NaBH_4$ /NaOH can also be used for the purpose. The reaction is called **oxymercuration-demercuration reaction** and proceeds through cyclic transition state formation involving mercury metal. It is contrary to hydration with H_2SO_4 where carbonium ion is produced. If the carbonium ion is intermediate then there always exists a possibility of rearrangement while such a possibility is not seen in the case of **oxymercuration demercuration**. *i.e.*, the addition is exactly localised here. The reaction can be seen as



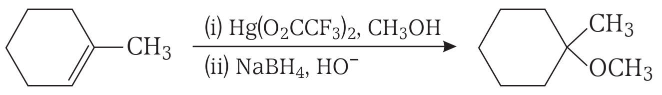
$$(CH_3)_3CCH{=}CH_2 \xrightarrow[\text{THF}]{Hg(OCOCH_3)_2} \xrightarrow{NaBH_4/NaOH} (CH_3)_3C\cdot \underset{\substack{|\\ OH}}{C}HCH_3$$

In this reaction, mercury diacetate first adds across the double bond in an oxymercuration step. Water then displaces the mercury acetate group. The mechanism involves the ring opening of a mercurinium ion by S_N2 attack of water; this result in the *anti* (or *trans*) hydroxy-substituted organomercury intermediate, which is then reduced to give the alcohol (Nucleophile attaches to the more substituted carbon from the side opposite the leaving mercury)

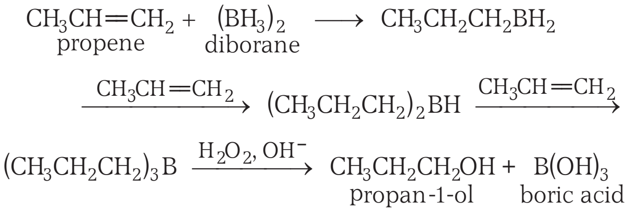




In alkoxy mercuration reaction, alcohol is the nucleophile and product formed is an ether.



(iii) **Hydroboration** A reaction of alkene with diborane followed by oxidation with alkaline H_2O_2, also give hydration product without rearrangement but in accordance with Kharash rule. This reaction looks as



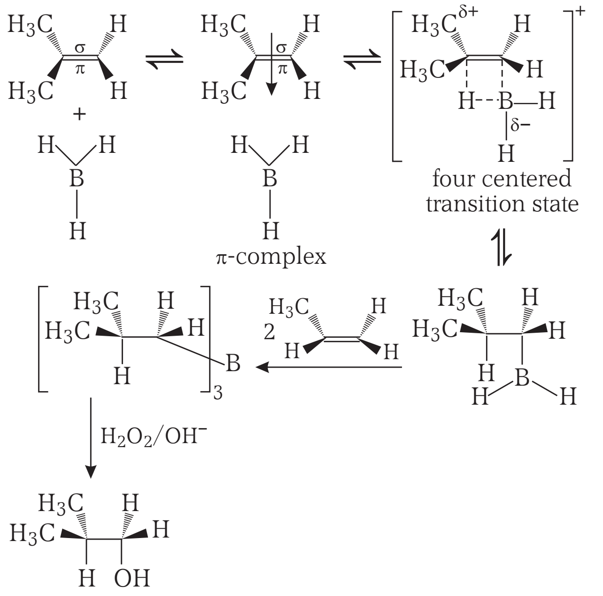
$$\underset{\text{propene}}{CH_3CH{=}CH_2} + \underset{\text{diborane}}{(BH_3)_2} \longrightarrow CH_3CH_2CH_2BH_2$$

$$\xrightarrow{CH_3CH=CH_2} (CH_3CH_2CH_2)_2BH \xrightarrow{CH_3CH=CH_2}$$

$$(CH_3CH_2CH_2)_3B \xrightarrow{H_2O_2,\, OH^-} \underset{\text{propan-1-ol}}{CH_3CH_2CH_2OH} + \underset{\text{boric acid}}{B(OH)_3}$$

This reaction involves two steps, *i.e., syn* addition of borane (BH_3) to double bond and oxidation followed by hydrolysis to give alcohol.

Mechanism



Addition takes place through the initial formation of a π-complex which changes into a cyclic four centre transition state with the boron atom adding to less hindered carbon atom. The dashed bonds in the transition state represent bonds that are partially formed or partially broken.

The overall hydration of the alkene has been shows to occur by the *syn*-addition.

Sample **Problem 3** *Alkene,* $CH_3CH_2OCH{=}CH_2$ *hydrolysed much faster as compared to ethene. The reason for this is*

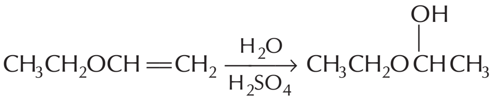
(a) *a more stable carbocation is generated in case of* $CH_3CH_2OCH{=}CH_2$

(b) $CH_3CH_2OCH{=}CH_2$ *is a more stable alkene as compared to* C_2H_4 *towards hydration.*

(c) *a more stable carbanion is generated in case of* $CH_3CH_2OCH{=}CH_2$

(d) *None of the above*

Interpret (*a*)



$$CH_3CH_2OCH{=}CH_2 \xrightarrow[H_2SO_4]{H_2O} CH_3CH_2O\overset{\overset{OH}{|}}{C}HCH_3$$

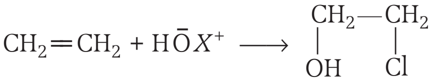
$$CH_3CH_2OCH{=}CH_2 \xrightarrow{H_3O^+} \underset{\text{carbocation } A \text{ (more stable)}}{CH_3CH_2O\overset{\oplus}{C}HCH_3}$$

$$CH_2{=}CH_2 \xrightarrow{H_3O^+} \underset{\text{carbocation } B \text{ (less stable)}}{CH_3\overset{\oplus}{C}H_2}$$

Stability of 2° carbocation is further increased by electron repelling ethoxy (CH_3CH_2O) group. Greater the stability of carbocation, easier is its formation, hence faster the reaction.

5. Reaction with Hypohalous Acid (HO*X*)

Halohydrins are obtained in the reaction. Halohydrins are the compounds containing —OH and —*X* groups at successive C–atoms. The hypohalous acid breaks as OH^- and X^+ and it is the halonium ion (X^+) which attacks on π bond. Reaction is **stereo-selective** (*anti*-addition is seen) and seen as

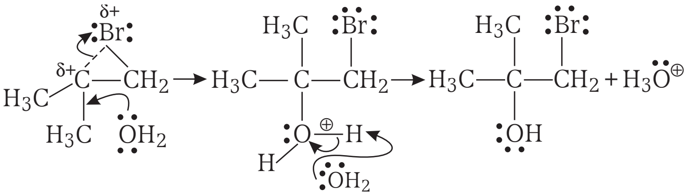


$$CH_2{=}CH_2 + H\bar{O}X^+ \longrightarrow \underset{OH}{\underset{|}{C}H_2}{-}\underset{Cl}{\underset{|}{C}H_2}$$

Markownikoff's rule is followed in the case of unsymmetrical alkenes.

The order of reactivity of different X_2/H_2O is $Cl_2/H_2O > Br_2/H_2O > I_2/H_2O$.

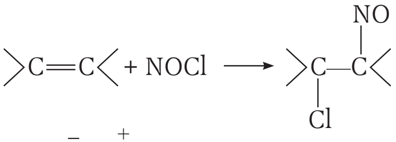
Mechanism



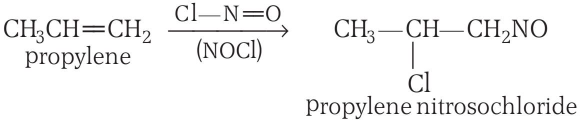
6. Addition of Nitrosyl Chloride (Tildens Reagent)

Nitrosyl chloride (NOCl) or bromide adds to a carbon-carbon double bond to yield halonitroso derivatives.

$$(NOCl \longrightarrow {}^-Cl{-}{}^+N{=}O);\ (NOBr \longrightarrow {}^-Br{-}{}^+NO)$$



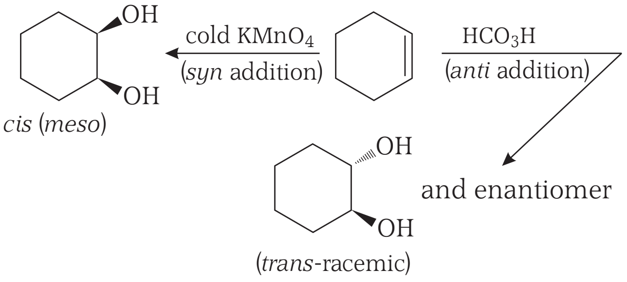
$$>C{=}C< + NOCl \longrightarrow >\underset{Cl}{\underset{|}{C}}{-}\overset{NO}{\overset{|}{C}}<$$

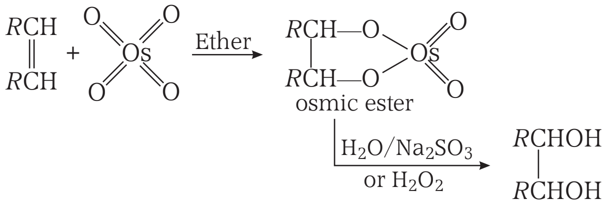


$$\underset{\text{propylene}}{CH_3CH{=}CH_2} \xrightarrow[(NOCl)]{\bar{C}l{-}\overset{+}{N}{=}O} \underset{\text{Propylene nitrosochloride}}{CH_3{-}\underset{Cl}{\underset{|}{C}H}{-}CH_2NO}$$

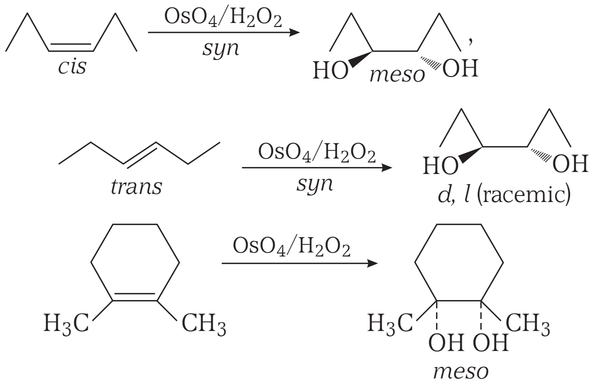
7. Hydroxylation (Insertion of —OH Group)

Hydroxylation with **Baeyer's reagent** ($KMnO_4$/NaOH or $KMnO_4$ cold or $KMnO_4$) and OsO_4 is *syn*-addition (stereo-selective) while with peroxyacids it is an *anti*-addition. Infact with peroxy acids oxiranes are produced in the beginning and peroxyformic acid (HCOOOH) is strong enough to break them into glycols. That means with rest peroxyacids oxiranes are the last product.

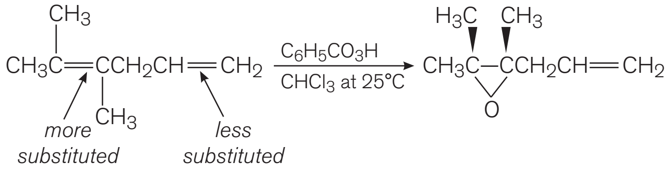




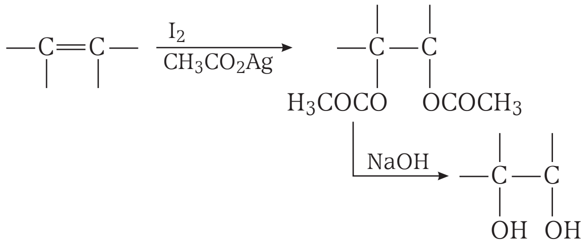
Like $KMnO_4$, in this case also, addition is *syn*.



Caution Point *If peroxybenzoic acid, $C_6H_5CO_3H$ or peroxy acetic acid CH_3CO_3H is used, oxiranes (epoxides) are formed. The more highly substituted double bond is more nucleophilic and therefore, reacts faster with the peroxy acid than the less substituted double bond.*

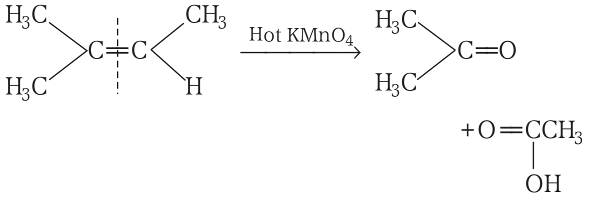


Besides, I_2 with silver acetate can also be used as hydroxylating agent and in this case also the addition is of *syn* type.



8. **Oxidation by Hot or Acidic** $KMnO_4$

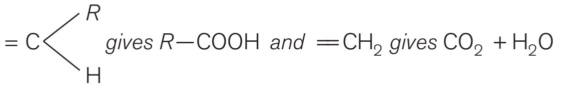
With hot or acidic $KMnO_4$, complete cleavage occurs at $>C{=}C<$ bond resulting to acids or ketone as



Caution Points

(*i*) *During oxidation of alkene with hot* $KMnO_4$.

$= CR_2$ *gets converted into* $O{=}CR_2$

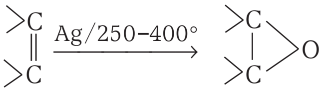


$=C\begin{matrix} R \\ H \end{matrix}$ *gives* $R{-}COOH$ *and* $=CH_2$ *gives* $CO_2 + H_2O$

(*ii*) *If* HCOOH *is formed in the above cleavage, it is further oxidised to* CO_2.

9. **Catalytic Oxidation**

This reaction produces cyclic ethers as



10. **Waker's Process**

In this process alkene is oxidised by treating it with Pd and $CuCl_2$ at 50°C, *e.g.*,

$$\underset{\text{ethene}}{H_2C{=}CH_2} + PdCl_2 + H_2O \xrightarrow{50°C} \underset{\text{acetaldehyde}}{CH_3CHO} + Pd + 2HCl$$

$$\left[\begin{array}{rcl} Pd + 2CuCl_2 & \longrightarrow & PdCl_2 + Cu_2Cl_2 \\ Cu_2Cl_2 + 2HCl + 1/2\,[O]_2 & \longrightarrow & 2CuCl_2 + H_2O \end{array}\right]$$

With propene, acetone is formed.

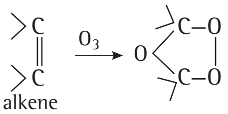
$$\underset{\text{propene}}{CH_3CH{=}CH_2} + PdCl_2 + H_2O \longrightarrow \underset{\text{acetone}}{CH_3COCH_3} + Pd + 2HCl$$

Hot Spot 2

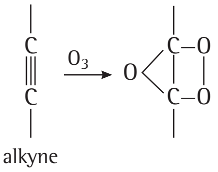
OZONOLYSIS

It is the most important topic for JEE Main examination. The importance of the topic is revealed by the fact that the question are not very difficult and with a small practice, you get mastery in it.

Ozonolysis is oxidation with O_3 (ozonide formation) followed by hydrolysis. In ozonide formation two bonds between carbon atoms are used as



Similarly,

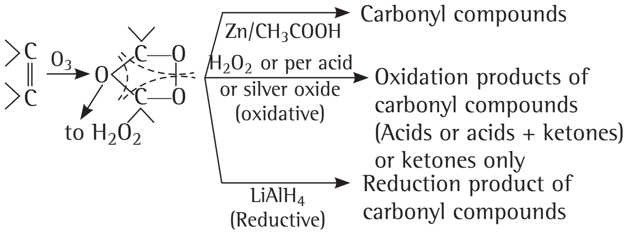


The normal products of this reaction are carbonyl compounds which are formed if hydrolysis is carried out in the presence of mild reducing agents like Zn / CH_3COOH which nullify the oxidising tendency of H_2O_2 formed as the by product of this reaction and have the tendency to oxidise carbonyl product formed.

The hydrolysis may be of oxidation type or reductive type

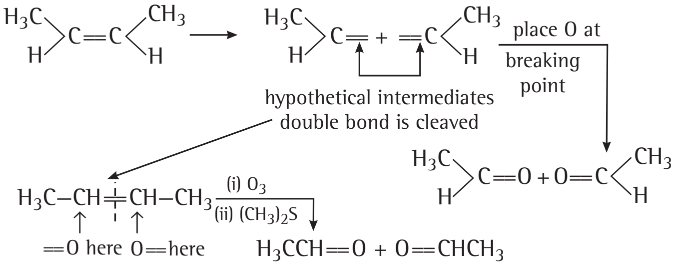
(i) The **oxidative type** hydrolysis results in oxidation products of carbonyl compounds *i.e.,* acids in the presence of oxidising agents like silver oxide or peroxy acids. H_2O_2 produced may also auto-oxidise the products. Among the carbonyl compounds, ketones are not easily oxidised. Thus, we may get either only **acids** or **acid + ketones** or only **ketones** as the product of oxidative hydrolysis.

(ii) The hydrolysis may be **reductive type** also with reagents like $LiAlH_4$ (strong reducing agents) and results to primary and secondary alcohols (reduction products of carbonyl compounds).

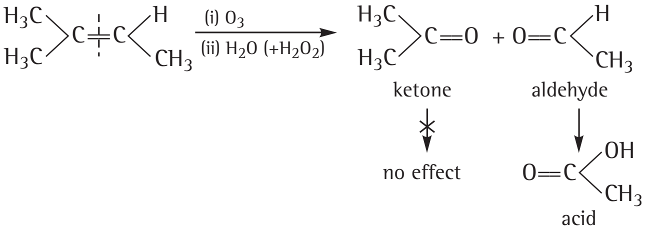


Thus, complete reaction looks as :

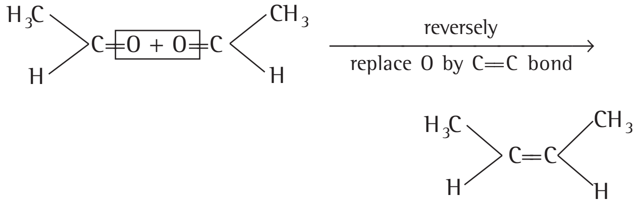
To determine product by ozonolysis of alkenes, break C═C bond and place oxygen at breaking point



If the ozonide is simply treated with water, H_2O_2 is formed as a by product. Under these conditions (or H_2O_2 is added from outside), aldehydes are converted into carboxylic acids, but ketones remain unaffected.



To decide the structure of alkene from ozonolysis products, bring the products together in such a way that O atoms are face to face, replace O by C═C bond. Thus,



Sample **Problem 4** *An alkene ' A' contains three C—C, eight C—H σ-bonds and one C—C π-bond. ' A' on ozonolysis gives two moles of an aldehyde of molar mass 44 u. Write the IUPAC name of ' A'.* [**NCERT**]

(*a*) *but*-1-*ene*

(*b*) 2-*methyl prop*-1-*ene*

(*c*) 2-*methyl prop*-2-*ene*

(*d*) *but*-2-*ene*

Interpret (*d*) To solve such problems, first identify the structure of aldehyde, *R*CHO from the molar mass (44 u) to find the structure of *A*. Join two molecules of aldehyde to find the structure of *A*. Count the number of σ and π-bonds in *A*. Are they satisfy the given data.

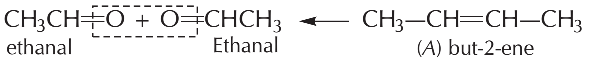
General formula for aldehyde is *R*CHO. Let mass of *R* is *x*.

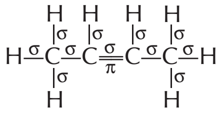
$$x + 12 + 1 + 16 = 44$$

$$x = 15$$

Mass of CH_3 group is 15, so $R = CH_3$ and aldehyde is CH_3CHO.

Now,

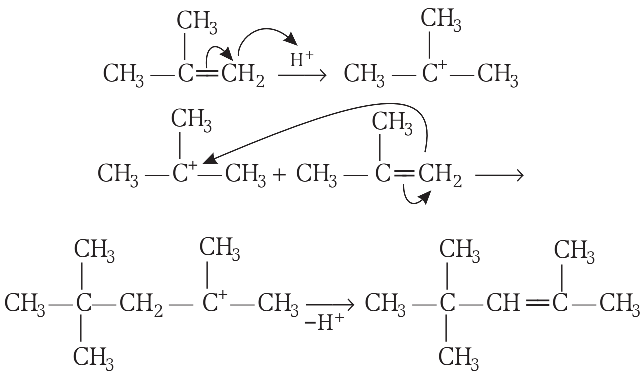




Hence, alkene (*A*), *i.e.,* but-2-ene contains three C—C, eight C—H,σ-bonds and one C—C π-bond (as given in the question).

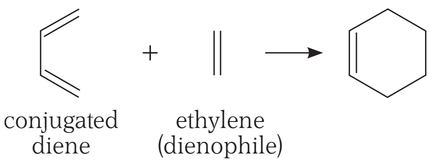
11. Dimerisation

Dimerisation have the similarity with alkylation.The first two steps are common for both the reactions. In the absence of branched alkane and at high temperature, the carbonium ion formed eliminates H^+ resulting to alkene formation again. Due to the presence of H^+ in the reaction yield of product is low. Thus, dimerisation looks as



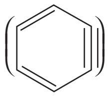
12. Diels-Alder Reaction

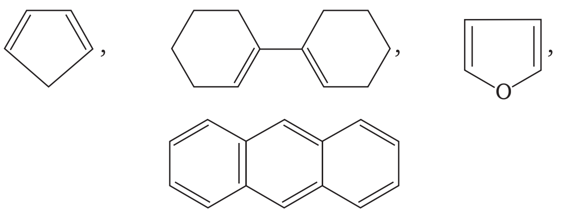
The reaction is also called **cycloaddition** as a new cycle is generated in this reaction. Basically in the reaction a conjugated diene is attacked by an olefin which is called **dienophile.** The reaction looks like as



No other conditions are specified but it is seen that

(i) Attachment of electron attracting groups in dienophile or electron releasing groups in conjugated diene increases the rate of reaction.

(ii) Besides olefins, alkynes, benzyne  and allenes ($>C═C═C<$) can be used as dienophiles.

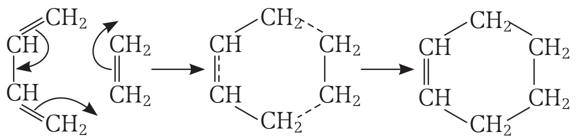
(iii) 

can be used as conjugated dienes.

(iv) Benzene, naphthalene and phenanthrene are quite unreactive.

(v) The reaction is strictly **stereospecific** *i.e.*, orientation of groups does not change from reactants to products.

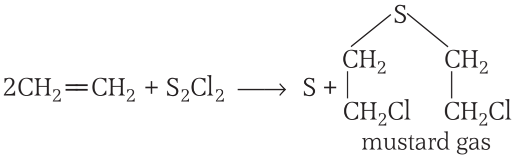
The mechanism of the reaction can be seen as



The bond breakage and formation may be **stepwise** or simultaneous (it is not definite).

13. With S_2Cl_2

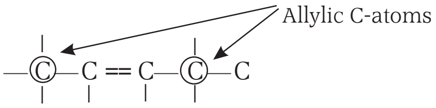
Ethylene on reaction with sulphur monochoride (S_2Cl_2) forms mustard gas which is highly poisonous and used in chemical warfare.



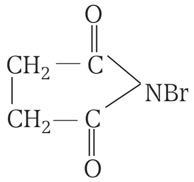
$$2CH_2{=}CH_2 + S_2Cl_2 \longrightarrow S + \underset{\text{mustard gas}}{S(CH_2CH_2Cl)_2}$$

14. Allylic Substitution

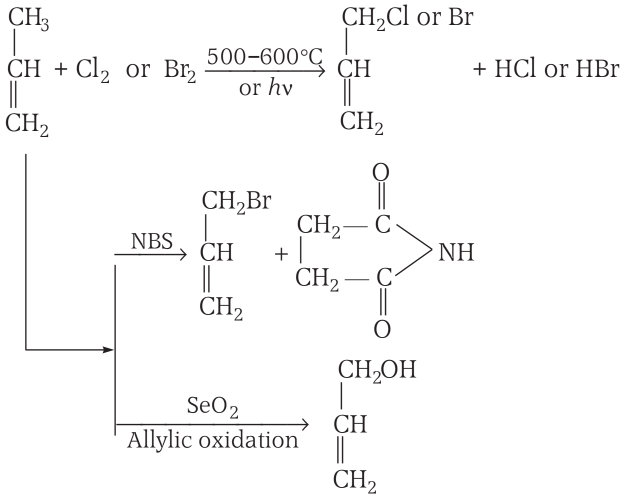
The C–atoms present alternate to carbon-carbon double bond are called **allylic C–atoms** *i.e.*,



NBS is called N–bromo succinimide with the structure



The reaction looks like

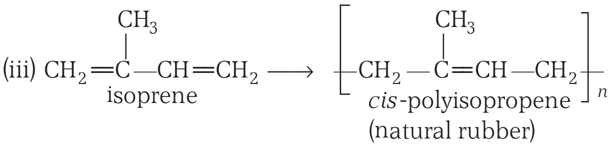


15. Polymerisation

When a large number of monomers combine to give a molecule bearing high molecular mass, called the polymer, the process is called polymerisation. The polymerisation reactions can be seen as

(i) $\underset{\text{ethene}}{nCH_2{=}CH_2} \longrightarrow \underset{\text{polyethene}}{\left[CH_2{-}CH_2\right]_n}$

(ii) $\underset{\text{butadiene}}{CH_2{=}CH{-}CH{=}CH_2} \longrightarrow \underset{\text{polybutadiene}}{\left[CH_2{-}CH{=}CH{-}CH_2\right]_n}$

(iii) 

$$\underset{\text{isoprene}}{CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH{=}CH_2} \longrightarrow \underset{\substack{cis\text{-polyisopropene}\\ \text{(natural rubber)}}}{\left[CH_2{-}\overset{CH_3}{\overset{|}{C}}{=}CH{-}CH_2\right]_n}$$

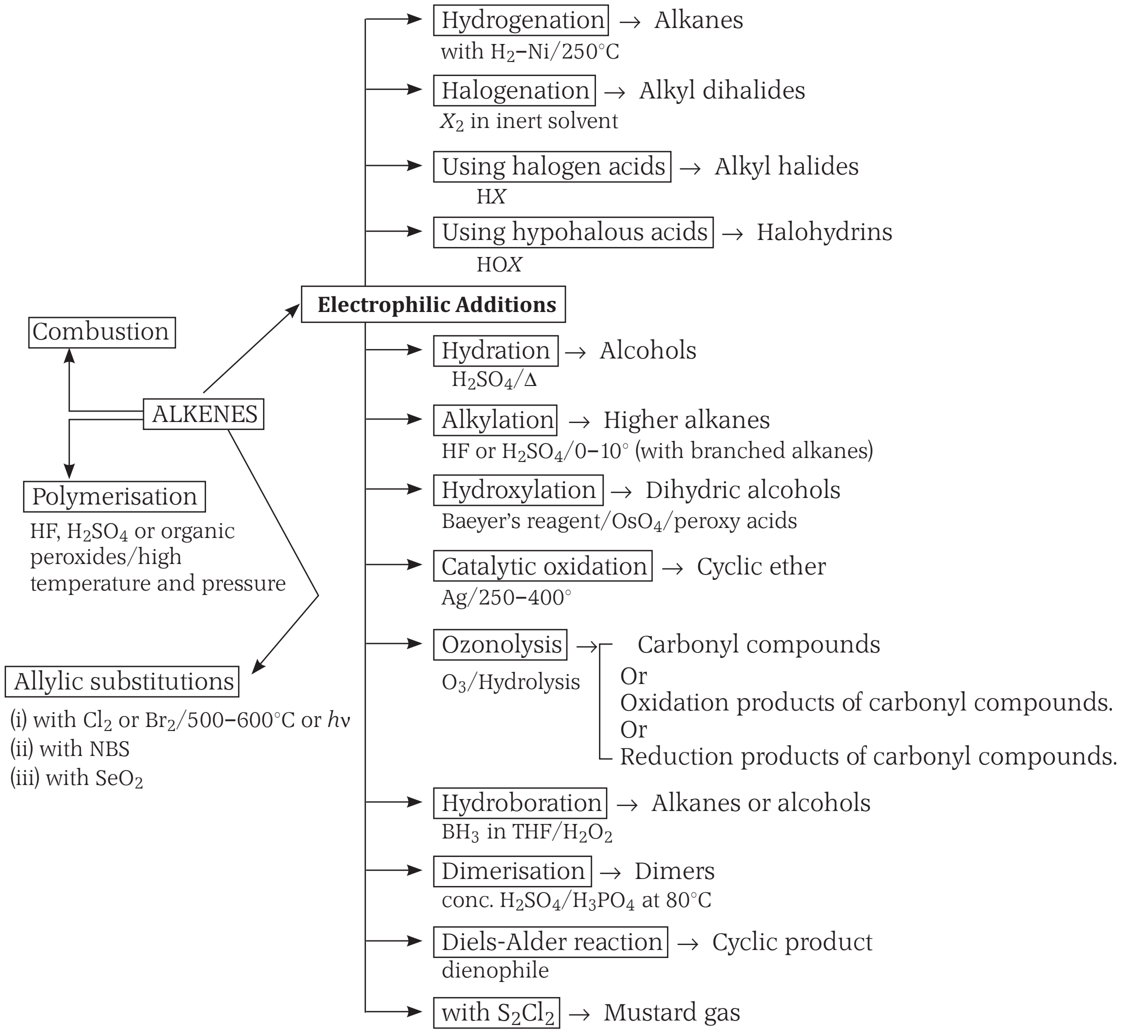
16. Combustion

The generalised combustion reaction can be seen as

$$C_nH_{2n} + \frac{3n}{2}O_2 \longrightarrow nCO_2 + nH_2O + \text{Heat}$$

Note All hydrocarbons on complete combustion gives CO_2 and H_2O.

The outline of the chemical properties of alkenes looks as



Check Point 2

1. The melting point of *cis* but-2-ene is lower than that of *trans* but-2-ene. Explain why?
2. The solubility of *cis*-alkenes is higher than the corresponding *trans* alkenes in a particular solvent. Explain.
3. Peroxide effect is not applicable in case of HF, HCl etc. Explain why?
4. Hydroxylation with $KMnO_4$ gives *syn*-addition whereas with peracid gives *anti*-addition why?
5. Hydration of propene with dilute H_2SO_4 gives 2-propanol but its hydroboration gives 1-propanol. Why?

15.4 Alkynes

These form the second series of **unsaturated hydrocarbons** with highest possible degree of unsaturation. Their general formula is C_nH_{2n-2}, with two π-bonds and one σ-bond between two C–atoms *i.e.*, total 3 bonds. This group of three bonds is often called **acetylenic bond.** (Acetylene is the first and most important member).

These are named by adding suffix 'yne' to the root word. These exhibit chain and functional isomerism (For details see Chapter 13 and 14).

Methods of Preparation

General methods of preparation of alkynes are as follows

1. By Hydrolysis of Metal Carbides

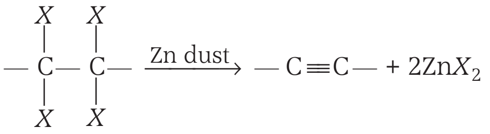
The metal carbides of group IInd elements give alkynes on reaction with H_2O

$$\text{(i)}\ \left.\begin{array}{l} MgC_2 \\ CaC_2 \\ SrC_2 \\ BaC_2 \end{array}\right\} + 2H_2O \longrightarrow C_2H_2 + \text{Metal hydroxide } [M(OH)_2]$$

$$\text{(ii)}\ Mg_2C_3 + 4H_2O \longrightarrow CH_3C{\equiv}CH + 2Mg(OH)_2$$

2. Dehalogenation

Dehalogenation of tetrahalides with Zn dust can be seen as



$$-\overset{X}{\underset{X}{C}}-\overset{X}{\underset{X}{C}}- \xrightarrow{\text{Zn dust}} -C{\equiv}C- + 2ZnX_2$$

In case of trihalides Ag is used.

$$CH\boxed{X_3 + 6Ag + X_3}CH \xrightarrow{\Delta} CH{\equiv}CH + 6AgX$$

3. Dehydrohalogenation

For dehydrohalogenation see alkenes (methods of preparation) and remember KNH_2, $NaNH_2$ in liquid NH_3 and NaH etc., are better dehydrohalogenating agents than alcoholic KOH.

4. Kolbe's Electrolytic Method

Electrolysis of potassium fumerate $\left(\begin{array}{l} CHCOO^-K^+ \\ \| \\ CHCOO^-K^+ \end{array}\right)$ produces acetylene with the liberation of CO_2 and H_2 at anode and cathode respectively.

5. From Sodium Acetylide

Reaction of sodium acetylide with alkyl halides is used to prepare higher alkynes from lower alkynes as

$$\begin{tikzcd} HC{\equiv}CH + Na \arrow[r, "\text{liquid}", "NH_3"'] & HC{\equiv}C^-Na^+ \arrow[r, "RX", "-NaX"'] & HC{\equiv}CR \arrow[d, "\text{Na in liquid}\ NH_3"] \\ R'{-}C{\equiv}C{-}R & & Na^+C^-{\equiv}CR \arrow[ll, "R'X"', "-NaX"] \end{tikzcd}$$

The reaction is seen only in acidic alkynes *i.e.,* the alkynes in which triply bonded C-atom contain atleast one replaceable H, for example acetylene and terminal alkynes.

6. From Grignard's Reagent

Grignard reagents also help in preparing higher alkynes from lower alkynes as

$$\begin{tikzcd} HC{\equiv}CH + RMgX \arrow[r] & HC{\equiv}C^-Mg^+X^- \arrow[d, "RX"] \\ & HC{\equiv}C{-}R + MgX_2 \end{tikzcd}$$

7. Other Methods

These are used to prepare acetylene and include

(i) By passing an electric discharge through graphite electrodes in the atmosphere of hydrogen.

$$\underset{\text{(graphite)}}{2C} + H_2 \xrightarrow{1200°C} CH{\equiv}CH$$

(ii) By the controlled oxidation of methane as

$$3CH_4 + 3O_2 \xrightarrow{1500°C} CH{\equiv}CH + CO + 5H_2O$$

The outline of the methods of preparation of alkynes are as

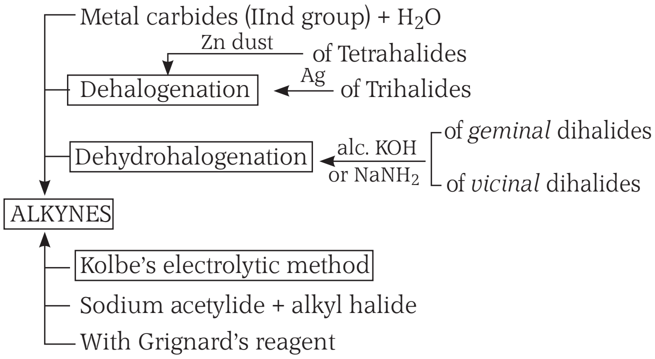


Fig. 15.3 Flow chart showing general methods of preparation of alkynes

Physical Properties

1. First three members of alkynes are gases, next eight are liquids and higher alkynes are solids.
2. All alkynes are colourless and odourless except acetylene which has garlic odour.
3. Melting and boiling points and densities of alkynes are slightly higher than that of corresponding alkenes and alkanes. These properties generally increases with increase in molecular mass.
4. These are lighter than water and also insoluble in it. However, they are soluble in non-polar solvents like benzene, ether etc.

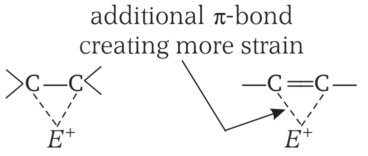
5. Acetylene and terminal alkynes $\left[\begin{array}{c}CH\\ |||\\ CH\end{array}\ \text{and}\ \begin{array}{c}CR\\ |||\\ CH\end{array}\right]$ are acidic in nature. *The acidic nature of alkynes is due to sp-hybridisation present in them because of which the electrons of* C—H *bond are held more strongly by* C–*nucleus*. Alkynes like $R—C\equiv C—R$ are non-acidic as these lack replaceable hydrogen in them.

Chemical Properties

Alkynes exhibit following chemical properties

1. Electrophilic Addition Reactions

As far as **electrophilic additions** are concerned in general alkenes are more reactive than alkynes. The reason is more strained (less stable) cyclic intermediate in the case of alkynes due to the presence of additional π-bond in alkynes.



less strained, more stable cyclic intermediate of alkenes

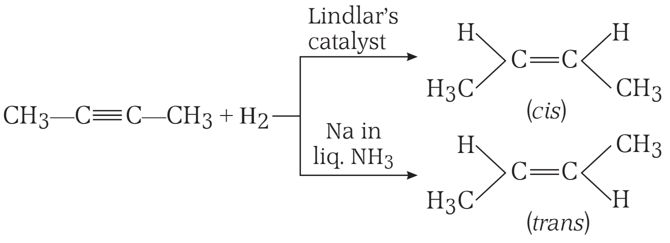
more strained, less stable cyclic intermediate of alkynes

(i) **Hydrogenation** For hydrogenation see alkene (Chemical properties;) and alkanes (Methods of preparation).

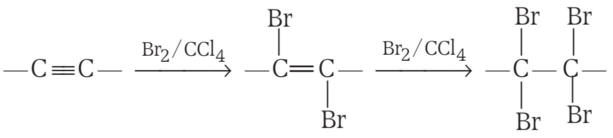
$$CH_3—C\equiv CH + 2H_2 \xrightarrow{\text{Ni or Pt or Pd}} CH_3CH_2CH_3$$

$$CH_3—C\equiv CH + H_2 \xrightarrow{\text{Lindlar's catalyst}} CH_3—CH=CH_2$$

2-butyne when reduced with Lindlar's catalyst gives nearly 100% *cis*-isomer while with Na in liquid ammonia gives nearly 100% *trans*-isomer.

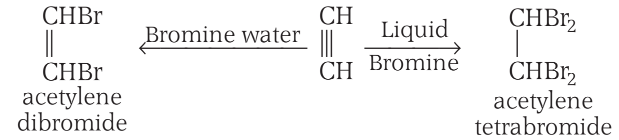


(ii) **Halogenation** Halogenation can be seen as :



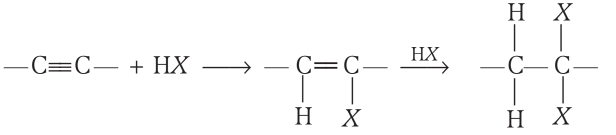
$$—C\equiv C— \xrightarrow{Br_2/CCl_4} —\overset{Br}{\overset{|}{C}}=\underset{Br}{\underset{|}{C}}— \xrightarrow{Br_2/CCl_4} —\overset{Br}{\overset{|}{\underset{Br}{\underset{|}{C}}}}—\overset{Br}{\overset{|}{\underset{Br}{\underset{|}{C}}}}—$$

Liquid bromine yields tetrabromo derivative while bromine water or Br_2/CCl_4 forms dibromo derivative.



$$\underset{\text{acetylene dibromide}}{\begin{array}{c}CHBr\\ \|\\ CHBr\end{array}} \xleftarrow{\text{Bromine water}} \begin{array}{c}CH\\ |||\\ CH\end{array} \xrightarrow[\text{Bromine}]{\text{Liquid}} \underset{\text{acetylene tetrabromide}}{\begin{array}{c}CHBr_2\\ |\\ CHBr_2\end{array}}$$

(iii) **Addition of Halogen Acids**

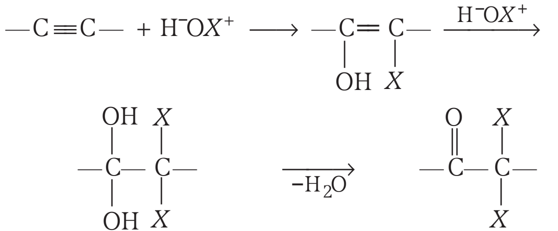


$$—C\equiv C— + HX \longrightarrow —\underset{H}{\underset{|}{C}}=\underset{X}{\underset{|}{C}}— \xrightarrow{HX} —\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}—\overset{X}{\overset{|}{\underset{X}{\underset{|}{C}}}}—$$

(*gem*-dihalide)

(also see alkene properties)

(iv) **Addition of Hypohalous Acids**



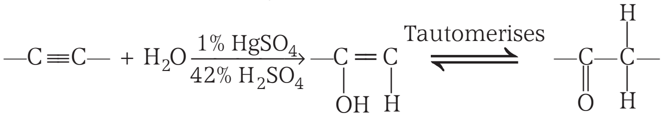
$$—C\equiv C— + H^-OX^+ \longrightarrow —\underset{OH}{\underset{|}{C}}=\underset{X}{\underset{|}{C}}— \xrightarrow{H^-OX^+}$$

$$—\overset{OH}{\overset{|}{\underset{OH}{\underset{|}{C}}}}—\overset{X}{\overset{|}{\underset{X}{\underset{|}{C}}}}— \xrightarrow{-H_2O} —\overset{O}{\overset{\|}{C}}—\overset{X}{\overset{|}{\underset{X}{\underset{|}{C}}}}—$$

(Alkynes exhibit following chemical properties)

halogen derivative of carbonyl compound

(v) **Hydration** Hydration occurs in the presence of 1% $HgSO_4$ and 42% H_2SO_4 as

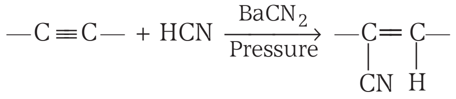


$$—C\equiv C— + H_2O \xrightarrow[42\%\ H_2SO_4]{1\%\ HgSO_4} —\underset{OH}{\underset{|}{C}}=\underset{H}{\underset{|}{C}} \overset{\text{Tautomerises}}{\rightleftharpoons} —\underset{O}{\underset{\|}{C}}—\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}—$$

carbonyl compound

Among the alkynes only acetylene gives aldehydes, rest all the alkynes gives ketones as the final product of this reaction.

(vi) **Addition of HCN** Addition of HCN occurs in the presence of $BaCN_2$ under pressure as



$$—C\equiv C— + HCN \xrightarrow[\text{Pressure}]{BaCN_2} —\underset{CN}{\underset{|}{C}}=\underset{H}{\underset{|}{C}}—$$

Acetylene gives vinyl cyanide (acrylonitrile) on the polymerisation of which synthetic fibre **orlon** is obtained.

$$HC\equiv CH + HCN \xrightarrow[\text{Pressure}]{BaCN_2} \underset{\text{acrylonitrile}}{CH_2=CH—CN}$$

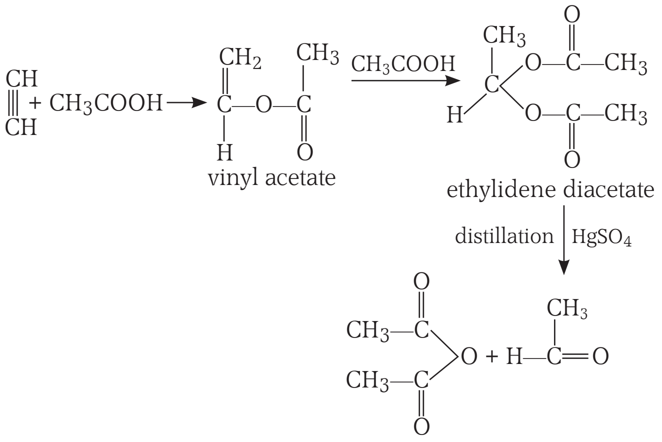
Some Addition Reactions Given by Acetylene

Only Acetylene (CH≡CH) especially undergo some more addition reactions which are

(i) **Addition of alcohols** Ethers are produced as

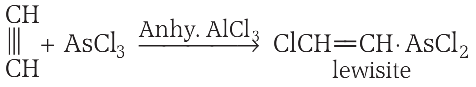
$$HC\equiv CH + ROH \xrightarrow[\substack{120\text{–}180°\\ \text{high pressure}}]{KOH\ \text{or}\ CH_3O^-K^+} \underset{\text{alkyl vinyl ether}}{CH_2=CH—OR}$$

(ii) **Addition of CH_3COOH** It is a very useful reaction used in the preparation of acetic anhydride. Ethylidene diacetate is produced in the beginning, which on distillation in the presence of $HgSO_4$, gives acetaldehyde and acetic anhydride as



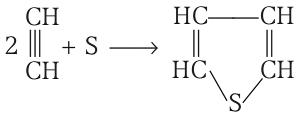
Vinyl acetate is used in the manufacture of synthetic rubber and plastic.

(iii) **Addition of arsenic trichloride** Reaction occur in the presence of $AlCl_3$ (anhydrous) to yield **lewisite** (a poisonous gas) used in chemical war as



$$CH\equiv CH + AsCl_3 \xrightarrow{\text{Anhy. }AlCl_3} \underset{\text{lewisite}}{ClCH{=}CH\cdot AsCl_2}$$

(iv) **Addition of sulphur** When acetylene is passed over heated iron pyrites (FeS_2) at 300°C, it combines with sulphur of iron pyrites to form **thiophene** as

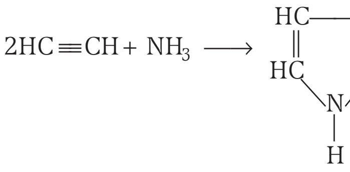


thiophene

(v) **Addition of N_2** When an electric spark is passed through a mixture of acetylene and nitrogen, HCN is produced as

$$HC\equiv CH + N_2 \xrightarrow[\text{spark}]{\text{Electric}} 2H{-}C\equiv N$$

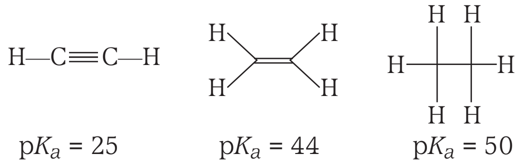
(vi) Addition of NH_3 At high temperatures, NH_3 combines with acetylene to form **pyrrole** as



pyrrole

2. Acidic Character of Alkynes

The hydrogen bonded to the carbon of terminal alkyne is considerably more acidic than those bonded to carbons of alkenes and alkanes. The pK_a values for ethyne, ethene and ethane illustrate this point.



Due to the presence of this acidic H atom, alkynes (terminal) exhibit the following reactions.

(i) **Reaction with Na in liquid NH_3** The reaction with Na in liquid NH_3 is considered as test of acidity. H_2 is released in the reaction as

$$H{-}C\equiv C{-}R + Na \xrightarrow[NH_3]{\text{In liquid}} Na^+C^-\equiv C{-}R + \frac{1}{2}H_2\uparrow$$

(ii) **Reaction with Tollen's reagent** With Tollen's reagent (ammoniacal $AgNO_3$), a white precipitate, of silver salt is obtained. The reaction is used to differentiate between terminal (acidic) alkynes with rest of the alkynes *i.e.*, helpful in detecting the position of triple bond (interstitial or terminal).

$$H{-}C\equiv C{-}H + 2AgNO_3 + 2NH_4OH \longrightarrow \underset{\substack{\text{silver acetylide}\\ \text{(white ppt.)}}}{Ag{-}C\equiv C{-}Ag} + 2NH_4NO_3 + 2H_2O$$

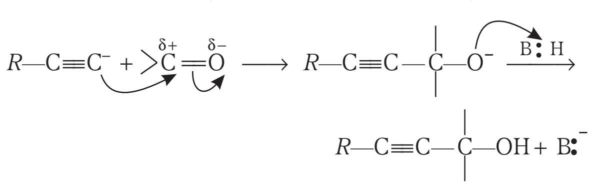
(iii) **Fehling's solution** It is also used for the same purpose as that Fehling's solution is used. Terminal alkynes with Fehling's solution give red precipitate of their copper salts.

$$H{-}C\equiv C{-}H + Cu_2Cl_2 + 2NH_4OH \longrightarrow \underset{\substack{\text{copper acetylide}\\ \text{(red ppt)}}}{Cu{-}C\equiv C{-}Cu} + 2NH_4Cl + 2H_2O$$

$$R{-}C\equiv C{-}H + Cu_2Cl_2 + 2NH_4OH \longrightarrow \underset{\text{copper alkynide}}{R{-}C\equiv C{-}Cu} + 2NH_4Cl + 2H_2O$$

3. Ethinylation

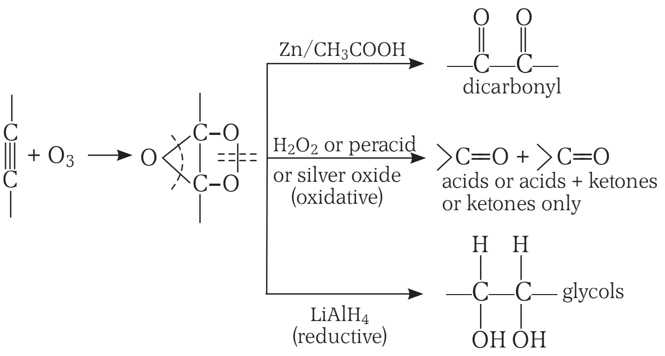
In this reaction terminal alkynes work as nucleophile, thus add to $>C{=}O$ group through nucleophilic addition, in the presence of base as :



Here, B$\colon^-$ is a base. The reaction is seen as a modification of **Aldol condensation.**

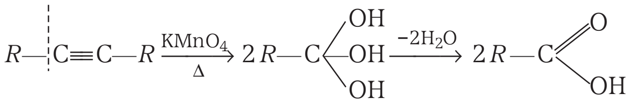
4. Ozonolysis

The ozonolysis in the case of alkynes can be seen as

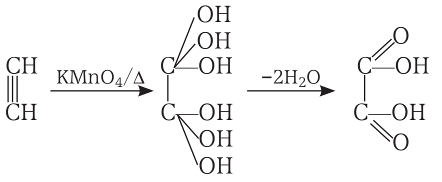


5. Oxidation with $KMnO_4$

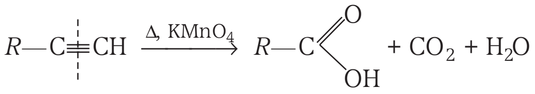
Oxidation with hot $KMnO_4$ produces carboxylic acids as



CH≡CH under these conditions gives oxalic acid as

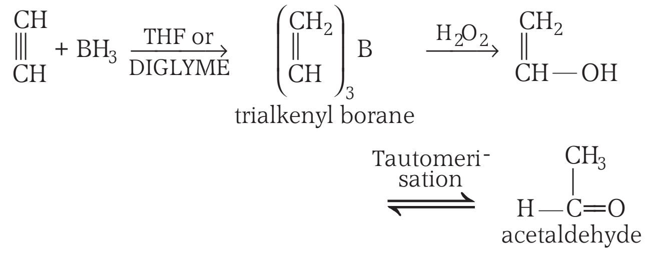


Rest of acidic alkynes produce CO_2 also along with acid as

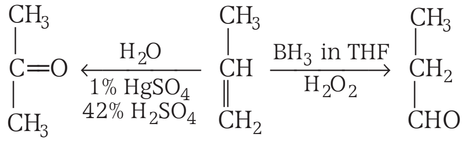


6. Hydroboration-oxidation

Hydroboration oxidation of alkyne can be seen as

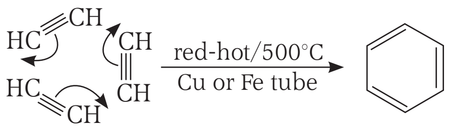


Contrary to hydration in this case all alkynes give aldehydes *i.e.,*



7. Polymerisation

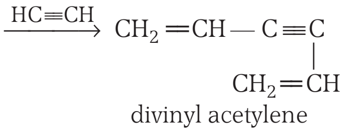
In the polymerisation reactions of alkynes, aromatic compounds are produced when their vapours are passed through red hot Cu or Fe tube as



When acetylene is passed through cuprous chloride solution containing NH_4Cl, linear polymerisation occurs resulting to mono vinyl and divinyl acetylene as

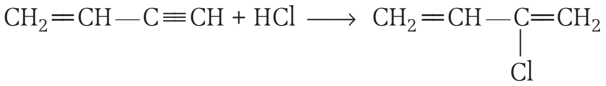
$$2HC\equiv CH \xrightarrow[NH_4Cl]{Cu_2Cl_2} CH_2{=}CH{-}C\equiv CH$$

monovinyl acetylene



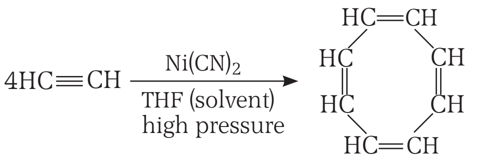
divinyl acetylene

Monovinyl acetylene is used for the synthesis of **chloroprene,** the constituent of **neoprene** (the synthetic rubber) as



chloroprene

In the presence of $Ni(CN)_2$ and under high pressure, acetylene dissolves in THF and polymerises to give cyclooctatetraene as



cyclooctatetraene

When acetylene is heated in the presence of spongy copper or its oxides, a cork like substance is produced which is called **cuprene.** It is used in the manufacture of linoleum.

Summary of the reactions of alkynes is given in the following flow chart.

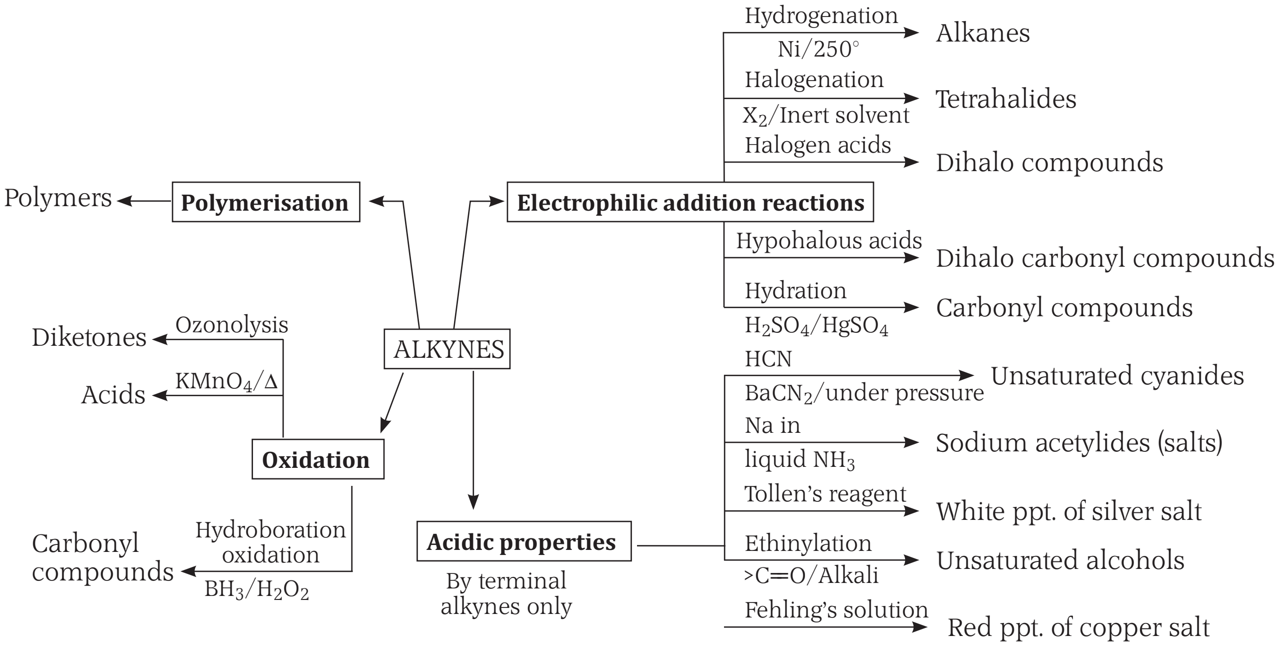


Fig. 15.4 Flow chart showing reactions of alkynes

Check Point 3

1. Explain why are alkynes less reactive than alkenes towards electrophilic addition reactions?
2. Explain why alkynes undergo nucleophilic addition reactions while simple alkenes do not?
3. $CH_2{=}CH^-$ is more basic than $HC{\equiv}C^-$. Explain.
4. Why does HF form H-bonding with ethyne even though it is non-polar in nature?

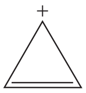
Aromatic Hydrocarbons

Aromatic hydrocarbons are specialised cyclic compounds which are known for their characteristic unique smell (*Aroma* = fragrance). The group is also called **arenes.** Although the name aromatic was given for their pleasant odour, but today, it is used for a class of compounds having a characteristic stability despite having unsaturation.

15.5 **Aromaticity**

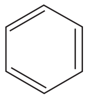
A compound can be considered as aromatic if it follows following three rules :

(i) An aromatic compound must be cyclic and planar.
(ii) An aromatic compound must have the conjugated system in it.
(iii) An aromatic compound must follow **Huckel rule** which states that the number of π-electrons = $(4n + 2)$; where n = integer 0, 1, 2, 3 etc. For example, in



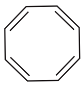
number of π-electrons = 2.

$(4n + 2) = 2$ and $n = 0$ thus Huckel rule is followed.



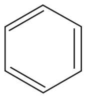
, Number of π-electron = 6.

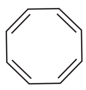
$(4n + 2) = 6$ and $n = 1$ thus Huckel rule is followed.

Those compounds which does not follow the above 3 rules are called **non-aromatic.** These non-aromatic compounds may be cyclic with conjugated system, for example,  (cyclooctatetraene) is cyclic with conjugated system but it does not follow Huckel rule and its plane is also distorted that's why it is non-aromatic.

Compounds which are monocyclic and contain ($4n$) π-electrons are much more reactive than expected even more reactive than their acyclic analogues. This decreased stability in ($4n$) molecules has been called *anti-aromaticity* (Breslow, 1967) for example, cyclooctatetraenide salts.

The name **annulene** has been proposed as a general name for monocyclic compounds having alternating single and double bonds (conjugated system of bonds) and the ring size is indicated with in brackets as a number before annulene as


benzene or [6] annulene
(aromatic)


cyclooctatetraene or
[8] annulene (non-aromatic)

15.6 Benzene

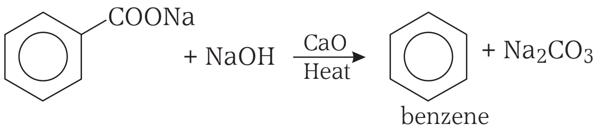
It is the first member of aromatic hydrocarbon series.

Methods of Preparation of Benzene

Following methods can be used to prepare benzene

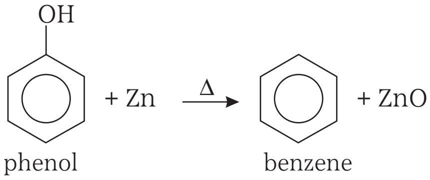
(i) Decarboxylation

It is prepared by heating the mixture of sodium benzoate and sodalime.



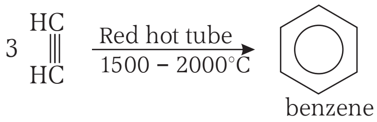
(ii) Dehydroxylation

Benzene is obtained by dehydroxylation of phenol with red hot zinc powder.



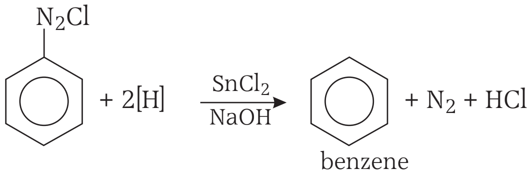
(iii) Polymerisation

When acetylene is passed through a red hot metallic tube, cyclic polymerisation takes place and benzene is formed.



(iv) Reduction of Benzene Diazonium Chloride

Benzene diazonium chloride is reduced to benzene by $SnCl_2$ and NaOH or absolute ethyl alcohol or hypophosphorous acid (H_3PO_2).



(v) Distillation

Distillation of coal-tar gives following fractions

(a) **Light oil** Below 200°C–contains BTX (Benzene, toluene and xylene) as its chief components.

(b) **Middle oil** 200–240°C–contains phenols, cresols and naphthalene.

(c) **Heavy oil** 245–280°C–contains cresols and naphthalene.

(d) **Anthracene oil** (green oil) 280–405°C-contains anthracene, phenanthrene and carbazole.

(e) **Pitch** The residue containing 5 and 6 membered fused rings and tar oils.

Benzene is obtained from light oil fraction as

$$\text{Light oil fraction} \xrightarrow[\substack{\text{(i) } H_2SO_4 \text{ (basic impurity remover)} \\ \text{(ii) NaOH (acidic impurity remover)}}]{\text{washed}} \text{Light oil fraction without impurities}$$

$$\downarrow \text{Washed with water, dried and distilled}$$

$$\text{Almost pure benzene between 80–82°C with traces of thiophene} \xleftarrow{\text{Refractioned}} \text{110°C fraction contains benzene, toluene and thiophene}$$

$$\downarrow \begin{array}{l} H_2 / 400°C \\ \text{Ni under pressure} \end{array}$$

Pure benzene + H_2S

(vi) Cracking of Petroleum

From petroleum, benzene is obtained through aromatisation or platforming of C_6-C_{10} fraction of petroleum naphtha as

$$\text{Hexane} \xrightarrow[500^\circ\text{C } 15 \text{ atm}]{\text{Pt, Al}_2\text{O}_3} \text{Benzene}$$

$$\text{Heptane} \xrightarrow[500^\circ\text{C, } 15 \text{ atm}]{\text{Pt, Al}_2\text{O}_3} \text{Toluene}$$

The reaction is the modified form of aromatisation reaction of alkanes (see properties of alkanes; reaction 6)

Summary of the methods of preparation of benzene is given below.

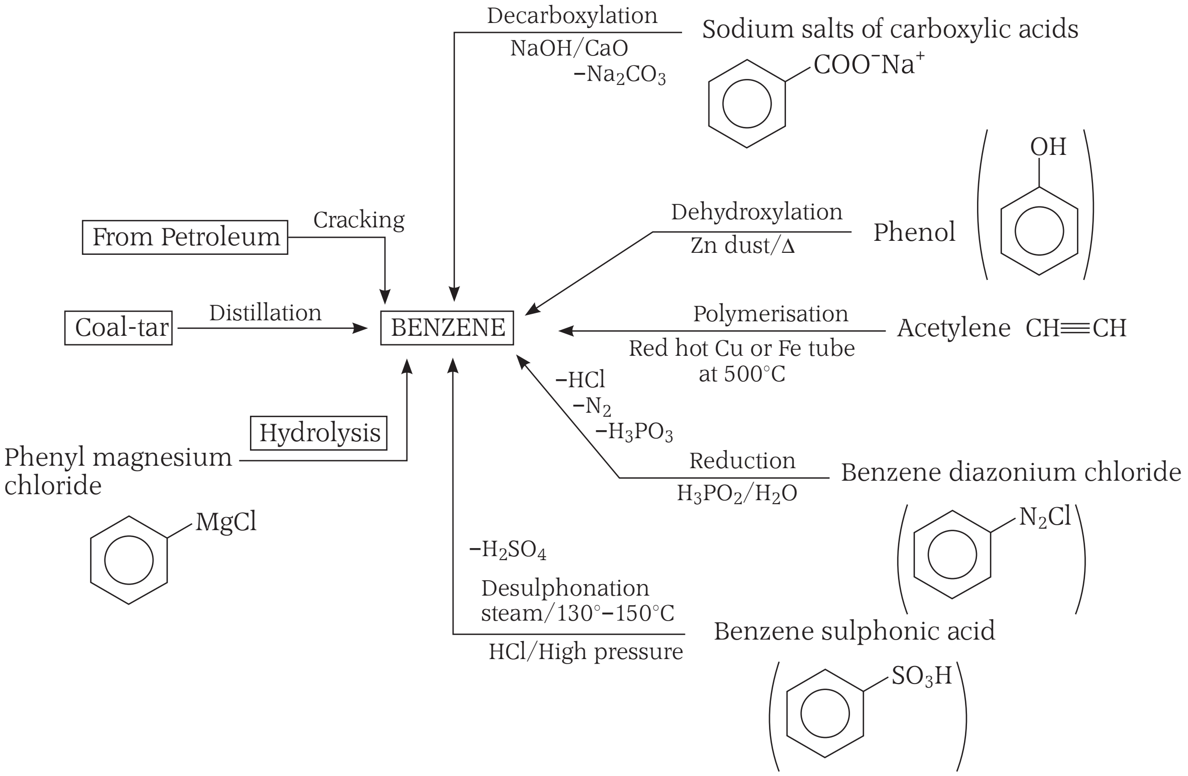


Fig. 15.5 Flow chart showing methods of preparation of benzene

Physical Properties of Benzene

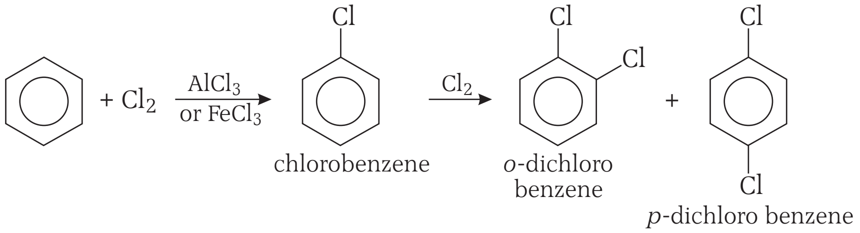
Benzene is a colourless liquid, b.p. 80.1°C, m.p. 5.5°C, insoluble in water, miscible with alcohol, ether and chloroform, itself a good solvent, vapours highly toxic, burns with a luminous sooty flame.

Chemical Properties of Benzene

Important chemical reactions exhibited by benzene are given below.

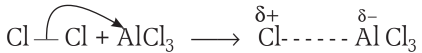
(i) Halogenation

Benzene undergo chlorination when it is treated with chlorine in the presence of catalyst aluminium chloride or ferric chloride and in the absence of light.



This reaction follows the following mechanism

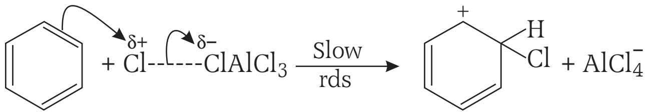
Step I Generation of an electrophile



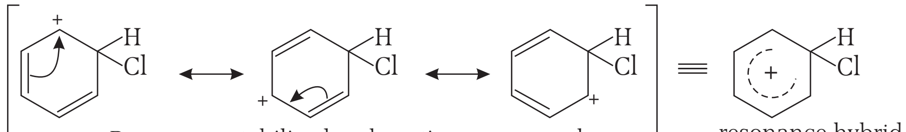
$$\mathrm{Cl{-}Cl + AlCl_3 \longrightarrow \overset{\delta+}{Cl}\text{------}\overset{\delta-}{Al}Cl_3}$$

electrophile

Step II Formation of σ-complex or carbocation intermediate.



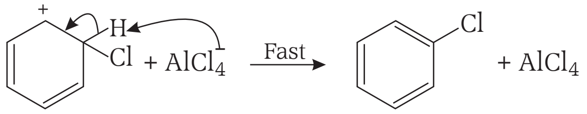
σ-complex



Resonance stabilized carbocation or σ-complex

resonance hybrid

Step III Loss of a proton from the carbocation intermediate.

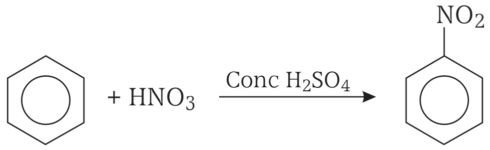


chlorobenzene

(This step is fast and hence, does not affect the rate of the reaction).

(ii) Nitration

Benzene undergoes nitration when treated with conc HNO_3 in the presence of conc sulphuric acid.

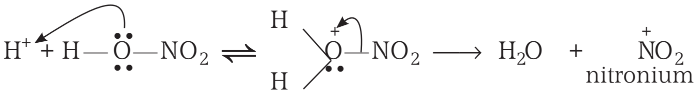


nitrobenzene

The steps involved during this reaction are as follows

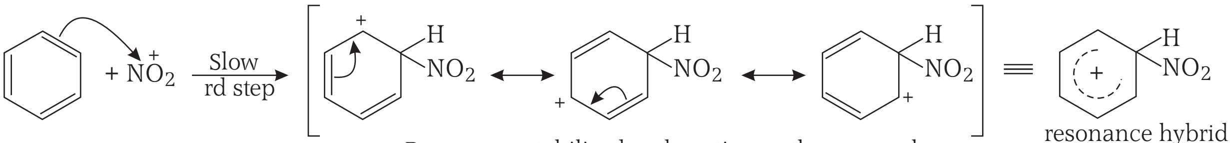
Step I Generation of an electrophile, *i.e.*, NO_2^+ (nitronium ion).

$$H_2SO_4 \longrightarrow H^+ + HSO_4^-$$



nitronium ion

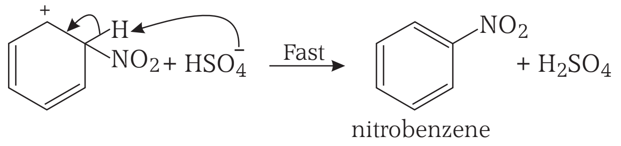
Step II Formation of σ-complex or carbocation intermediate.



Resonance stabilized carbocation or the σ-complex

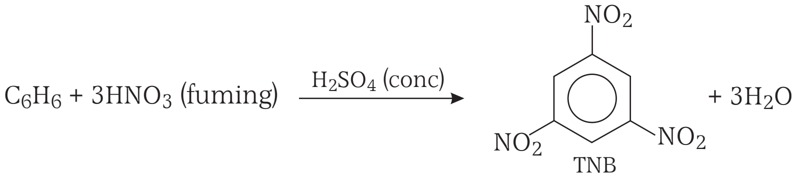
resonance hybrid

Step III Loss of a proton from the carbocation intermediate.



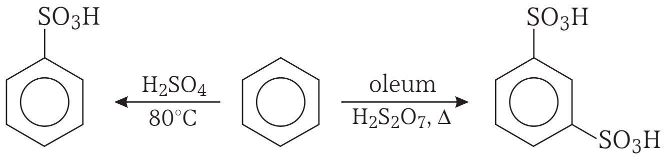
(This step is fast and hence does not affect the rate of the reaction.)

On heating benzene with fuming nitric acid and conc H_2SO_4, 1,3,5-trinitrobenzene (TNB) is formed



(iii) **Sulphonation**

Benzene forms benzene sulphonic acid with hot conc H_2SO_4, while with fuming H_2SO_4 or oleum at high temperature, *m*-benzene disulphonic acid is formed.



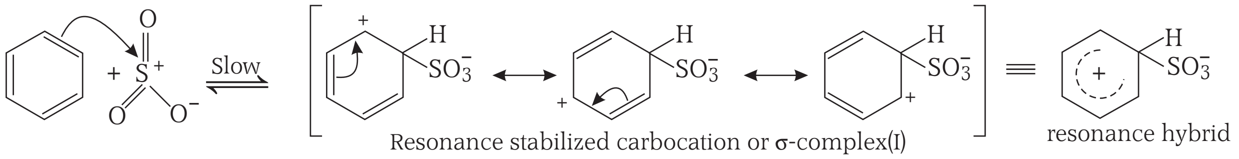
For sulphonation the attacking species is SO_3 or $\overset{+}{S}O_3H$.

This reaction involves the following mechanism

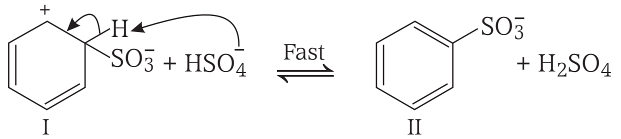
Step I Generation of an electrophile, *i.e.,* sulphur trioxide (SO_3).

$$2H_2SO_4 \rightleftharpoons SO_3 + HSO_4^- + H_3O^+$$

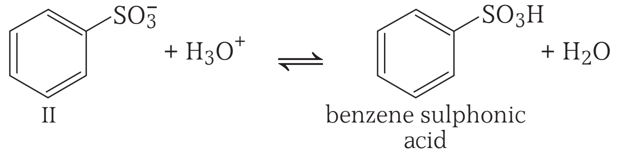
Step II Formation of σ-complex or carbocation intermediate.



Step III Loss of a proton from the carbocation.



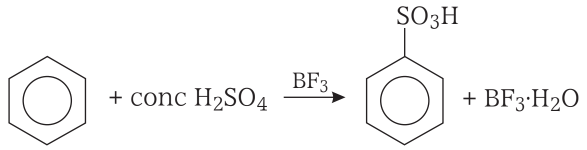
Step IV Addition of proton to the benzenesulphonic acid anion (II) gives the final product.



This equilibrium lies far to the left since sulphonic acid is a strong acid.

It may be pointed out here that unlike other electrophilic aromatic substitution reactions, sulphonation is reversible.

Sulphonation can also be carried out at room temperaure in the presence of BF_3 catalyst.



(iv) Friedel-Crafts Alkylation, Acylation or Carboxylation

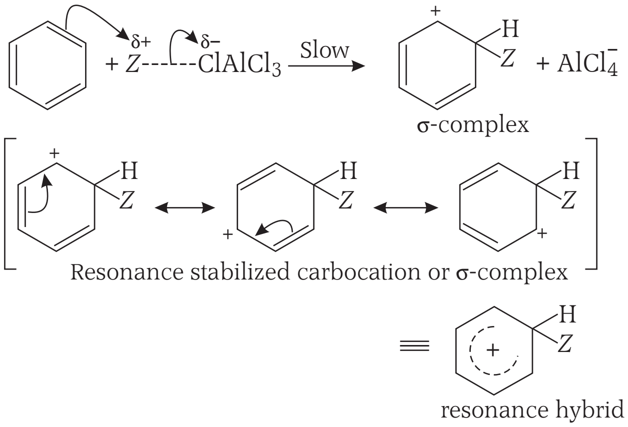
Lewis acids can be used for these reactions are $AlCl_3$, $FeCl_3$, $SnCl_2$, $SnCl_4$, BF_3, HF etc.

These reactions involve the following step

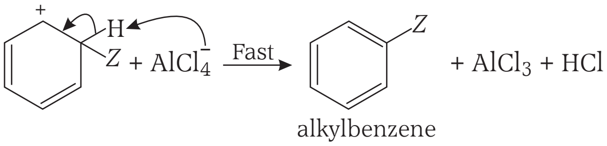
Step I Generation of an electrophile

$$Z\text{—}Cl + AlCl_3 \longrightarrow \underset{\text{electrophile}}{\overset{\delta+}{Z}\text{------}\overset{\delta-}{Cl}AlCl_3}$$

Step II Formation of σ-complex or carbocation intermediate.



Step III Loss of a proton from the carbocation intermediate.



(This step is fast and hence does not affect the rate of the reaction)

(where, $Z = -R$, —COR)

(v) Formylation

The attacking electrophile is $\overset{\overset{\displaystyle O}{\|}}{C^+}\text{—}H$, which is produced as

$$CO + HCl \rightleftharpoons H\text{—}\underset{\underset{\displaystyle O}{\|}}{C}\text{—}Cl$$

$$H\text{—}\underset{\underset{\displaystyle O}{\|}}{C}\text{—}Cl + AlCl_3 \rightleftharpoons H\text{—}\underset{\underset{\displaystyle O}{\|}}{C^+} + AlCl_4^-$$

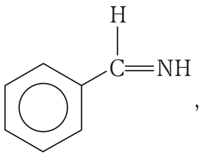
Gattermann synthesis

(a) The attacking electrophile is $\overset{+}{C}H{=}NH$, which is produced as

$$HC{\equiv}N + HCl \rightleftharpoons H\text{—}\underset{\underset{\displaystyle Cl}{|}}{C}{=}NH$$

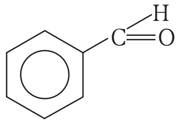
$$H\text{—}\underset{\underset{\displaystyle Cl}{|}}{C}{=}NH + AlCl_3 \rightleftharpoons H\text{—}C^+{=}NH + AlCl_4^-$$

(b) The product formed initially is



,

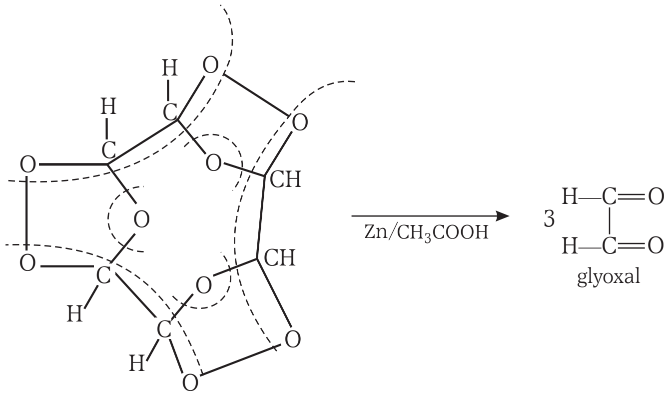
which on hydrolysis gave



and NH_3.

(vi) Ozonolysis

The ozonide formed in this reaction looks like

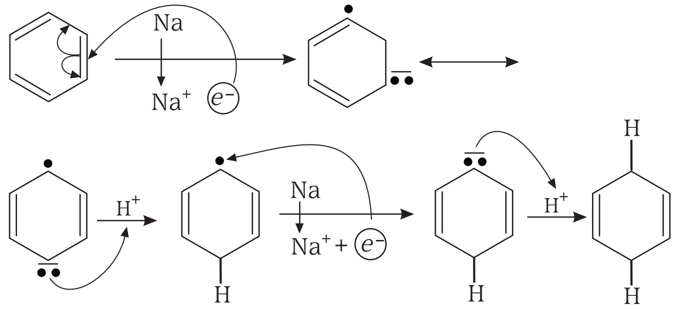


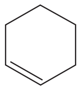
(vii) Vapour Phase Oxidation

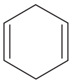
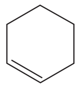
Maleic acid $\left(\begin{array}{l}CHCOOH\\ \|\\ CHCOOH\end{array}\right)$ is first produced in the reaction which looses water at such a high temperature and converted into anhydride.

(viii) Addition Reactions

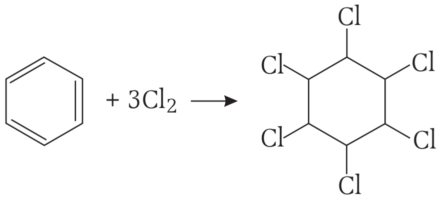
(a) Halogenation and hydrogenation operate through free radical mechanisms while in **Birch reduction** the metal used is of Ist group *i.e.*, Li, Na (mostly Na) and alcohol normally CH_3OH (or C_2H_5OH). Here metal works for electron donation and alcohol for proton donation as :



The H^+ is provided here by alcohol. At high temperature even alcohol is not needed. NH_3 provides H^+ at high temperatures and the product at high temperatures is .

The uniqueness of pathway here is that the addition is throughout 1,4-addition, *i.e.*, initially  is formed which on further 1,4-addition gave .

(b) The product of halogenation is $C_6H_6Cl_6$ (Benzene hexachloride or BHC). It is also called **Lindane** or **Gammexane** or 666 and is used as insecticide.



Sample **Problem 7** *Benzene undergoes electrophilic substitution reactions easily and nucleophilic substitution with difficulty. This is because* **[NCERT]**

(*a*) *of* $6\pi e^-s$
(*b*) *benzene is* e^- *deficient*
(*c*) *benzene is* e^- *rich*
(*d*) *both* (a) *and* (c)

Interpret (*d*) Due to the presence of delocalized 6π-electrons, benzene acts as a rich source of electrons. So, it attracts the electrophilic reagent (electron deficient species) towards itself but repels the nucleophilic reagents. That's why benzene gives electrophilic substitution reactions easily and nucleophilic substitution reactions with difficulty.

The outline of chemical properties of benzene looks like

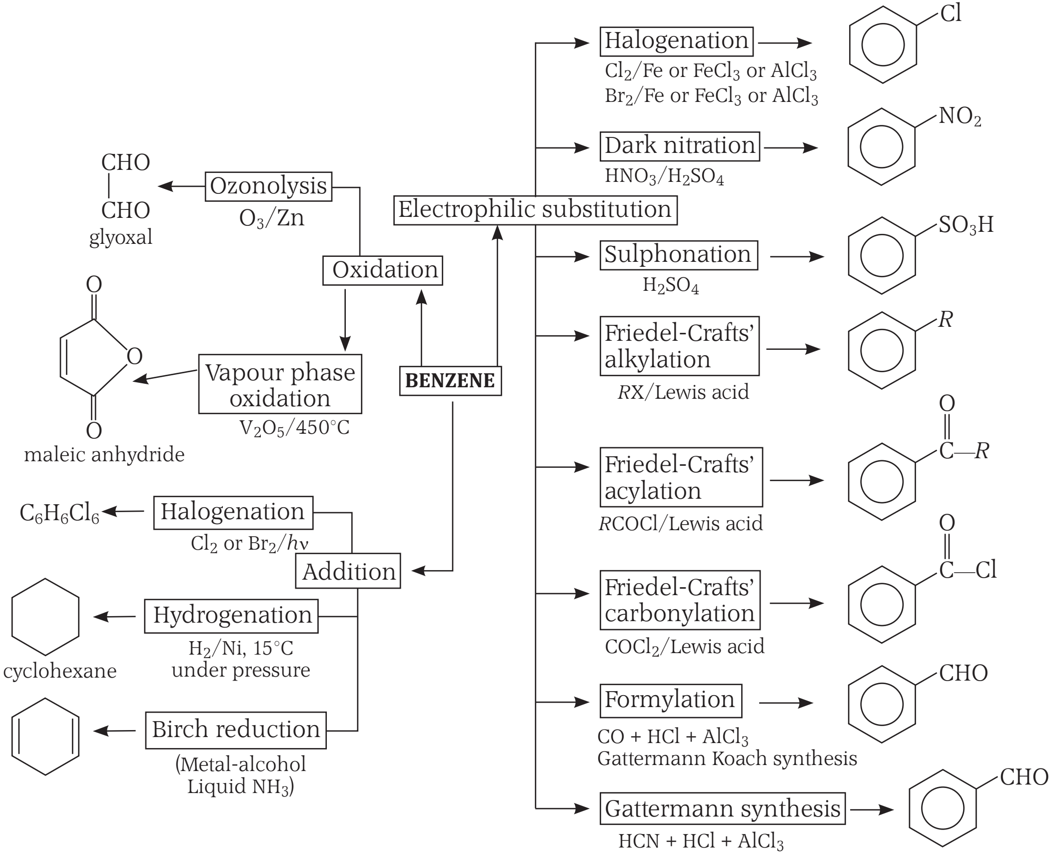


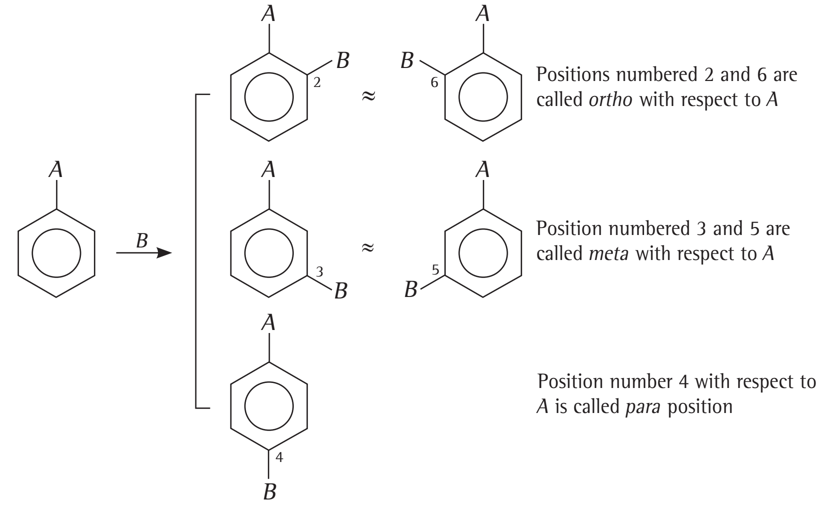
Fig. 15.6 Flow chart showing chemical reactions of benzene

Hot Spot 3

DIRECTIVE Influence of Groups

It is also an important topic for JEE Main point of view and also a simple topic. So small practice may help you to score high marks. The questions are generally 'find the product' type.

All H-atoms of benzene ring are equivalent, thus only one monosubstitution product is possible.
For the second substituent following 3 positions are possible, i.e.



Positions numbered 2 and 6 are called *ortho* with respect to *A*

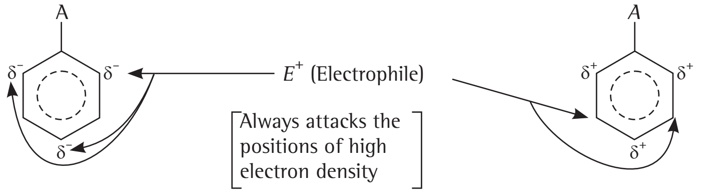
Position numbered 3 and 5 are called *meta* with respect to *A*

Position number 4 with respect to *A* is called *para* position

The first substituent (after monosubstitution) directs the next substituent as follows

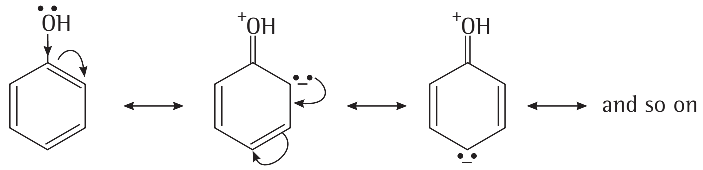
(i) if electron density at *ortho* and *para* position is increased due to first substituent *i.e.*,

(ii) if electron density at *ortho* and *para* position is decreased due to first substituent *i.e.*,



A is *ortho* and *para* **directing as electron density is highest at these positions**

A is *meta* **directing as now electron density is maximum at these positions**



The substituent which increases electron density at the ring is called **ring activator** for further electrophilic substitution while the group which decreases electron density on the ring is called **ring deactivator** for further electrophilic substitution. Thus, normally *ortho* and *para* directing groups are ring activators and *meta* directing groups are ring deactivators. (With halogens as exception because these are *ortho* and *para* directing but ring deactivators)**. The *ortho* and *para* directive influence of halogens is attributed to their ability of donating lone pair while their ring deactivation influence is attributed to their high electronegativity.**

Of all the haloarenes, fluorobenzene deviates the benzene ring to the least extent towards further electrophilic substitution reactions because the electron-donating resonance effect of F is only slightly outweighted by its electron withdrawing inductive effect.

The various ring activator and deactivator groups in the order of their activity are given below

***o/p* directing group or activating group**

(i) strongly activating $—NH_2 > —NHR > —NR_2 > —OH > —OR$

(ii) moderately activating $—NHCOR > —OCOR$,

(iii) weakly activating $—R > —Ar > —CH{=}CR_2$

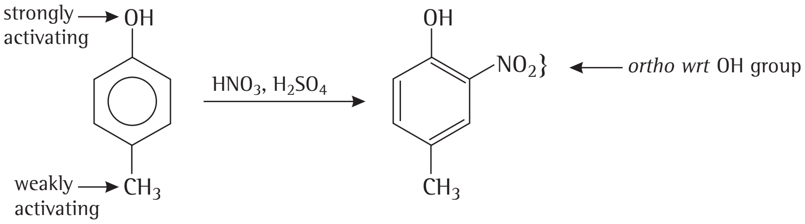
***m*-directing or deactivating**

(i) weakly deactivating $—F > —Cl > —Br > —I$

(ii) moderately deactivating $—CHO > —COR > —COOR > —COOH$

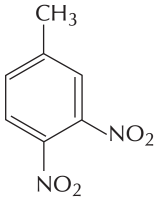
(iii) strongly deactivating $—CN < —SO_3 < \overset{+}{N}H_3 < \overset{+}{N}H_2R_2 < \overset{+}{N}HR_2 < \overset{+}{N}R_3 < —NO_2$ most deactivating.

Remember that if two groups are present, the strongly activating groups generally win over the deactivating or weakly activating group. *e.g.*,

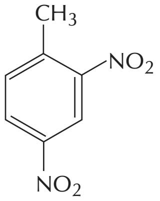


***Sample* Problem 7** *p-nitrotoluene on further nitration gives*

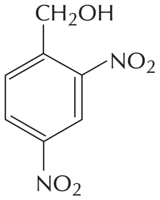
(*a*)



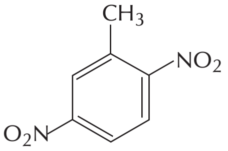
(*b*)



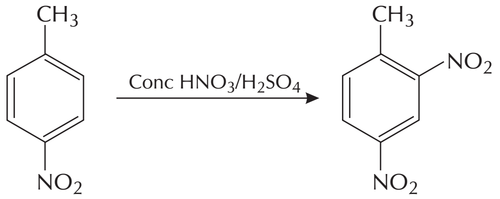
(*c*)



(*d*)



Solution (*b*) $—CH_3$ is a *o*/*p* directing group and $—NO_2$ is a *m*- directing group, thus the electrophile attacks at the position which is *ortho* to CH_3 and *meta* to NO_2 as *p*-position is already occupied.



Caution Point *When ethyl benzene or propyl benzene is chlorinated in the presence of sunlight at high temperature, the reaction proceeds through the formation of benzenylic radical, not by 1° radical.*

Check Point 4

1. Nitrobenzene does not undergo Friedel-Crafts alkylation. Explain it.
2. Why does tertiary butyl benzene not give benzoic acid on oxidation with acidic $KMnO_4$?
3. In the nitration reaction of benzene, HNO_3 acts as a base. Explain.

WORKED **OUT**
Examples

Example 1 *When bromoethane is subjected to Wurtz reaction, the hydrocarbon mixture so obtained consists of*

(*a*) *butane only*
(*b*) *butane and ethane*
(*c*) *butane and ethene*
(*d*) *butane, ethane and ethene*

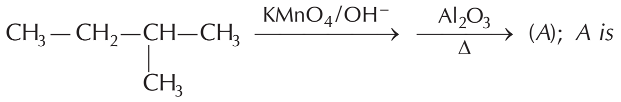
Solution (*d*) Butane is formed by Wurtz reaction whereas ethane and ethene are formed by a bimolecular elimination reaction.

$$2C_2H_5Br + 2Na \xrightarrow{\text{Dry ether}} C_2H_5-C_2H_5 + 2NaBr$$

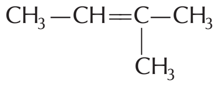
$$C_2H_5Br + Na \longrightarrow C_2H_5^-Na^+$$

$$C_2H_5^-Na^+ + C_2H_5Br \xrightarrow[-NaBr]{} C_2H_6 + CH_2{=}CH_2$$

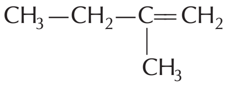
Example 2 *In the given sequence*



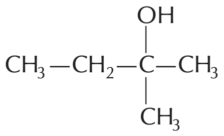
$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3 \xrightarrow{KMnO_4/OH^-} \xrightarrow[\Delta]{Al_2O_3} (A);\ A \text{ is}$$

(*a*)


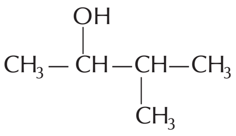
$$CH_3-CH{=}\underset{\underset{CH_3}{|}}{C}-CH_3$$

(*b*)


$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{C}{=}CH_2$$

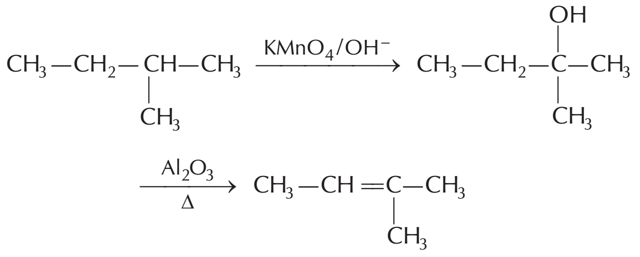
(*c*)


$$CH_3-CH_2-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

(*d*)


$$CH_3-\overset{\overset{OH}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

Solution (*a*) The reaction is oxidation followed by Saytzeff elimination, as the compound contains 3° H atom.



$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3 \xrightarrow{KMnO_4/OH^-} CH_3-CH_2-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

$$\xrightarrow[\Delta]{Al_2O_3} CH_3-CH{=}\underset{\underset{CH_3}{|}}{C}-CH_3$$

(*A*)

Example 3 *1-butene and 2-butene can be distinguished by their reaction with*

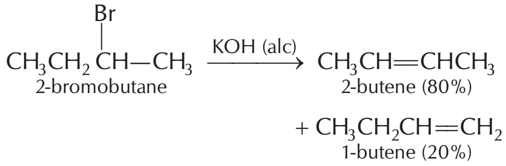
(*a*) *ammoniacal solution of* $AgNO_3$
(*b*) *alkaline solution of* $KMnO_4$
(*c*) *ammoniacal solution of* Cu_2Cl_2
(*d*) *None of the above*

Solution (*d*) In but-2-ene there is symmetry and in case of symmetrical alkenes *anti*-Markownikoff's rule is not obeyed.

Example 4 *Elimination of bromine from 2-bromobutane results in the formation of*

(*a*) *predominantly* 1-*butene*
(*b*) *predominantly* 2-*butyne*
(*c*) *predominantly* 2-*butene*
(*d*) *equimolar mixture of* 1 *and* 2-*butene*

Solution (*c*)



$$\underset{\text{2-bromobutane}}{CH_3CH_2\overset{\overset{Br}{|}}{CH}-CH_3} \xrightarrow{\text{KOH (alc)}} \underset{\text{2-butene (80\%)}}{CH_3CH{=}CHCH_3} + \underset{\text{1-butene (20\%)}}{CH_3CH_2CH{=}CH_2}$$

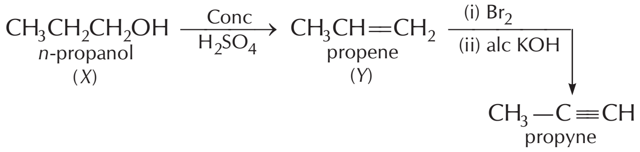
(∵ The elimination takes place according to Saytzeff's rule)

Example 5 *In the following reaction, what is X?*

$$X \xrightarrow[H_2SO_4]{\text{Conc}} Y \xrightarrow[\text{(ii) alc KOH}]{\text{(i) }Br_2} CH_3C{\equiv}CH$$

(*a*) $CH_3CH_2CH_3$
(*b*) $CH_3CH_2CH_2OH$
(*c*) $(CH_3)_2CHBr$
(*d*) CH_3CH_2Br

Solution (*b*) Since, the final product is alkyne which is obtained by dehydrohalogenation of respective halide which in turn obtained by the addition of halogen over double bond, thus, *Y* must be an alkene having three carbon atoms and alkene is obtained by dehydration of alcohols having the same number of carbon atoms. Thus, alcohol is propanol. The reactions are as follows



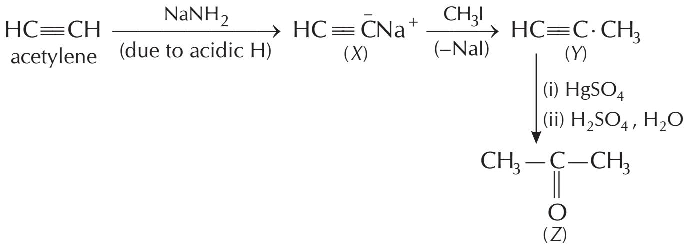
$$\underset{(X)}{\underset{n\text{-propanol}}{CH_3CH_2CH_2OH}} \xrightarrow[H_2SO_4]{\text{Conc}} \underset{(Y)}{\underset{\text{propene}}{CH_3CH{=}CH_2}} \xrightarrow[\text{(ii) alc KOH}]{\text{(i) }Br_2} \underset{\text{propyne}}{CH_3-C{\equiv}CH}$$

Example 6 *In the series,*

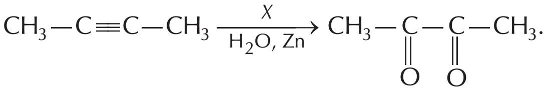
$$C_2H_2 \xrightarrow{NaNH_2} X \xrightarrow{CH_3I} Y \xrightarrow[H_2SO_4,\ H_2O]{HgSO_4} Z, \text{ the compound } Z \text{ is}$$

(*a*) $CH_3CH_2CH{=}CH_2$
(*b*) CH_3COCH_3
(*c*) CH_3CHO
(*d*) $CH_3CH_2CH_2CHO$

Solution (*b*)



Example 7



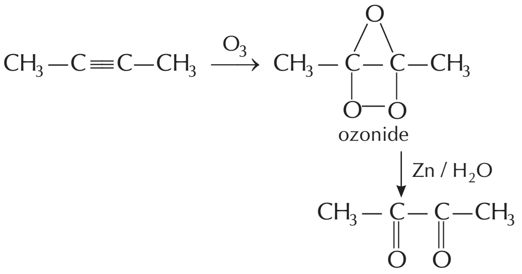
$$CH_3-C\equiv C-CH_3 \xrightarrow[H_2O,\ Zn]{X} CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3.$$

In the given reaction reagent X will be

(*a*) $KMnO_4$ (*b*) HIO_4

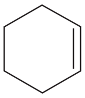
(*c*) O_3 (*d*) O_2

Solution (*c*) The reagent is O_3 as it is the reagent that introduces two O atoms at the successive triple bonded carbon atoms.

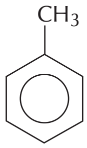


Example 8 *Which one of the following on ozonolysis followed by oxidation will give adipic acid?*

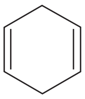
(*a*)



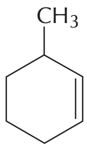
(*b*)



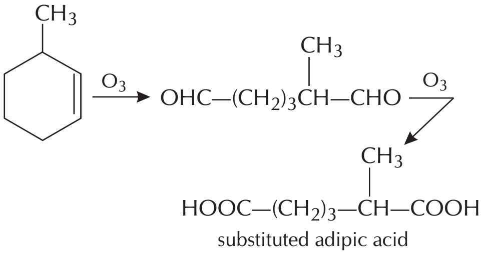
(*c*)



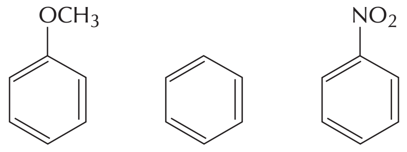
(*d*)



Solution (*d*)



Example 9 *Among the following compounds* (I – III) *the correct order of reaction with electrophile is*

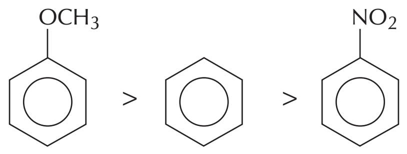


I II III

(*a*) $II > III > I$ (*b*) $III < I < II$

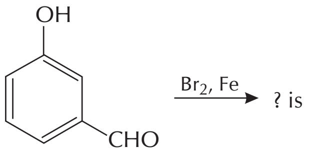
(*c*) $I > II > III$ (*d*) $I \approx II > III$

Solution (*c*) Activating groups like $—OCH_3$, —OH etc., activates the benzene ring towards electrophilic substitution while deactivating groups like NO_2, COOH etc., deactivates the benzene ring towards electrophilic substitution. Thus, order of reaction with electrophile (of the given compounds) is as

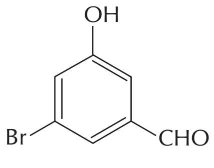


I II III

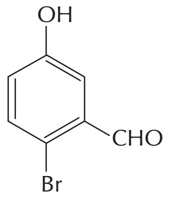
Example 10 *The product of the following reaction*



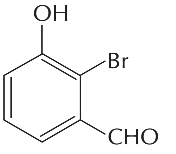
(*a*)



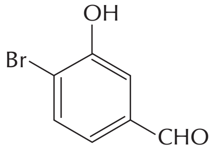
(*b*)



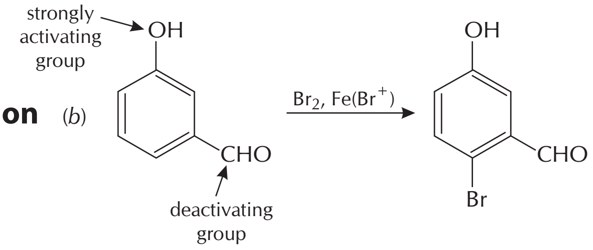
(*c*)



(*d*)



Solution (*b*)



(∵ Strongly activating group generally win over the deactivating group and —OH is a *ortho/para* directing group. *p*-product predominates.)

Start Practice *for* JEE Main

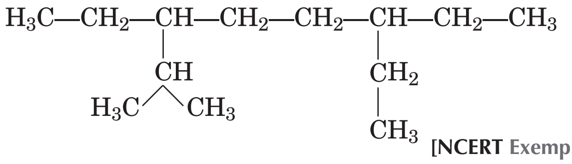
Round I (Topically Divided Problems)

Alkanes

1. In cyclopropane, cyclobutane and cyclohexane, the common group is

(a) $-\overset{|}{\underset{|}{C}}-$ (b) $\overset{|}{\underset{|}{CH_2}}$ (c) $-CH_3$ (d) $-\overset{|}{\underset{|}{CH}}$

2. The correct IUPAC name of the following alkane is



[NCERT Exemplar]

(a) 3,6-diethyl-2-methyloctane
(b) 5-*iso*-propyl-3-ethyloctane
(c) 5-ethyl-5-*iso*-propyloctane
(d) 3-*iso*-propyl-6-ethyloctane

3. Which of the following liberates methane on treatment with water?

(a) Silicon carbide (b) Calcium carbide
(c) Beryllium carbide (d) Magnesium carbide

4. Which of the following reactions of methane is incomplete combustion? **[NCERT Exemplar]**

(a) $2CH_4 + O_2 \xrightarrow{Cu/523\ K/100\ atm} 2CH_3OH$
(b) $CH_4 + O_2 \xrightarrow{Mo_2O_3} HCHO + H_2O$
(c) $CH_4 + O_2 \longrightarrow C(s) + 2H_2O(l)$
(d) $CH_4 + 2O_2 \longrightarrow CO_2(g) + 2H_2O(l)$

5. Which of the following will not produce ethane?

(a) Reduction of CH_3COOH with HI and red P
(b) Reduction of CH_3COCH_3 with HI and red P
(c) Sodalime decarboxylation of sodium propionate
(d) Hydrogenation of ethane in the presence of Raney-Ni

6. Which of the following reactions can be used to prepare methane?

(a) Clemmensen reduction
(b) Wurtz reaction
(c) Reduction of $CH_2{=}CH_2$ by $LiAlH_4$
(d) Reduction of methyl iodide by using a zinc-copper couple

7. Which of the following compounds cannot be prepared singly by the Wurtz reaction?

(a) C_2H_6
(b) $(CH_3)_2CHCH_3$
(c) $CH_3CH_2CH_2CH_3$
(d) All can be prepared

8. Both methane and ethane may be obtained by a suitable one-step reaction from

(a) CH_3I (b) C_2H_5I
(c) CH_3OH (d) C_2H_5OH

9. Arrange the halogens F_2, Cl_2, Br_2, I_2 in order of their increasing reactivity with alkanes **[NCERT Exemplar]**

(a) $I_2 < Br_2 < Cl_2 < F_2$ (b) $Br_2 < Cl_2 < F_2 < I_2$
(c) $F_2 < Cl_2 < Br_2 < I_2$ (d) $Br_2 < I_2 < Cl_2 < F_2$

10. The increasing order of reduction of alkyl halides with zinc and dilute HCl is **[NCERT Exemplar]**

(a) $R{-}Cl < R{-}I < R{-}Br$
(b) $R{-}Cl < R{-}Br < R{-}I$
(c) $R{-}I < R{-}Br < R{-}Cl$
(d) $R{-}Br < R{-}I < R{-}Cl$

11. An alkyl bromide, RBr of molecular weight 151 is the exclusive product of bromination of which hydrocarbon?

(a) Dodecane
(b) 2,2-dimethylpropane
(c) 2,2-dimethylhexane
(d) 2,2,3-trimethylheptane

12. Several hydrocarbon radicals can be formed as intermediates during monochlorination of 2-methylpropane. Which of them is the most stable? **[NCERT Exemplar]**

(a) $(CH_3)_2\dot{C}CH_3$ (b) $(CH_3)_2CH\dot{C}H_2$
(c) $(CH_3)\dot{C}HCH_2CH_3$ (d) All are equally stable

13. The products obtained in the reaction of sodium with a mixture of 1-iodo-2-methylpropane and 2-iodopropane is/are **[NCERT Exemplar]**

(a) 2,5-dimethyl hexane (b) 2,3-dimethylbutane
(c) 2,4-dimethyl pentane (d) All of these

14. Hydrocarbon which is liquid at room temperature is

(a) pentane (b) butane
(c) propane (d) ethane

15. On mixing a certain alkane with chlorine and irradiating it with UV light, it forms one monochloro alkane. The alkane could be

(a) *neo*-pentane (b) propane
(c) pentane (d) *iso*-pentane

16. Which of the following react with Cl_2 and Br_2 at room temperature and in the absence of diffused sunlight to produce dihalogen derivatives?

(a) Cyclobutane (b) Cyclopentane
(c) Cyclohexane (d) All of these

17. Which of the following alkanes can be easily sulphonated?

(a) *n*-butane (b) *iso*-butane
(c) *n*-pentane (d) *n*-hexane

18. $CH_3CH_2CH_3 \xrightarrow{400-600^\circ C} X + Y$

X and Y are

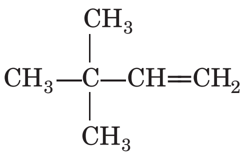
(a) hydrogen, methane (b) methane, ethylene
(c) hydrogen, ethylene (d) ethylene, ethane

Alkenes

19. The best method to prepare cyclohexene from cyclohexanol is by using

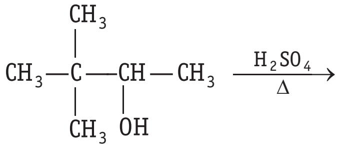
(a) conc. HCl + $ZnCl_2$ (b) conc. H_3PO_4
(c) HBr (d) conc. HCl

20. Which of the following reactions is not expected to give

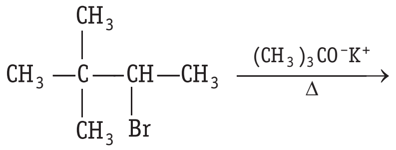


$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=CH_2$

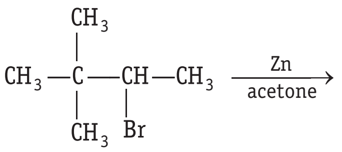
in yields of more than 50%?

(a) 

$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{OH}{CH}-CH_3 \xrightarrow[\Delta]{H_2SO_4}$

(b) 

$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{Br}{CH}-CH_3 \xrightarrow[\Delta]{(CH_3)_3CO^-K^+}$

(c) 

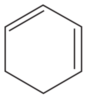
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{Br}{CH}-CH_3 \xrightarrow[\text{acetone}]{Zn}$

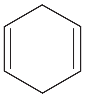
(d) None of the above

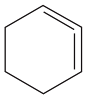
21. Allene (C_3H_4) contains

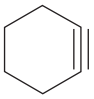
(a) one double bond, one triple bond and one single bond
(b) one triple and two double bonds
(c) two triple and one double bond
(d) two double and four single bonds

22. Which of the following compounds is the most stable?

(a) 

(b) 

(c) 

(d) 

23. Which one of the following has the smallest heat of hydrogenation per mole?

(a) 1-butene (b) *Trans*-but-2-ene
(c) *Cis*-but-2-ene (d) Buta-1,3-diene

24. The addition of HCl to 3,3,3-trichloropropene gives

(a) $Cl_3CCH_2CH_2Cl$
(b) $Cl_3CCH_2CHCl_2$
(c) $Cl_2CHCH_2CHCl_2$
(d) $Cl_2CHCH(Cl)CH_2Cl$

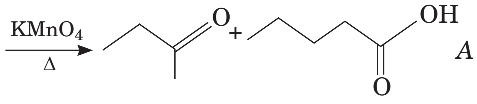
25. Arrange the following hydrogen halides in the order of their decreasing reactivity with propene. **[NCERT Exemplar]**

(a) HCl > HBr > HI (b) HBr > HI > HCl
(c) HI > HBr > HCl (d) HCl > HI > HBr

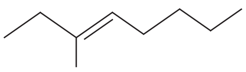
26. The addition of HBr to an alkene in the presence of peroxide is the example of

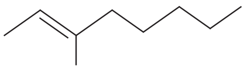
(a) electrophilic addition reaction
(b) nucleophilic addition reaction
(c) free radical addition reaction
(d) the formation of carbocation as an intermediate

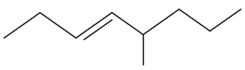
27. Alkene (*A*)

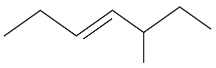


A is

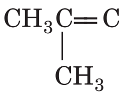
(a) 

(b) 

(c) 

(d) 

28. The treatment of



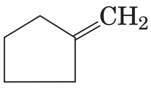
$CH_3\underset{\substack{|\\ CH_3}}{C}=CHCH_3$ with $NaIO_4$ or boiling $KMnO_4$ produces

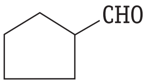
(a) $CH_3COCH_3 + CH_3COOH$

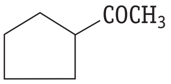
(b) $CH_3COCH_3 + CH_3CHO$

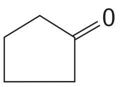
(c) $CH_3CHO + CO_2$

(d) CH_3COCH_3 only

29.  on ozonolysis gives

(a) 

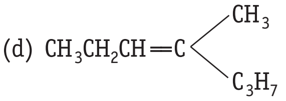
(b) 

(c)  + HCHO

(d) None of these

30. Propanal and pentan-3-one are ozonolysis product of an alkene. What is the structural formula of the alkene? **[NCERT]**

(a) $CH_3CH_2CH{=}C(C_2H_5)_2$ (b) $CH_3CH{=}CHCH(C_2H_5)_2$

(c) $CH_3CH_2CH{=}CHCH_2C_3H_7$ (d) 

$CH_3CH_2CH{=}C\begin{matrix} CH_3 \\ C_3H_7 \end{matrix}$

31. An unsaturated hydrocarbon '*A*' adds two molecules of H_2 and on reductive ozonolysis gives butane-1,4-dial, ethanol and propanone. Give the IUPAC name of *A*. **[NCERT Exemplar]**

(a) 3-methylocta-2,6-diene

(b) 2-methylocta-2,5-diene

(c) 2-methylocta-2,6-diene

(d) 2-methylocta-3,5-diene

32. The alkene which on hydrogenation give 2-methyl butane is **[NCERT]**

(a) 2-methylbut-1-ene

(b) 2-methylbut-2-ene

(c) 3-methylbut-1-ene

(d) All of the above

33. The reaction of propene with HOCl proceeds *via* the addition of

(a) Cl^+ and OH^- in a single step

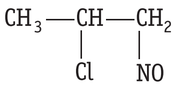
(b) Cl^+ in the first step

(c) H^+ in the first step

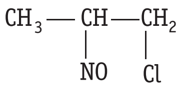
(d) OH^- in the first step

34. $CH_3{-}CH{=}CH_2 + NOCl \longrightarrow P$

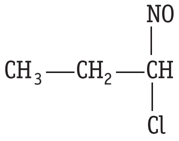
Identify the adduct.

(a) 

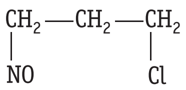
$CH_3{-}\underset{\substack{|\\ Cl}}{CH}{-}\underset{\substack{|\\ NO}}{CH_2}$

(b) 

$CH_3{-}\underset{\substack{|\\ NO}}{CH}{-}\underset{\substack{|\\ Cl}}{CH_2}$

(c) 

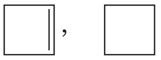
$CH_3{-}CH_2{-}\overset{\substack{NO\\ |}}{\underset{\substack{|\\ Cl}}{CH}}$

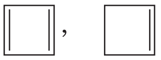
(d) 

$\underset{\substack{|\\ NO}}{CH_2}{-}CH_2{-}\underset{\substack{|\\ Cl}}{CH_2}$

35. $A\,(C_4H_6) \xrightarrow[\text{1 mole}]{H_2,\,Ni} B\,(C_4H_8) \xrightarrow{O_3/H_2O/Zn} CH_3CHO.$

Thus, *A* and *B* are

(a) 

(b) 

(c) $CH_3CH_2C{\equiv}CH,\ CH_3CH{=}CHCH_3$

(d) $CH_2{=}CH{-}CH{=}CH_2,\ CH_3CH{=}CH{-}CH_3$

Alkynes

36. The number of possible alkynes with molecular formula C_5H_8 is

(a) 3	(b) 4
(c) 5	(d) 6

37. $CaC_2 + H_2O \longrightarrow A \xrightarrow{H_2SO_4/HgSO_4} B$

Identify *A* and *B* in the given reaction.

(a) C_2H_2 and CH_3CHO	(b) CH_4 and HCOOH
(c) C_2H_4 and CH_3COOH	(d) C_2H_2 and CH_3COOH

38. The reduction of 4-octyne with H_2 in the presence of $Pd/CaCO_3$ quinoline gives

(a) *trans*-4-octene

(b) *cis*-4-octene

(c) a mixture of *cis*-and *trans*-4-octene

(d) a completely reduced product C_8H_{18}

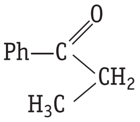
39. Water can be added across a triple bond in the presence of

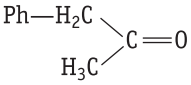
(a) acidic medium	(b) alkaline medium
(c) neutral medium	(d) acid and $HgSO_4$

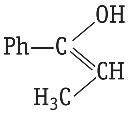
40. The product(s) obtained *via* oxymercuration ($HgSO_4 + H_2SO_4$) of but-1-yne would be

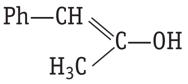
(a) $CH_3CH_2COCH_3$	(b) $CH_3CH_2CH_2CHO$
(c) $CH_3CH_2CHO + HCHO$	(d) $CH_3CH_2COOH + HCOOH$

41. $Ph—C\equiv C—CH_3 \xrightarrow{Hg^{2+}/H^+} A$,

(a)


(b)


(c)


(d)


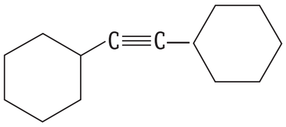
42. The final product in the following sequence of reaction is

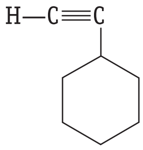
$$CH\equiv CH \xrightarrow{NaNH_2} A \xrightarrow{CH_3Br} B$$

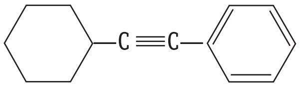
(a) $CH_2{=}CH—CH{=}CH_2$ (b) $HC\equiv C—CH_3$
(c) $CH_2{=}CH—CH_3$ (d) $CH_3—CH_2—CH_3$

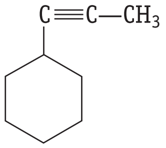
43. Acetylene and HCHO reacts in the presence of copper acetylide catalyst to form
(a) 1-butyne-1, 4-diol (b) 2-butyne-1, 2-diol
(c) 2-butyne-1, 4-diol (d) None of these

44. Which of the following form alkynide?

(a)


(b)


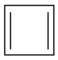
(c)


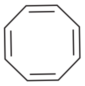
(d)


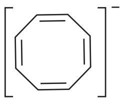
45. Ammoniacal silver nitrate form a white precipitate easily with
(a) $CH_3C\equiv CH$ (b) $CH_3C\equiv C—CH_3$
(c) $CH_3CH{=}CH_2$ (d) $CH_2{=}CH_2$

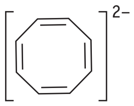
Aromatic Hydrocarbons

46. Which among the following is aromatic?

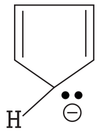
(a)


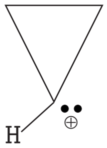
(b)


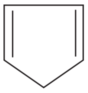
(c)


(d)


47. Which of the following species will be aromatic?

(a)


(b)


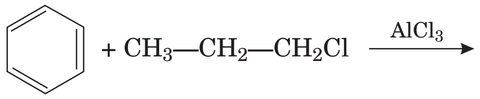
(c)


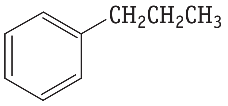
(d) None of these

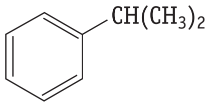
48. Which of the following annulenes is anti-aromatic?
(a) Benzene
(b) Cyclobutadiene
(c) Cyclodecapentene
(d) Cyclooctatetraene

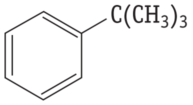
49. An activating group
(a) activates only *ortho* and *para* positions
(b) deactivates *meta* position
(c) activates *ortho* and *para* more than *meta*
(d) deactivates *meta* more than *ortho* and *para*

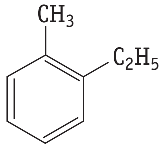
50. What will be the product obtained as a result of the following reaction and why? **[NCERT Exemplar]**


$$+ CH_3—CH_2—CH_2Cl \xrightarrow{AlCl_3}$$

(a)


(b)


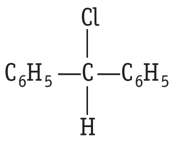
(c)


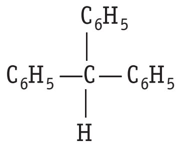
(d)


51. The treatment of benzene with benzoyl chloride in the presence of $AlCl_3$ gives
(a) benzaldehyde (b) benzophenone
(c) diphenyl (d) cyclohexane

52. A Friedel-Crafts reaction of benzene with chloroform produces

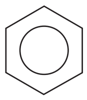
(a) $C_6H_5CHCl_2$

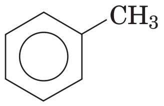
(b)

$$C_6H_5—\underset{H}{\overset{Cl}{C}}—C_6H_5$$

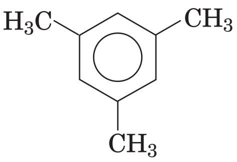
(c)

$$C_6H_5—\underset{H}{\overset{C_6H_5}{C}}—C_6H_5$$

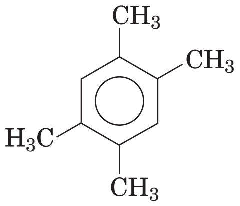
(d) All of these

53. Arrange the following in the order of decreasing boiling point.


I

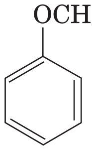

II

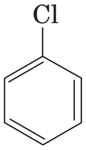

III

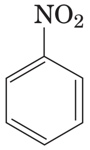

IV

(a) I > II > III > IV (b) IV > III > II > I
(c) I > III > IV > II (d) II > III > I > IV

54. Arrange the following set of compounds in the order of their decreasing relative reactivity with an electrophile. **[NCERT Exemplar]**


I


II


III

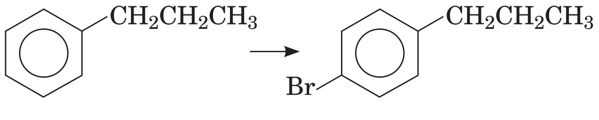
(a) I > II > III
(b) I > III > II
(c) II > I > III
(d) II > III > I

55. Among the following statements on the nitration of aromatic compounds, the false one is
(a) the rate of nitration of benzene is almost the same as that of hexadeuterobenzene
(b) the rate of nitration of toluene is greater than that of benzene
(c) the rate of nitration of benzene is greater than that of hexadeuterobenzene
(d) nitration is an electrophilic substitution reaction

56. Among the following, the compound that can be most readily sulphonated is
(a) benzene (b) nitrobenzene
(c) toluene (d) chlorobenzene

57. Toluene, when treated with Br_2/Fe, gives *p*-bromotoluene as the major product because the —CH_3 group

58. The conversion



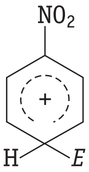
can be achieved by using
(a) Br_2/CCl_4 (b) Br_2/H_2O
(c) Br_2/Fe (d) Br_2/benzoyl peroxide

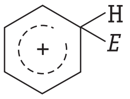
59. Nitrobenzene can be prepared from benzene by using a mixture of concentrated HNO_3 and concentrated H_2SO_4. In the nitrating mixture, HNO_3 acts as
(a) base (b) acid
(c) reducing agent (d) catalyst

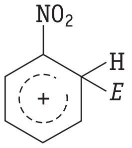
60. The reaction of toluene with chlorine in the presence of ferric chloride gives predominantly
(a) benzoyl chloride (b) *m*-chlorotoluene
(c) benzyl chloride (d) *o*-and *p*-chlorotoluene

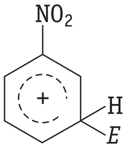
61. Benzyl chloride ($C_6H_5CH_2Cl$) can be prepared from toluene by chlorination with
(a) SO_2Cl_2 (b) $SOCl_2$
(c) Cl_2 (d) NaOCl

62. The electrophile, $E^{\oplus}$ attacks the benzene ring to generate the intermediate σ-complex of the following, which σ-complex is of lowest energy?

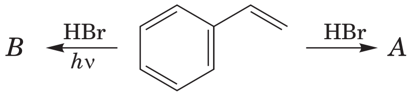
(a)


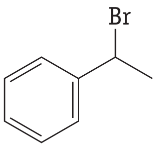
(b)


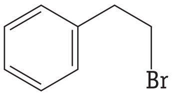
(c)


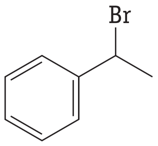
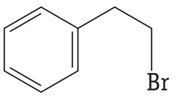
(d)


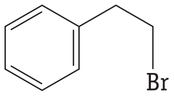
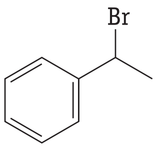
63. Observe the following reactions and predict the nature of *A* and *B*



(a) *A* and *B* both are


(b) *A* and *B* both are


(c) *A* is

and *B* is


(d) *A* is

and *B* is


64. Arrange the following set of compounds in the order of their decreasing relative reactivity with an electrophile, E^+

I. chlorobenzene
II. 2,4-dinitrochlorobenzene
III. *p*-nitrochlorobenzene
IV. toluene
V. *p*-$H_3C—C_6H_4—NO_2$, **[NCERT]**

(a) I > II > III > IV > V (b) IV > V > I > III > II
(c) V > IV > III > II > I (d) I > III > II > V > IV

Miscellaneous

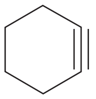
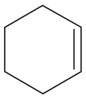
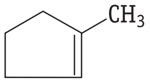
65. Which of the following will react with sodium metal?
(a) Ethene (b) Propyne (c) But-2-yne (d) Ethane

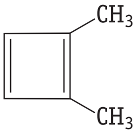
66. The treatment of aluminium carbide with water or dilute acid produces
(a) acetylene (b) ethene (c) methane (d) ethane

67. The reactivities of ethane, ethylene and acetylene are of the order
(a) ethane < ethene < ethyne
(b) ethane < ethyne < ethene
(c) ethyne = ethene > ethane
(d) Any of the above

68. Which of the following statements is true for ethane, ethene and acetylene?
(a) Acetylene is the weakest acid and has the longest C—H bond distance
(b) Acetylene is the strongest acid and has the shortest C—H bond distance
(c) Ethane is the strongest acid and has the shortest C—H bond distance
(d) Ethene is the strongest acid and has the shortest C—H bond distance

69. Compound (*A*) on oxidation with $OsO_4/NaIO_4$ gives hexanedinal. Structure of compound (*A*) will be

(a) 
(b) 
(c) 

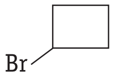
(d) 

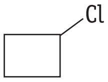
70. Choose the correct statement.
(a) Acetylene is more reactive than ethylene to an electrophilic attack
(b) Acetylene and ethylene show similar reactivities towards an electrophilic attack with different rates
(c) The reactivities of acetylene and ethylene towards an electrophilic attack depend on the electrophilic reagent
(d) Acetylene is less reactive than ethylene to an electrophilic attack

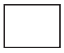
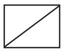
Round II (Mixed Bag)

Only One Correct Option

1. What would be the product formed when 1-bromo-3-chloro cyclobutane reacts with two equivalents of metallic sodium in ether?

(a) 

(b) 

(c) 
(d) 

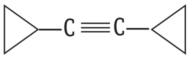
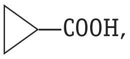
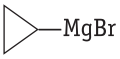
2. An alkene, C_8H_{18} is obtained as the only product on subjecting a primary alkyl halide to Wurtz reaction. On monobromination this alkane yields a single isomer of a tertiary bromide. The primary alkyl halide is **[NCERT Exemplar]**
(a) 1-chloro butane
(b) *iso*-butyl halide
(c) *iso*-pentyl halide
(d) *neo*-pentyl halide

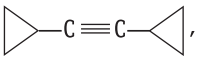
3. The relative reactivity of 1°, 2°, 3° hydrogen's towards chlorination is 1 : 3.8 : 5. The percentages of 2° monochlorinated products obtained from 2-methylbutane is **[NCERT Exemplar]**
(a) 41.67 (b) 35.18 (c) 23.15 (d) 48.5

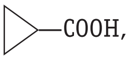
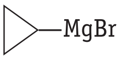
4. $C_8H_{10}(A) \xrightarrow{O_3/H_2O} \text{acid } (B)$

$C_3H_5MgBr(C) \xrightarrow{CO_2,\, H_3O^+} \text{acid } B$

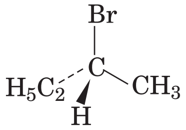
Identify *A*, *B* and *C*.

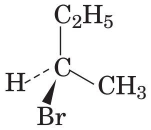
(a) , , 

(b) , $CH_3CH_2CH_2COOH$,
$CH_2{=}CH—CH_2MgBr$

(c) $CH_3—CH_2—CH_2—CH_3$, $CH_3CH_2CH_2COOH$, $CH_2{=}CH—CH_2MgBr$
(d) $CH_3CH_2CH_2CH_3$, , 

5. The addition of HBr to 1-butene gives a mixture of products *A*, *B* and *C*


(*A*)


(*B*)

$CH_3CH_2CH_2CH_2Br$
(*C*)

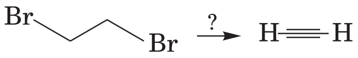
The mixture consists of **[NCERT Exemplar]**

(a) *A* and *B* as major and *C* as minor products
(b) *B* as major, *A* and *C* as minor products
(c) *B* as minor, *A* and *C* as major products
(d) *A* and *B* as minor and *C* as major products

6. Alkyne, C_7H_{12}, when reacted with alkaline $KMnO_4$ followed by acidification with HCl gives a mixture of $(CH_3)_2CHCOOH + CH_3CH_2COOH$. The alkyne C_7H_{12} is

(a) 3-hexyne (b) 2-methyl-2-hexene
(c) 2-methyl-3-hexyne (d) 3-methyl-2-hexyne

7. The reagent(s) for the following conversion,



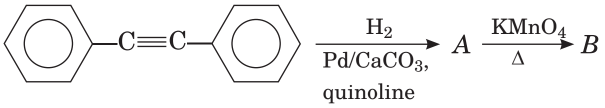
is/are

(a) alcoholic KOH
(b) alcoholic KOH followed by $NaNH_2$
(c) aqueous KOH followed by $NaNH_2$
(d) Zn/CH_3OH

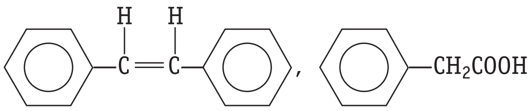
8. $$A \xleftarrow[\text{(ii) } H_2O_2,\ OH^-]{\text{(i) } BH_3,\ THF} CH_3C{\equiv}CH \xrightarrow[H_2SO_4]{HgSO_4} B$$

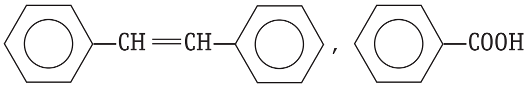
Identify *A* and *B*.

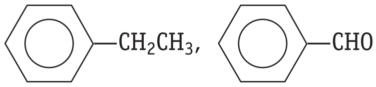
(a) CH_3CHO, CH_3COCH_3
(b) CH_3CH_2CHO, CH_3COCH_3
(c) CH_3CH_2CHO, $CH_3COCH_2CH_3$
(d) HCHO, CH_3COCH_3

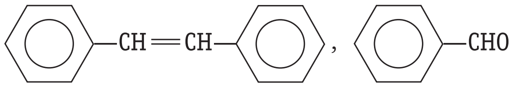
9. 

Identify *A* and *B*.

(a) 

(b) 

(c) 

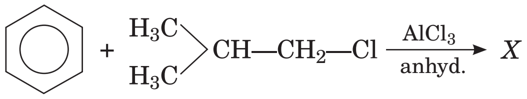
(d) 

10. Propyne and propene can be distinguished by

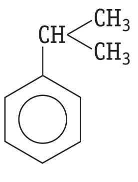
(a) conc. H_2SO_4
(b) Br_2 in CCl_4
(c) alk. $KMnO_4$
(d) $AgNO_3$ in NH_3

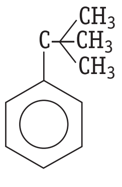
11. Arrange benzene, *n*-hexane and ethyne in the decreasing order of acidic behaviour. **[NCERT]**

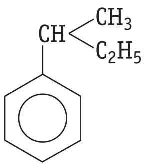
(a) Ethyne > benzene > hexane
(b) Hexane > benzene > ethyne
(c) Ethyne > hexane > benzene
(d) Benzene > hexane > ethyne

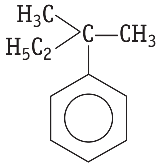
12. 

Identify the *X* in the above reaction

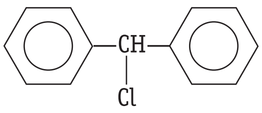
(a) 

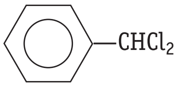
(b) 

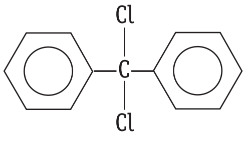
(c) 

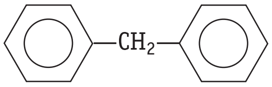
(d) 

13. When excess of C_6H_6 reacts with CH_2Cl_2 in the presence of anhydrous $AlCl_3$, the following compound is obtained

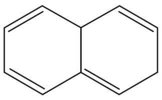
(a) 

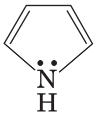
(b) 

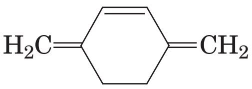
(c) 

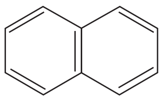
(d) 

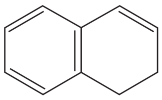
14. Which of the following compounds are aromatic according to Huckel's rule? **[NCERT Exemplar]**

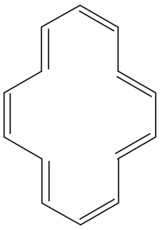
I. 

II. 

III. 

IV. 

V. 

VI. 

(a) I, II, IV, V
(b) II, IV, V, VI
(c) II, III, V only
(d) IV, V and VI

15. 896 mL vapour of a hydrocarbon '*A*' having carbon 87.80% and hydrogen 12.19% weighs 3.28 g at STP. Hydrogenation of '*A*' gives 2-methylpentane. Also '*A*' on hydration in the presence of H_2SO_4 and $HgSO_4$ gives a ketone '*B*' having molecular formula $C_6H_{12}O$. The ketone '*B*' gives a positive iodoform test. Find the structure of '*A*'. **[NCERT Exemplar]**

(a) $(CH_3)_3CC{\equiv}C{-}CH_2CH_3$
(b) $(CH_3)_2CHCH_2C{\equiv}CH$
(c) $CH_3CH_2C{\equiv}CCH_2CH_2CH_2CH_3$
(d) $(CH_3)_2CHCH_2CH_2C{\equiv}CH$

16. Match the reagent from Column I which on reaction with $CH_3{-}CH{=}CH_2$ gives some product given in Column II as per the codes given below **[NCERT Exemplar]**

	Column I		Column II
A.	$O_3/Zn + H_2O$	1.	Acetic acid and CO_2
B.	$KMnO_4/H^+$	2.	Propan-1-ol
C.	$KMnO_4/OH^-$	3.	Propan-2-ol
D.	H_2O/H^+	4.	Acetaldehyde and formaldehyde
E.	B_2H_6/NaOH and H_2O_2	5.	Propane-1,2- diol

Codes

	A	B	C	D	E
(a)	4	1	5	2	3
(b)	4	5	1	2	3
(c)	3	2	1	5	4
(d)	4	1	5	3	2

17. Match the following reactants in Column I with the corresponding reaction products in Column II. **[NCERT Exemplar]**

	Column I		Column II
A.	Benzene + $Cl_2 \xrightarrow{AlCl_3}$	1.	Benzoic acid
B.	Benzene + $CH_3Cl \xrightarrow{AlCl_3}$	2.	Methyl phenyl ketone
C.	Benzene + $CH_3COCl \xrightarrow{AlCl_3}$	3.	Toluene
D.	Toluene $\xrightarrow{KMnO_4/NaOH}$	4.	Chlorobenzene
		5.	Benzene hexachloride

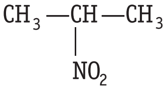
Codes

	A	B	C	D
(a)	4	3	2	1
(b)	1	2	3	4
(c)	4	3	1	5
(d)	1	5	2	3

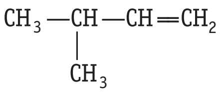
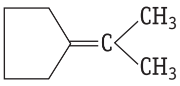
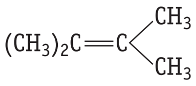
More than One Correct Option

18. Some oxidation reactions of methane are given below. Which of them is/are controlled oxidation reactions? **[NCERT Exemplar]**

(a) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$
(b) $CH_4(g) + O_2(g) \longrightarrow C(s) + 2H_2O(l)$
(c) $CH_4(g) + O_2(g) \xrightarrow{Mo_2O_3} HCHO + H_2O$
(d) $2CH_4(g) + O_2(g) \xrightarrow{Cu/523/100\ atm} 2CH_3OH$

19. Nitration of propane with concentrated HNO_3 gives
(a) CH_3NO_2
(b) $CH_3CH_2CH_2NO_2$
(c) 
$CH_3{-}CH(NO_2){-}CH_3$
(d) $CH_3CH_2NO_2$

20. Which of the following alkenes on ozonolysis give a mixture of ketones only? **[NCERT Exemplar]**

(a) $CH_3{-}CH{=}CH{-}CH_3$
(b) 
$CH_3{-}CH(CH_3){-}CH{=}CH_2$
(c) 
(d) 

21. The molecules having dipole moment are …… . **[NCERT Exemplar]**

(a) 2,2-dimethylpropane
(b) *trans*-pent-2-ene
(c) *cis*-hex-3-ene
(d) 2,2,3,3-tetramethylbutane

22. For an electrophilic substitution reaction, the presence of a halogen atom in the benzene ring …… . **[NCERT Exemplar]**

(a) deactivates the ring by inductive effect
(b) deactivates the ring by resonance
(c) Increases the charge density at *ortho* and *para* position relative to *meta* position by resonance
(d) directs the incoming electrophile to *meta* position by increasing the charge density relative to *ortho* and *para* position.

Assertion and Reason

Directions (Q. Nos. 23 to 27) *Each of these questions contains two statements : Statement* I (*Assertion*) *and Statement* II (*Reason*). *Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes* (*a*), (*b*), (*c*), (*d*) *given below :*

(a) Statement I is true; Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true; Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

23. **Statement I** Cycloalkenes decolourise the purple colour of dilute and cold $KMnO_4$ or red colour of bromine in carbon tetrachloride.

Statement II Cycloalkenes undergo the electrophilic addition reactions which are characteristic of alkenes.

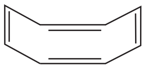
24. **Statement I** Among isomeric pentanes, 2,2-dimethylpropane has the lowest boiling point.

Statement II Branching does not affect the boiling point. **[NCERT Exemplar]**

25. **Statement I** Acetylene is more reactive than ethylene.

Statement II In acetylene, there is greater strain.

26. **Statement I** The compound cyclooctane has the following structural formula



It is cyclic and has conjugated 8π-electron system but it is not an aromatic compound.

Statement II $(4n+2)\,\pi$ electrons rule does not hold good and ring is not planar. **[NCERT Exemplar]**

27. **Statement I** The repalcement of hydrogen atom by sulphonic acid group (—SO_3H) is known as sulphonation.

Statement II Sulphonation follows free radical mechanism.

Comprehension Based Questions

Directions (Q. Nos. 28 to 30) Dehydration of 1-butanol and 2-butanol with conc H_2SO_4 gives the same mixture of 1-butene and 2-butene in which the more highly substituted alkene, *i.e.,* 2-butene predominates (Saytzeff rule). The formation of this mixture from 1-butanol can be explained by the rearrangement of the initially formed less stable 1° carbocation to the more stable 2° carbocation, which then loses a proton in accordance with Saytzeff rule to afford a mixture of 2-butene and 1-butene.

28. In the acid catalysed dehydration of alcohols to alkenes, the reactive intermediate involved is a

(a) carbene
(b) free radical
(c) carbocation
(d) carbanion

29. When ethyl alcohol is heated with conc H_2SO_4 at 443 K, ethylene is formed by

(a) intermolecular dehydration
(b) intramolecular dehydration
(c) intermolecular hydration
(d) intramolecular hydration

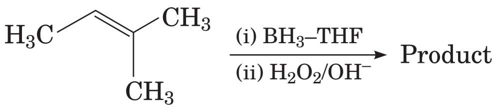
30. Which one of the following heptanols can be dehydrated to hept-3-ene only?

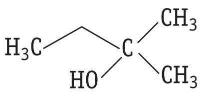
(a) Heptan-3-ol
(b) Heptan-4-ol
(c) Heptan-2-ol
(d) Heptan-1-ol

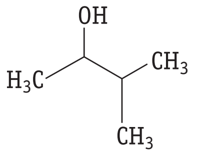
Directions (Q. Nos. 31 to 33) Acid catalysed hydration of alkene gives alcohol. In this reaction addition of water takes place according to Markownikoff's rule. Since intermediate carbocation is formed in this reaction, rearrangement of carbocation takes place. In oxymercuration-demercuration reaction hydration of alkene takes place according to Markownikoff's rule. Oxymercuration-demercuration is a better process than the catalytic hydration of alkene because in oxymercuration-demercuration, no rearrangement is possible. In hydroboration oxidation, (HBO) hydration of alkene takes place according to anti-Markownikoff's addition. In HBO reaction rearrangement is not possible. Both in oxymercuration-demercuration and hydroboration oxidation intermediate carbocation are not formed.

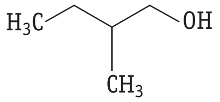
31. 2-phenyl propene on acidic hydration gives
- (a) 2-phenyl-2-propanol
- (b) 2-phenyl-1-propanol
- (c) 3-phenyl-1-propanol
- (d) 1-phenyl-2-propanol

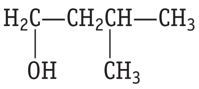
32. The product formed in the following reaction is



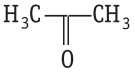
(a)


(b)


(c)


(d)


$\underset{OH}{H_2C}—CH_2\underset{CH_3}{CH}—CH_3$

33. $CH_3—C≡C—H \xrightarrow[\text{(ii) } H_2O_2/OH^-]{\text{(i) } B_2H_6} A$, A is
- (a) $CH_3—CH_2—CHO$
- (b)  $H_3C—\underset{\underset{O}{\|}}{C}—CH_3$
- (c) $CH_3—CHO$
- (d) $CH_3—CH_2—CH_2—OH$

Previous Years' Questions

34. How many chiral compounds are possible on monochlorination of 2-methyl butane? **[AIEEE 2012]**
- (a) 8
- (b) 2
- (c) 4
- (d) 6

35. Which branched chain isomer of the hydrocarbon with molecular mass 72 u gives only one isomer of mono substituted alkyl halide? **[AIEEE 2012]**
- (a) *Tert*-butyl chloride
- (b) *Neo*-pentane
- (c) *Iso*-hexane
- (d) *Neo*-hexane

36. 2-hexyne gives *trans*-2-hexene on treatment with **[AIEEE 2012]**
- (a) Pt/H_2
- (b) Li/NH_3
- (c) $Pd/BaSO_4$
- (d) $LiAlH_4$

37. Ozonolysis of an organic compound gives formaldehyde as one of the products. This confirms the presence of **[AIEEE 2011]**
- (a) two ethylenic double bonds
- (b) a vinyl group
- (c) an *iso* propyl group
- (d) an acetylenic triple bond

38. Ozonolysis of an organic compound *A* produces acetone and propionaldehyde in equimolar mixture. Identify *A* from the following compounds. **[AIEEE 2011]**
- (a) 2-methyl-1-pentene
- (b) 1-pentene
- (c) 2-pentene
- (d) 2-methyl-2-pentene

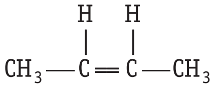
39. One mole of a symmetrical alkene on ozonolysis gives two moles of an aldehyde having a molecular mass of 44 u. The alkene is **[AIEEE 2010]**
- (a) propene
- (b) 1-butene
- (c) 2-butene
- (d) ethene

40. In the following sequence of reactions, the alkene affords the compound '*B*'

$$CH_3CH{=}CHCH_3 \xrightarrow{O_3} A \xrightarrow[Zn]{H_2O} B.$$

The compound *B* is **[AIEEE 2008]**
- (a) CH_3CH_2CHO
- (b) CH_3COCH_3
- (c) $CH_3CH_2COCH_3$
- (d) CH_3CHO

41. The hydrocarbon which can react with sodium in liquid ammonia is **[AIEEE 2008]**
- (a) $CH_3CH_2CH_2C≡CCH_2CH_2CH_3$
- (b) $CH_3CH_2C≡CH$
- (c) $CH_3CH{=}CHCH_3$
- (d) $CH_3CH_2C≡CCH_2CH_3$

42. The treatment of CH_3MgX with $CH_3C≡C—H$ produces **[AIEEE 2008]**
- (a) $CH_3—CH{=}CH_2$
- (b) $CH_3C≡C—CH_3$
- (c)  $CH_3—\overset{\overset{H}{|}}{C}{=}\overset{\overset{H}{|}}{C}—CH_3$
- (d) CH_4

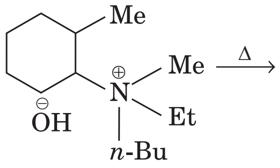
43. Which of the following reactions will yield 2, 2-dibromopropane? **[AIEEE 2007]**
- (a) $CH_3—C≡CH + 2HBr \longrightarrow$
- (b) $CH_3CH{=}CHBr + HBr \longrightarrow$
- (c) $CH≡CH + 2HBr \longrightarrow$
- (d) $CH_3—CH{=}CH_2 + HBr \longrightarrow$

44. Presence of a nitro group in a benzene ring **[AIEEE 2007]**
- (a) activates the ring towards electrophilic substitution
- (b) renders the ring basic
- (c) deactivates the ring towards nucleophilic substitution
- (d) deactivates the ring towards electrophilic substitution

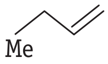
45. HBr reacts with $CH_2{=}CH{-}OCH_3$ under anhydrous conditions at room temperature to give **[AIEEE 2006]**

(a) CH_3CHO and CH_3Br (b) $BrCH_2CHO$ and CH_3OH
(c) $BrCH_2{-}CH_2{-}OCH_3$ (d) $H_3C{-}CHBr{-}OCH_3$

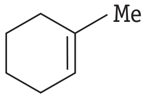
46.

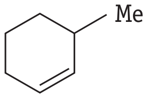


The alkene formed as a major product in the above elimination reaction is **[AIEEE 2006]**

(a)


(b) $CH_2{=}CH_2$

(c)


(d)


47. Of the five isomeric hexanes , the isomer which can give two monochlorinated compounds, is **[AIEEE 2005]**

(a) 2-methylpentane
(b) 2, 2-dimethylbutane
(c) 2, 3-dimethylbutane
(d) *n*-hexane

48. Reaction of one molecule of HBr with one molecule of 1, 3-butadiene at 40°C gives predominantly **[AIEEE 2005]**

(a) 1-bromo-2-butene under kinetically controlled conditions
(b) 3-bromobutene under thermodynamically controlled conditions
(c) 1-bromo-2-butene under thermodynamically controlled conditions
(d) 3-bromobutene under kinetically controlled conditions

49. Which one of the following has the minimum boiling point? **[AIEEE 2004]**

(a) *n*-butane (b) 1-butyne
(c) 1-butene (d) *Iso*-butene

50. Butene-1 may be converted to butane by reaction with **[AIEEE 2003]**

(a) Zn-HCl (b) Sn-HCl
(c) Zn-Hg (d) Pd/H_2

51. Acetylene does not react with **[AIEEE 2002]**

(a) Na (b) ammoniacal $AgNO_3$
(c) HCl (d) NaOH

Answers

Round I

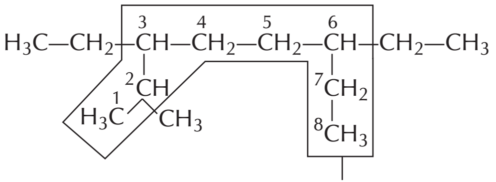
1. (b)	**2.** (a)	**3.** (c)	**4.** (c)	**5.** (b)	**6.** (d)	**7.** (b)	**8.** (a)	**9.** (a)	**10.** (b)
11. (b)	**12.** (a)	**13.** (d)	**14.** (a)	**15.** (a)	**16.** (a)	**17.** (d)	**18.** (b)	**19.** (b)	**20.** (a)
21. (d)	**22.** (a)	**23.** (d)	**24.** (a)	**25.** (c)	**26.** (c)	**27.** (a)	**28.** (a)	**29.** (c)	**30.** (a)
31. (c)	**32.** (d)	**33.** (b)	**34.** (b)	**35.** (d)	**36.** (a)	**37.** (a)	**38.** (b)	**39.** (d)	**40.** (a)
41. (a)	**42.** (b)	**43.** (c)	**44.** (b)	**45.** (a)	**46.** (d)	**47.** (a)	**48.** (b)	**49.** (c)	**50.** (b)
51. (b)	**52.** (c)	**53.** (a)	**54.** (a)	**55.** (a)	**56.** (c)	**57.** (c)	**58.** (c)	**59.** (a)	**60.** (d)
61. (c)	**62.** (b)	**63.** (c)	**64.** (b)	**65.** (b)	**66.** (c)	**67.** (a)	**68.** (b)	**69.** (b)	**70.** (d)

Round II

1. (d)	**2.** (b)	**3.** (b)	**4.** (a)	**5.** (a)	**6.** (c)	**7.** (b)	**8.** (b)	**9.** (b)	**10.** (d)
11. (a)	**12.** (b)	**13.** (d)	**14.** (b)	**15.** (b)	**16.** (d)	**17.** (a)	**18.** (c,d)	**19.** (a,b,c,d)	**20.** (c,d)
21. (b,c)	**22.** (a,c)	**23.** (b)	**24.** (c)	**25.** (a)	**26.** (a)	**27.** (b)	**28.** (c)	**29.** (b)	**30.** (b)
31. (a)	**32.** (b)	**33.** (a)	**34.** (c)	**35.** (b)	**36.** (b)	**37.** (b)	**38.** (d)	**39.** (c)	**40.** (d)
41. (b)	**42.** (d)	**43.** (a)	**44.** (d)	**45.** (d)	**46.** (b)	**47.** (c)	**48.** (c)	**49.** (d)	**50.** (d)
51. (d)									

the Guidance

Round I

2. 

longest chain with eight carbons

3,6-diethyl-3-methyloctane

Note Name of the substituent are given alphabetically when more than one substituent are present.

3. Beryllium carbide gives CH_4, magnesium carbide (MgC_2) and calcium carbide (CaC_2) give acetylene on hydrolysis while silicon carbide being covalent does not undergo hydrolysis.

4. Incomplete combustion of methane results in the formation of carbon black C(s).

5. Reduction of CH_3COCH_3 with HI and red P will give propane.

$$CH_3COCH_3 \xrightarrow{\text{HI, Red P}} CH_3CH_2CH_3$$

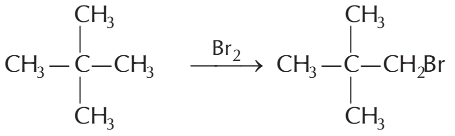
7. If two different alkyl halides (R_1—X and R_2—X) are used, a mixture of three alkanes is obtained which is difficult to separate.

8. $$CH_3I + 2[H] \xrightarrow{\text{Zn–Cu}} \underset{\text{methane}}{CH_4} + HI$$

$$2CH_3I \xrightarrow{\text{Na}} \underset{\text{ethane}}{CH_3CH_3}$$

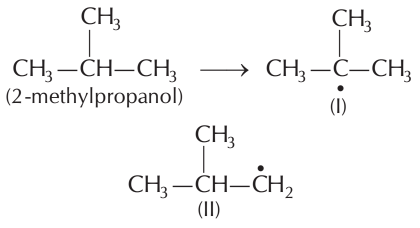
9. Among the halogens, fluorine being most electronegative is highly reactive and reactivity decreases on moving down the group. Thus, the correct order is $I_2 < Br_2 < Cl_2 < F_2$.

10. As the size of halogen atom increases, R—X bond length increases, thus, reactivity of RX increases.

11. 

$$\underset{\text{2,2-dimethyl propane}}{CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_3} \xrightarrow{Br_2} \underset{(C_5H_{11}Br = 151)}{CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2Br}$$

12. 2-methylpropane gives two types of radicals.

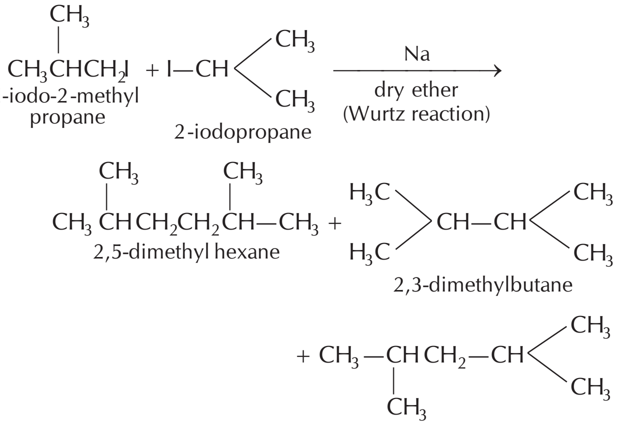


$$\underset{\text{(2-methylpropanol)}}{CH_3-\overset{CH_3}{CH}-CH_3} \longrightarrow \underset{\text{(I)}}{CH_3-\overset{CH_3}{\underset{\bullet}{C}}-CH_3}$$

and $$\underset{\text{(II)}}{CH_3-\overset{CH_3}{CH}-\dot{C}H_2}$$

Radical (I) is more stable because it is 3° and stabilized by nine hyperconjugative structures (as it has 9α-hydrogens).

Radical (II) is less stable because it is 1° and stabilized by only one hyperconjugative structure (as it has only 1α-hydrogen).

13. 

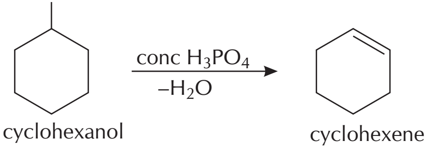
2,4-dimethyl pentane

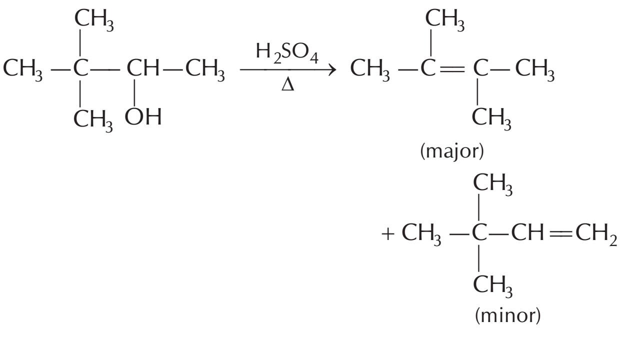
15. All H-atoms in *neo*-pentane are equivalent thus, it will yield monochloro product.

18. The thermal decomposition of alkanes is known as cracking. It leads to the formation of lower alkanes, alkenes and hydrogen.

$$\underset{\text{propane}}{CH_3CH_2CH_3} \xrightarrow{400\text{–}600°C} \underset{\underset{(X)}{\text{ethylene}}}{CH_2=CH_2} + \underset{\underset{(Y)}{\text{methane}}}{CH_4}$$

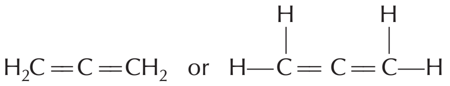
19. The best method to prepare cyclohexene from cyclohexanol is by using conc. H_3PO_4 because among given options dehydrating agent is only conc. H_3PO_4.



20. 

$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{OH}{CH}-CH_3 \xrightarrow[\Delta]{H_2SO_4} \underset{\text{(major)}}{CH_3-\overset{CH_3}{C}=\underset{CH_3}{C}-CH_3}$$

$$+ \underset{\text{(minor)}}{CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH=CH_2}$$



21. $H_2C{=}C{=}CH_2$ or $H{-}\overset{H}{C}{=}C{=}\overset{H}{C}{-}H$

allene (C_3H_4)

It has two double and four single bonds.

22. Conjugate dienes are more stable than the other dienes.

23. Heat of hydrogenation $\propto \dfrac{1}{\text{stability}}$

Among the given buta-1,3-diene is resonance stabilised, *i.e.*, more stable, thus it has the lowest heat of hydrogenation.

24. $Cl_3C{-}CH{=}CH_2 \xrightarrow[\text{anti-Markownikoff's rule}]{HCl} Cl_3C{-}CH_2{-}CH_2Cl$

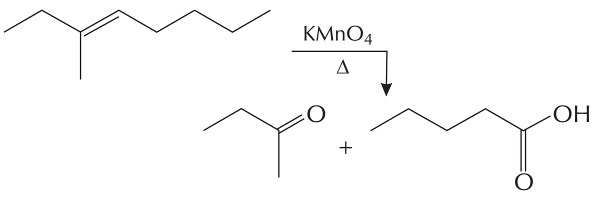
($\because$ CCl_3 is highly electron attracting group.)

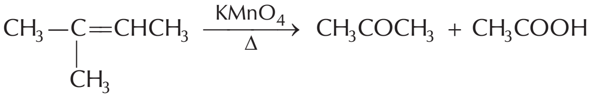
25. Reactivity of halogen acids towards addition reactions increases with increase in the size of halogen atoms as this reaction involves dissociation of H—*X* bond.

26. Addition of HBr to an alkene in the presence of peroxide is the example of free radical addition reaction.

$$R{-}O{-}O{-}R \longrightarrow 2R{-}O^{\bullet}$$
$$R{-}O^{\bullet} + HBr \longrightarrow R{-}OH + Br^{\bullet}$$
$$R{-}CH{=}CH_2 + Br^{\bullet} \longrightarrow R{-}\dot{C}H{-}CH_2Br$$
$$R{-}\dot{C}H{-}CH_2Br \xrightarrow{HBr} RCH_2CH_2Br + Br^{\bullet}$$
$$Br^{\bullet} + Br^{\bullet} \longrightarrow Br_2$$

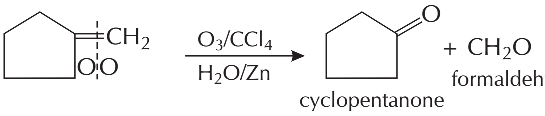
27.



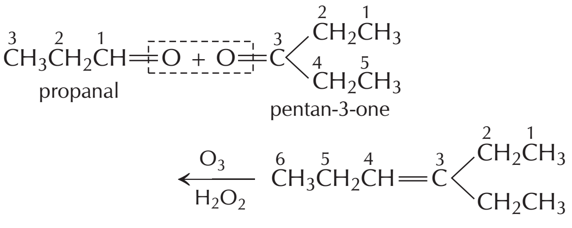


28. $CH_3{-}\underset{CH_3}{\underset{|}{C}}{=}CHCH_3 \xrightarrow[\Delta]{KMnO_4} CH_3COCH_3 + CH_3COOH$

29.



cyclopentanone formaldehyde



30. $\overset{3}{C}H_3\overset{2}{C}H_2\overset{1}{C}H{=}\boxed{O + O}{=}\overset{3}{C}(\overset{2}{C}H_2\overset{1}{C}H_3)(\overset{4}{C}H_2\overset{5}{C}H_3)$

propanal pentan-3-one

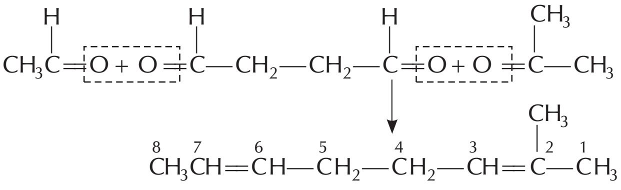
$\xleftarrow[H_2O_2]{O_3}$ $\overset{6}{C}H_3\overset{5}{C}H_2\overset{4}{C}H{=}\overset{3}{C}(\overset{2}{C}H_2\overset{1}{C}H_3)(CH_2CH_3)$

3-ethylhex-3-ene

31. $OHC{-}CH_2{-}CH_2{-}CHO$, CH_3CHO and CH_3COCH_3

(butane-1,4-dial) (ethanal) (propanone)

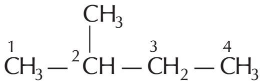
Hence, the structure of compound *A* is



$$CH_3\overset{H}{C}{=}\boxed{O + O}{=}\overset{H}{C}{-}CH_2{-}CH_2{-}\overset{H}{C}{=}\boxed{O + O}{=}\overset{CH_3}{C}{-}CH_3$$
$$\downarrow$$
$$\overset{8}{C}H_3\overset{7}{C}H{=}\overset{6}{C}H{-}\overset{5}{C}H_2{-}\overset{4}{C}H_2{-}\overset{3}{C}H{=}\overset{CH_3}{\overset{2}{C}}{-}\overset{1}{C}H_3$$

(*A*) 2-methylocta-2,6-diene

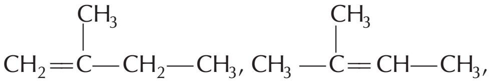
32. Structure of 2-methyl butane is



$$\overset{1}{C}H_3{-}\overset{CH_3}{\overset{2}{C}H}{-}\overset{3}{C}H_2{-}\overset{4}{C}H_3$$

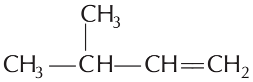
2-methyl butane

The structures of the given alkenes are as



$$CH_2{=}\overset{CH_3}{C}{-}CH_2{-}CH_3,\ CH_3{-}\overset{CH_3}{C}{=}CH{-}CH_3,$$

2-methylbut-1-ene 2-methylbut-2-ene

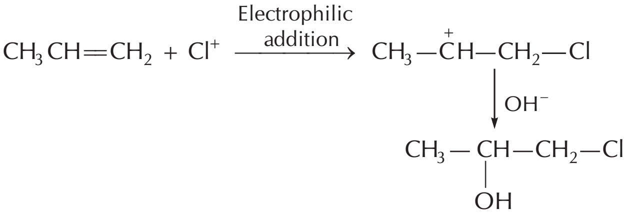


$$CH_3{-}\overset{CH_3}{C}H{-}CH{=}CH_2$$

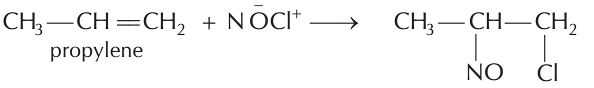
3-methylbut-1-ene

Thus, all give 2-methyl butane on hydrogenation.

33. HOCl has Cl^+ and OH^- ions.



$$CH_3CH{=}CH_2 + Cl^+ \xrightarrow[\text{addition}]{\text{Electrophilic}} CH_3{-}\overset{+}{C}H{-}CH_2{-}Cl$$
$$\downarrow OH^-$$
$$CH_3{-}\underset{OH}{\underset{|}{C}H}{-}CH_2{-}Cl$$



34. $CH_3{-}CH{=}CH_2 + N\overset{-}{O}Cl^+ \longrightarrow CH_3{-}\underset{NO}{\underset{|}{C}H}{-}\underset{Cl}{\underset{|}{C}H_2}$

propylene propylene nitroso chloride

35. $CH_2{=}CH{-}CH{=}CH_2 \xrightarrow[\text{1 mole}]{H_2,\ Ni} CH_3CH{=}CH{-}CH_3$

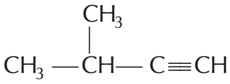
1,3-butadiene (*A*) 1,4-addition product (*B*)

$\xrightarrow[\text{(ii) } H_2O/Zn]{\text{(i) } O_3} CH_3CHO$

36. C_5H_8 has three possible alkynes. These are

$CH_3CH_2CH_2C{\equiv}CH$, $CH_3CH_2C{\equiv}C{-}CH_3$,

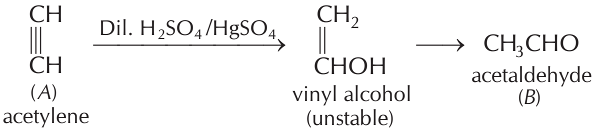
pent-1-yne pent-2-yne



$$CH_3{-}\overset{CH_3}{C}H{-}C{\equiv}CH$$

3-methylbut-1-yne

37. $CaC_2 + 2H_2O \longrightarrow \underset{(A)}{C_2H_2} + Ca(OH)_2$

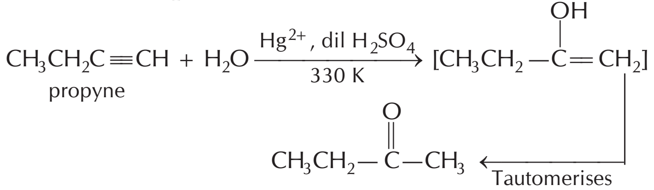


$$\begin{matrix}CH\\ |||\\ CH\end{matrix} \xrightarrow{\text{Dil. } H_2SO_4/HgSO_4} \begin{matrix}CH_2\\ ||\\ CHOH\end{matrix} \longrightarrow CH_3CHO$$

(*A*) acetylene vinyl alcohol (unstable) acetaldehyde (*B*)

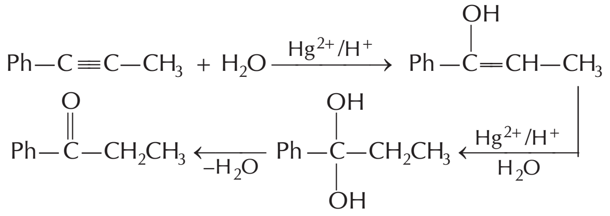
38. Reaction of 4-octyne and H_2 can be arrested at the alkene stage only by using palladium partially inactivated with trace of quinoline. The product is *cis*-alkene.

40. In the presence of dil H_2SO_4 and mercury salts, alkynes add a molecule of H_2O to form aldehydes or ketones.



$$\underset{\text{propyne}}{CH_3CH_2C\equiv CH} + H_2O \xrightarrow[330\text{ K}]{Hg^{2+},\ \text{dil }H_2SO_4} [CH_3CH_2-\overset{OH}{\overset{|}{C}}=CH_2] \xrightarrow{\text{Tautomerises}} CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_3$$

41.

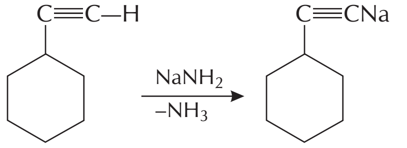


$$Ph-C\equiv C-CH_3 + H_2O \xrightarrow{Hg^{2+}/H^+} Ph-\overset{OH}{\overset{|}{C}}=CH-CH_3 \xrightarrow[H_2O]{Hg^{2+}/H^+} Ph-\underset{OH}{\overset{OH}{C}}-CH_2CH_3 \xrightarrow{-H_2O} Ph-\overset{O}{\overset{\|}{C}}-CH_2CH_3$$

42. $CH\equiv CH \xrightarrow{NaNH_2} \underset{'A'}{CH\equiv C^-Na^+} \xrightarrow[-NaBr]{CH_3Br} \underset{'B'}{CH\equiv C-CH_3}$

43. $\underset{\text{acetylene}}{CH\equiv CH} + 2HCHO \longrightarrow \underset{\text{2-butyne-1, 4-diol}}{OHH_2C-C\equiv C-CH_2OH}$

44. Only terminal alkynes when heated with sodamide ($NaNH_2$ in liq. NH_3), result in the formation of alkynide

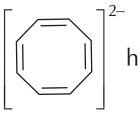


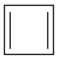
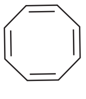
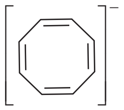
sodium alkynide

45. C_2H_2 and all 1-alkynes give white precipitate with ammoniacal silver nitrate.

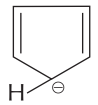
Propyne-1 ($CH_3C\equiv CH$) will give white precipitate with ammoniacal silver nitrate.

$$\underset{\text{propyne-1}}{CH_3C\equiv CH} + NH_4OH + AgNO_3 \longrightarrow \underset{\text{white ppt.}}{CH_3C\equiv CAg} + NH_4NO_3 + H_2O$$

46. Compound  has $8+2=10\pi$-electrons, hence is aromatic.

 has 4 πe^-,  has $8\pi e^-$, while  has $8+1=9\pi e^-$, hence, all these species are not aromatic.

47.



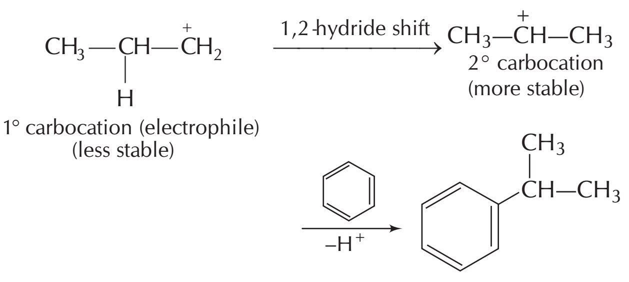
cyclopentadienyl anion

π electrons $= 4+2=6$

As it obeys Huckel rule, it is aromatic.

48. Cyclodecapentene and cyclooctatetraene both are non-aromatic. Cyclobutadiene is anti-aromatic while benzene having 6π-electrons is aromatic.

50. $CH_3-CH_2-CH_2-Cl + AlCl_3 \xrightarrow[-AlCl_4^-]{}$

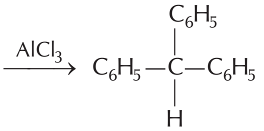


Iso-propyl benzene

51. Benzophenone (diphenyl ketone) can be prepared by the Friedel-Crafts condensation between benzoyl chloride and benzene.

$$C_6H_6 + C_6H_5COCl \xrightarrow{AlCl_3} C_6H_5COC_6H_5 + HCl(80\%)$$

52.

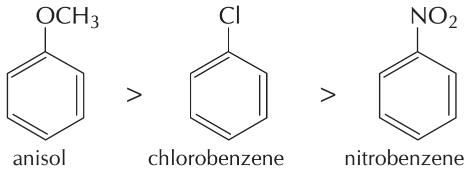


$$C_6H_6 + CHCl_3 \xrightarrow{AlCl_3} C_6H_5-\underset{H}{\overset{C_6H_5}{C}}-C_6H_5$$

53. As the number of $-CH_3$ group increases, boiling point decreases.

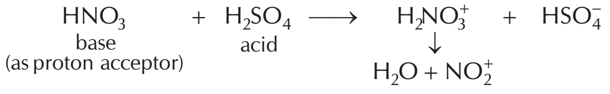
54. $-OCH_3$ (methoxy group) is an electron releasing group. It increases electron density in benzene nucleus due to resonance effect (+ *R* effect). Hence, makes anisole more reactive than benzene towards electrophiles.

In case of aryl halides, halogens are moderately deactivating because of their strong $-I$ effect and $+R$ effect thus, overall electron density on benzene ring decreases. It makes further substitution difficult. $-NO_2$ group is electron withdrawing group. It decreases the electron density in benzene nucleus due to strong $-I$ effect. Hence, makes nitrobenzene less reactive. Therefore, overall reactivity of these three compounds towards electrophiles decreases in the following order



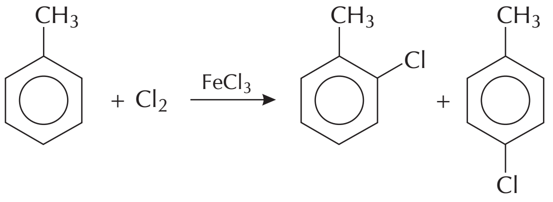
56. Reactivity towards electrophilic substitution increases as the electron density in the benzene ring increases. Since CH_3 is a strong electron donating group thus toluene ($C_6H_5CH_3$) can be most readily sulphonated.

59. In the laboratory, nitrobenzene is prepared by nitration of benzene with the mixture of nitric acid and sulphuric acid at temperature below 60°C. In which HNO_3 acts as a base.

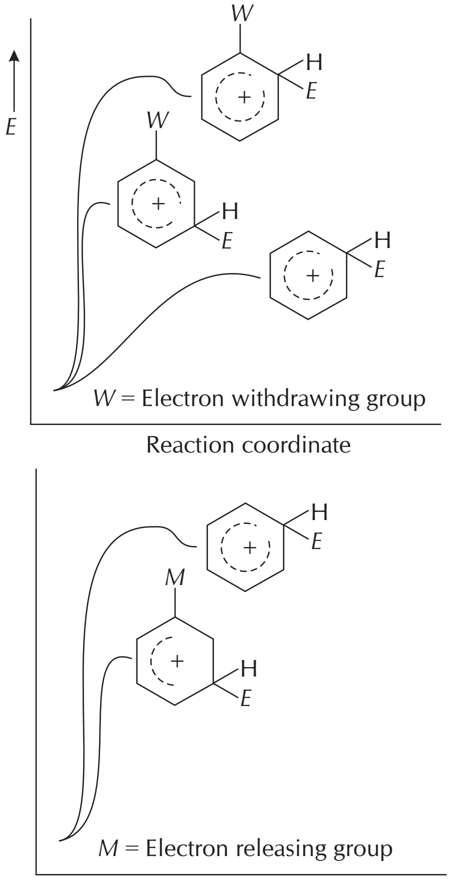


$$\underset{\substack{\text{base}\\\text{(as proton acceptor)}}}{HNO_3} + \underset{\text{acid}}{H_2SO_4} \longrightarrow \underset{\substack{\downarrow\\ H_2O + NO_2^+}}{H_2NO_3^+} + HSO_4^-$$

60.



62.



Electron withdrawing group destabilises the arenium ion σ-complex.

64. Presence of electron releasing group (or activating group) increases the electron density in benzene nucleus. Therefore, electrophile will attack benzene nucleus easily. But the presence of electron withdrawing group like $-NO_2$ decreases the electron density in benzene ring. Therefore, electrophile will attack benzene nucleus with difficulty.

The order of reactivity towards electrophile, E^+ in the order of their decreasing relative reactivity is

Toluene > $p\text{-}CH_3-C_6H_4-NO_2$

Chlorobenzene > *p*-nitrochlorobenzene
> 2,4-dinitrochlorobenzene

65. $$\underset{\substack{\text{propyne}\\ \text{(terminal alkyne)}}}{CH_3-C\equiv C-H} + Na \xrightarrow{\text{Liq. }NH_3} CH_3-C\equiv C-Na$$

$$CH_3-C\equiv C-Na + BrCH_3 \longrightarrow \underset{\text{but-2-yne}}{CH_3-C\equiv C-CH_3} + NaBr$$

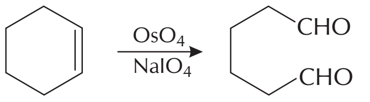
This reaction is utilised for the preparation of higher alkynes.

68. C_4H_6 may contains either two double bond or a triple bond.

$$CH_2=CH-CH=CH_2$$

or $$CH_3-CH_2-C\equiv CH$$

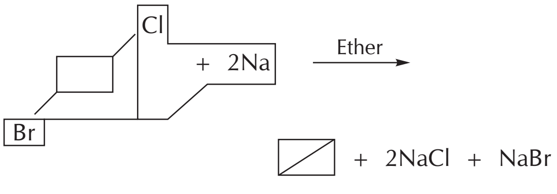
69.



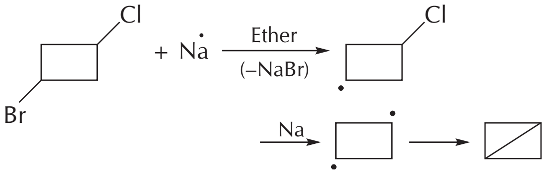
hexane-1,6-dial

Round II

1. This reaction is of Wurtz's type reaction.

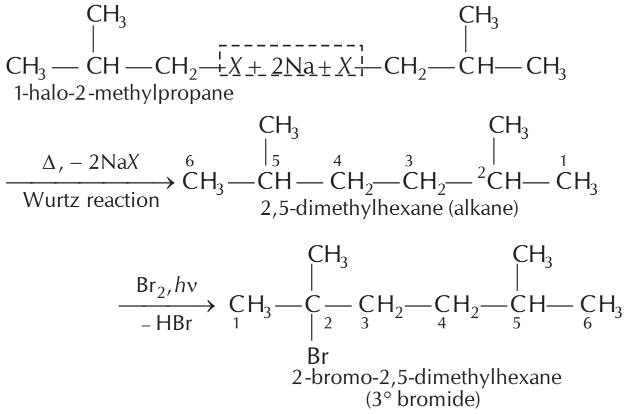


In this reaction, following mechanism is possible.



(Order of removal of halogen I > Br > Cl).

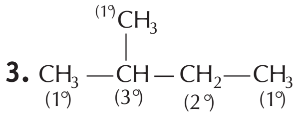
2. Since, alkane C_8H_{18} on monobromination yields a single isomer of a tertiary bromide, therefore alkane must contain tertiary hydrogen. This is possible if primary alkyl halide (which undergoes Wurtz reaction) has a tertiary hydrogen.



$$\underset{\text{1-halo-2-methylpropane}}{CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-}\boxed{X+2Na+X}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_3$$

$$\xrightarrow[\text{Wurtz reaction}]{\Delta,\,-2NaX} \underset{\text{2,5-dimethylhexane (alkane)}}{\overset{6}{CH_3}-\overset{CH_3}{\overset{|}{\overset{5}{CH}}}-\overset{4}{CH_2}-\overset{3}{CH_2}-\overset{CH_3}{\overset{|}{{}^2CH}}-\overset{1}{CH_3}}$$

$$\xrightarrow[-HBr]{Br_2,h\nu} \underset{\substack{\text{2-bromo-2,5-dimethylhexane}\\ (3^\circ\text{ bromide})}}{\underset{1}{CH_3}-\underset{\underset{Br}{|}}{\overset{CH_3}{\overset{|}{\underset{2}{C}}}}-\underset{3}{CH_2}-\underset{4}{CH_2}-\overset{CH_3}{\overset{|}{\underset{5}{CH}}}-\underset{6}{CH_3}}$$

3. 

$\overset{(1°)\,CH_3}{\underset{(1°)}{CH_3}—\underset{(3°)}{CH}—\underset{(2°)}{CH_2}—\underset{(1°)}{CH_3}}$

Relative amount of monochlorinated product

= Number of hydrogen × relative reactivity

For (1°) monochlorinated product $= 9 \times 1 = 9$

(2°) monochlorinated product $= 2 \times 3.8 = 7.6$

(3°) monochlorinated product $= 1 \times 5 = 5$

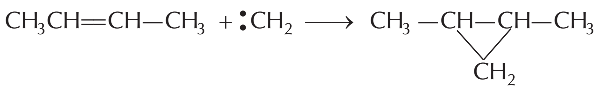
Total amount of monochlorinated compounds

$= 9 + 7.6 + 5 = 21.6$

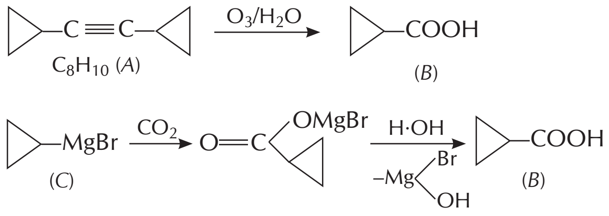
% of 1° monochlorinated product $= \frac{9 \times 100}{21.6} = 41.67$

% of 2° monochlorinated product $= \frac{7.6 \times 100}{21.6} = 35.18$

% of 3° monochlorinated product $= \frac{5 \times 100}{21.6} = 23.15$



$CH_3CH{=}CH—CH_3 + {:}CH_2 \longrightarrow CH_3—\underset{\diagdown\ CH_2\ \diagup}{CH—CH}—CH_3$

4. 

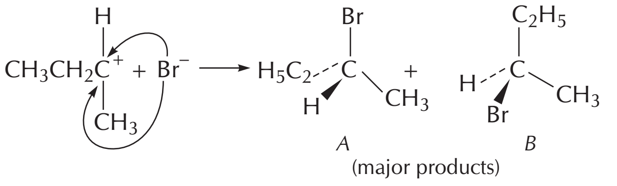
5. $CH_3CH_2CH{=}CH_2 + H^+ \longrightarrow CH_3CH_2\overset{+}{C}H—CH_3$

2° (planar)
(more stable major)

$+ CH_3CH_2CH_2—\overset{+}{C}H_2$

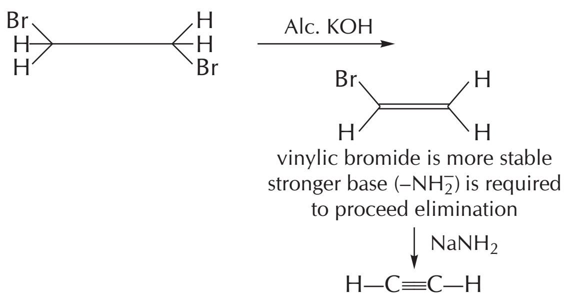
1°
(less stable)

$CH_3CH_2CH_2\overset{+}{C}H_2 + Br^- \longrightarrow \underset{(C)}{CH_3CH_2CH_2CH_2Br}$

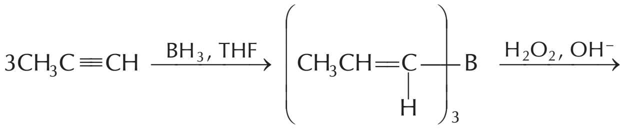


(major products)

6. $\underset{\text{2-methyl-3-hexyne}}{(CH_3)_2CH—C{\equiv}C—CH_2CH_3} \xrightarrow{[O]} (CH_3)_2CHCOOH + CH_3CH_2COOH$

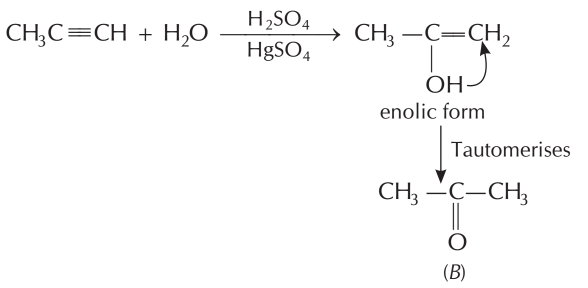
7. 

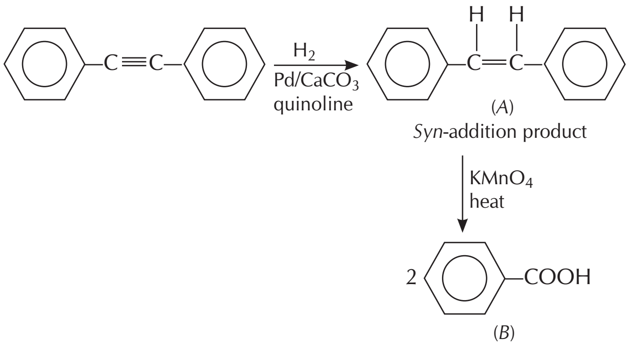
vinylic bromide is more stable stronger base ($–NH_2^-$) is required to proceed elimination

8. 

$3CH_3C{\equiv}CH \xrightarrow{BH_3,\ THF} \left(CH_3CH{=}\underset{H}{C}—B\right)_3 \xrightarrow{H_2O_2,\ OH^-}$

$CH_3CH{=}CHOH \xrightarrow{\text{Tautomerises}} \underset{(A)}{CH_3CH_2CHO}$



9. 

10. The two compounds should react differently with the reagent used to distinguish them.

∵ Propyne ($CH_3—C{\equiv}CH$) and propene ($CH_3CH{=}CH_2$) both are unsaturated compounds.

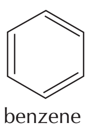
∴ Both of them decolourise alk. $KMnO_4$ and Br_2 in CCl_4 and both of them give addition reaction with conc. H_2SO_4.

∵ Propyne reacts with $AgNO_3$ in NH_3 to give white ppt. of silver acetylide and propene does not react with it. (only terminal alkynes react with $AgNO_3$ in NH_3.

$\underset{\text{(propyne)}}{CH_3—C{\equiv}CH} + AgNO_3 + NH_3 \longrightarrow \underset{\substack{\text{silver acetylide}\\ \text{(white ppt.)}}}{CH_3—C{\equiv}CAg}$

$CH_3—CH{=}CH_2 + AgNO_3 + NH_3 \longrightarrow$ No reaction

11. The hybridisation state of carbon in the given compounds is



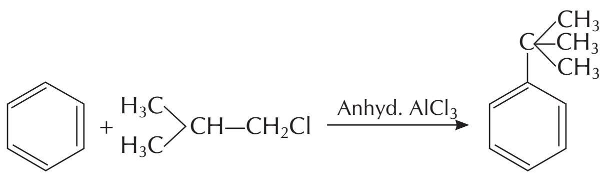
; $CH_3—(CH_2)_4—CH_3$; $HC{\equiv}CH$

	benzene	hexane	ethyne
Type of hybridisation	sp^2	sp^3	sp
s-character	33.33%	25%	50%

Acidic character increases with increase in *s*-character of the orbital. Hence, decreasing order of acidic behaviour of benzene, *n*-hexane and ethyne is as follows

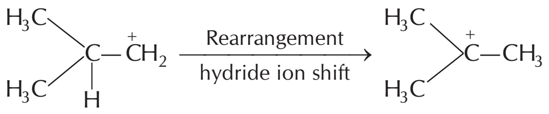
Ethyne > Benzene > Hexane

12.

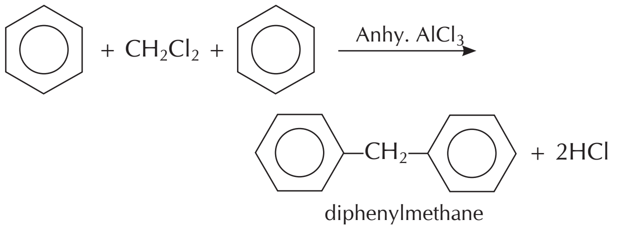


This reaction is an example of Friedel-Crafts reaction.

Mechanism



13. When excess of benzene reacts with CH_2Cl_2 in the presence of anhy. $AlCl_3$, diphenylmethane is obtained.



This reaction is an example of Friedel-Crafts reaction.

14. I. has 8π electrons, does not follow Huckel rule. Orbitals of one carbon atom are not in conjugation. It is not aromatic.

II. has 6π delocalised electrons. Hence, is aromatic.

III. has 6π electrons in conjugation but not in the ring. Non aromatic.

IV. 10π electrons in planar rings, aromatic.

V. Out of 8π electrons it has delocalised 6π electrons in one six membered planar ring, which follows Huckel's rule due to which it will be aromatic.

VI. 14π electrons are in conjugation and are present in a ring. Huckel's rule is being followed. Compound will be aromatic if ring is planar.

15. (i) Determination of empirical formula of hydrocarbon *A*

Element	Percentage	Atomic mass	Relative ratio	Relative number of atoms	Simplest ratio
C	87.8	12	$\frac{87.8}{12} = 7.31$	$\frac{7.31}{7.31} = 1$	$1 \times 3 = 3$
H	12.19	1	$\frac{12.19}{1} = 12.19$	$\frac{12.19}{7.31} = 1.66$	$1.66 \times 3 = 5$

∴ Empirical formula of hydrocarbon (*A*) = C_3H_5

Empirical formula mass $= 12 \times 3 + 5 \times 1 = 41$ u

(ii) Determination of molecular mass of hydrocarbon (*A*)

896 mL vapours of hydrocarbon (*A*) weigh at STP = 3.28 g

∴ 22400 mL vapours of *A* will weigh at STP

$$= \frac{3.28 \times 22400}{896} \text{ g mol}^{-1} = 82 \text{ g}$$

∴ Molecular mass of hydrocarbon (*A*) = 82 g mol^{-1}

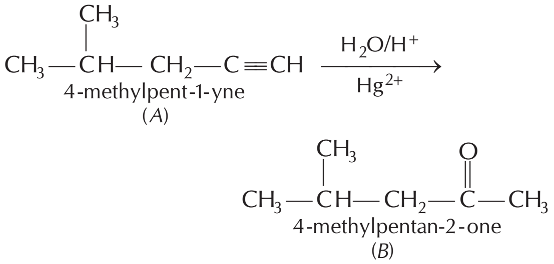
(iii) Determination of molecular formula of hydrocarbon *A*.

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{82}{41} = 2$$

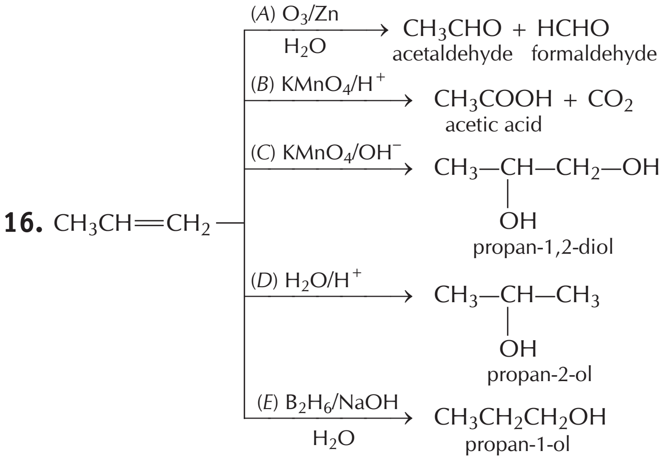
Therefore, molecular formula of hydrocarbon

$$(A) = n \times \text{Empirical formula} = 2 \times C_3H_5 = C_6H_{10}$$

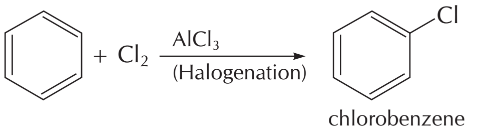
Since, hydrogenation of *A* gives 2-methyl pentane therefore compound '*A*' have 5 carbon atoms in straight chain. It should be an alkyne because compound '*A*' adds a molecule of H_2O in the presence of Hg^{2+} and H^+ to give a ketone '*B*'. Ketone '*B*' gives iodoform test so it should be a methyl ketone. Therefore, the structures of compound *A* and compound *B* are as follows



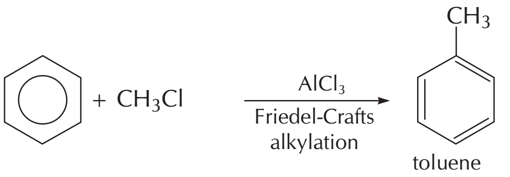
16.

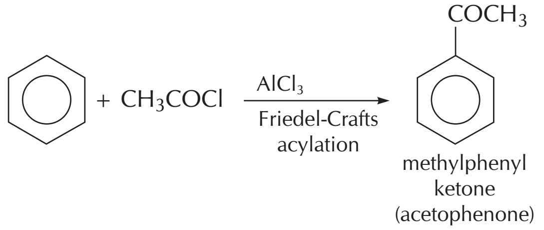


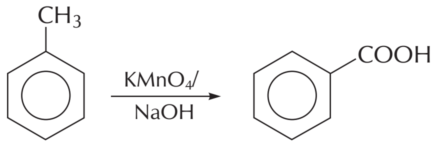
17. (A)



(B)

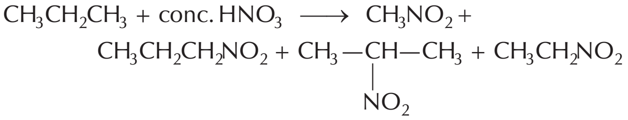


(C) 

(D) 

18. The controlled oxidation of methane results in the formation of aldehyde or alcohol.

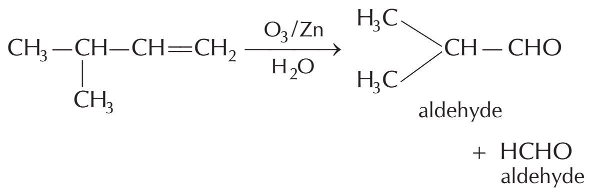
19. The reaction occurs by a free radical mechanism and so a mixture of products is obtained.

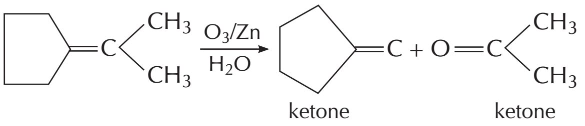


$$CH_3CH_2CH_3 + \text{conc. } HNO_3 \longrightarrow CH_3NO_2 + CH_3CH_2CH_2NO_2 + CH_3{-}\underset{NO_2}{\underset{|}{CH}}{-}CH_3 + CH_3CH_2NO_2$$

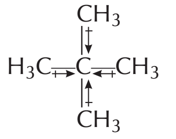
20. (a) $CH_3CH{=}CH{-}CH_3 \xrightarrow[H_2O]{O_3/Zn} 2CH_3CHO$

two moles of aldehyde

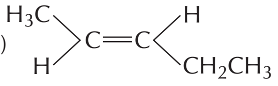
(b) 

(c) 

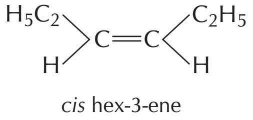
(d) $(CH_3)_2C{=}C(CH_3)_2 \xrightarrow[H_2O]{O_3/Zn} 2(CH_3)_2C{=}O$

21. (a) 

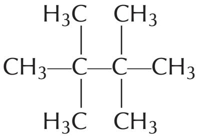
symmetrical molecule
(μ = 0)

(b) 

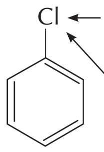
trans-pent-2-ene
(μ ≠ 0)
(as it is unsymmetrical)

(c) 

cis hex-3-ene
(unsymmetrical μ ≠ 0)

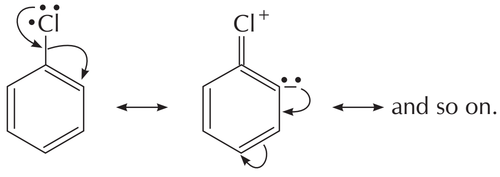
(d) 

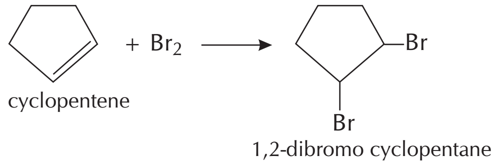
(symmetrical so μ = 0)

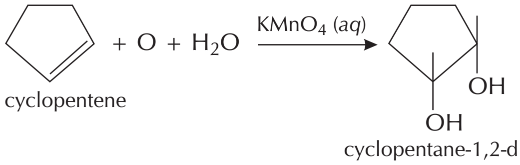
22. 

Cl ← due to –*I* effect deactivate the ring towards $E^{\oplus}$.

due to electron donating resonance effect increase charge density at *o*/*p* position.

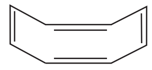


23. 



24. With branching boiling point decreases, due to decrease in van der Waals' forces.

25. When carbon atoms are linked by triple bond, the valency bonds undergo bending and are distorted from their normal directions. This bending produces strain in the molecule with the result that it becomes unstable and hence, more reactive.

26. 

8πe⁻ and non-planar
so non-aromatic

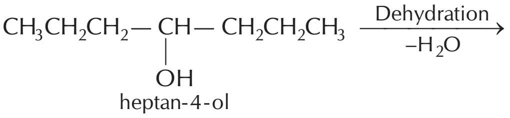
27. Lower alkanes do not undergo sulphonation but higher members are sulphonated slowly when treated with fuming sulphuric acid at about 400°C.

$$R{-}H + HOSO_3H \xrightarrow[\text{Prolonged heating}]{SO_3} R{-}SO_3H + H_2O$$

This reaction occur by free radical mechanism.

28. Dehydration of alcohols to alkene is carried out through carbocation formation.

29. Intramolecular dehydration since H_2O is lost from one molecule of ethyl alcohol.

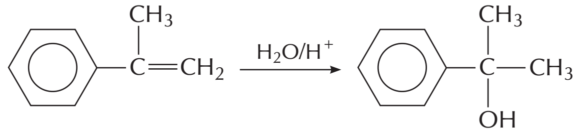
30. 

$$CH_3CH_2CH_2{-}\underset{OH}{\underset{|}{CH}}{-}CH_2CH_2CH_3 \xrightarrow[-H_2O]{\text{Dehydration}}$$

heptan-4-ol

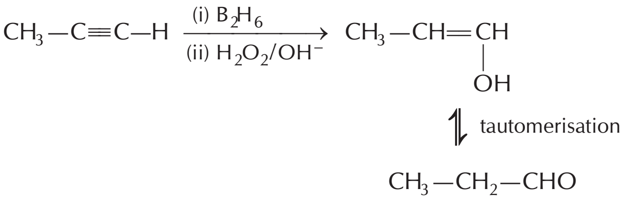
$CH_3CH_2CH{=}CHCH_2CH_2CH_3$
hept-3-ene

31.



32. Hydroboration oxidation, anti-Markownikoff's addition of water gives product.

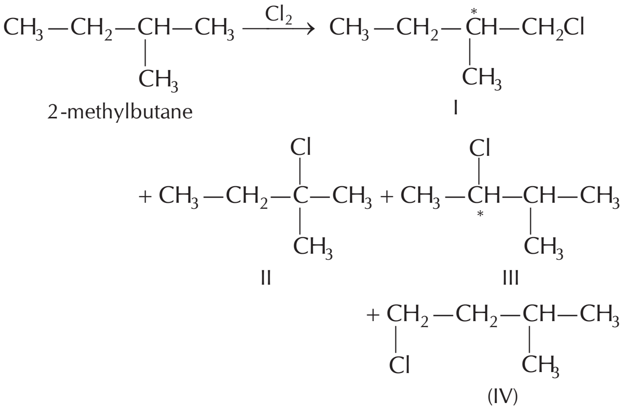
33.



$$CH_3-C\equiv C-H \xrightarrow[\text{(ii) } H_2O_2/OH^-]{\text{(i) } B_2H_6} CH_3-CH=CH(OH) \rightleftharpoons CH_3-CH_2-CHO$$

tautomerisation

34.



$$CH_3-CH_2-CH(CH_3)-CH_3 \xrightarrow{Cl_2} \underset{\text{I}}{CH_3-CH_2-\overset{*}{C}H(CH_3)-CH_2Cl} + \underset{\text{II}}{CH_3-CH_2-CCl(CH_3)-CH_3} + \underset{\text{III}}{CH_3-\overset{*}{C}HCl-CH(CH_3)-CH_3} + \underset{\text{(IV)}}{CH_2Cl-CH_2-CH(CH_3)-CH_3}$$

2-methylbutane

I and III have chirality (*). Thus, in all four (including enantiomers) optical isomers are obtained.

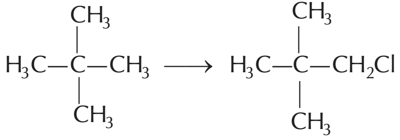
35. Molar mass = 72 = $C_nH_{2n+2} = 12n + (2n+2)$

$$n = 5$$

Thus, hydrocarbon is C_5H_{12}.

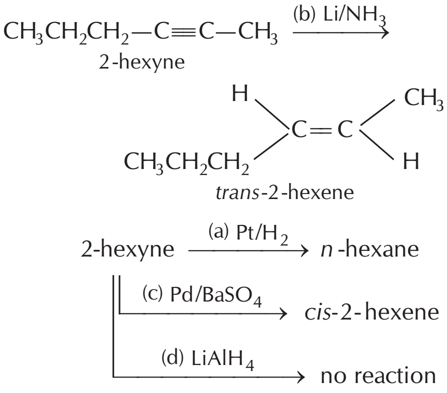
Since, it gives only single $C_5H_{11}Cl$, thus C_5H_{12} is symmetrical.

It is ***neo*-pentane**



$$H_3C-C(CH_3)_2-CH_3 \longrightarrow H_3C-C(CH_3)_2-CH_2Cl$$

36.



$CH_3CH_2CH_2-C\equiv C-CH_3 \xrightarrow{\text{(b) Li/NH}_3}$

2-hexyne

trans-2-hexene

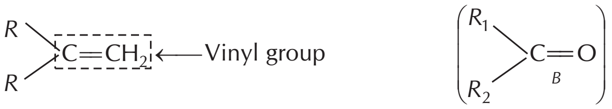
2-hexyne $\xrightarrow{\text{(a) Pt/H}_2}$ *n*-hexane

$\xrightarrow{\text{(c) Pd/BaSO}_4}$ *cis*-2-hexene

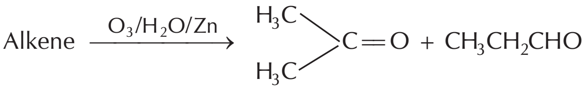
$\xrightarrow{\text{(d) LiAlH}_4}$ no reaction

37. Alkenes give carbonyl compounds on ozonolysis

$$\text{Alkene} \xrightarrow{O_3/Zn/H_2O} \underset{(A)}{HCHO} + \text{other carbonyl compound}$$

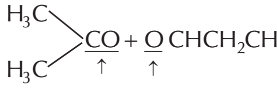


38.



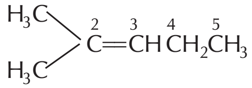
$$\text{Alkene} \xrightarrow{O_3/H_2O/Zn} (H_3C)_2C=O + CH_3CH_2CHO$$

To identify alkene (from ozonolysis products) place these products with O-atoms face to face. Replace O-atoms by = (double) bond.



$$(H_3C)_2\underline{CO} + \underline{O}\,CHCH_2CH_3$$

O-atom face to face



$$(H_3C)_2\overset{2}{C}=\overset{3}{C}H\overset{4}{C}H_2\overset{5}{C}H_3$$

2-methyl-2-pentene

39. $C_nH_{2n}O = 44$

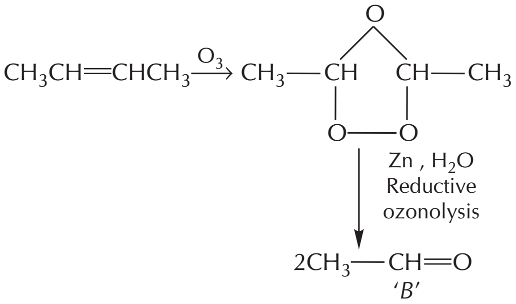
$$C_nH_{2n} = 44 - 16 = 28$$

$\therefore$ $n = 2$

So, $CH_3-CH=CH-CH_3$ is the symmetrical alkene.

Thus, $\underset{\text{2-butene}}{CH_3-CH=CH-CH_3} \xrightarrow[\text{(ii) Zn/H}_2O]{\text{(i) } O_3} \underset{\text{acetaldehyde}}{2CH_3-CH=O}$

40.



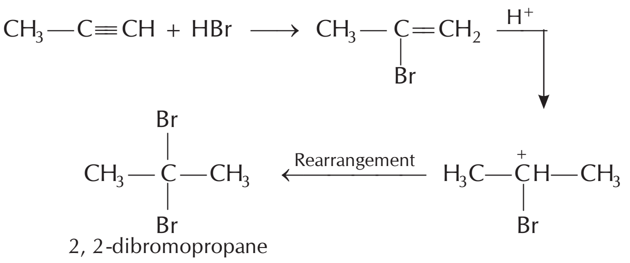
$$CH_3CH=CHCH_3 \xrightarrow{O_3} CH_3-CH(-O-O-)(-O-)CH-CH_3 \xrightarrow[\text{Reductive ozonolysis}]{Zn,\ H_2O} \underset{'B'}{2CH_3-CH=O}$$

41. $CH_3CH_2C\equiv CH \xrightarrow[\Delta]{\text{Na/Liq. NH}_3} CH_3CH_2C\equiv CNa^+$

Considering the options given it appears correct. Na/liq NH_3 is known for metal dissolved reduction. Actually it is truth that Na/liq NH_3 reduces internal triple bond and terminal double bond and do not reduce the terminal alkyne due to such alkylide formation.

42. Terminal alkyne has acidic hydrogen which is enough to protonate the Grignard reagent.

$$CH_3MgX + CH_3C\equiv CH \longrightarrow CH_4 + CH_3C\equiv CMgX$$

43. 

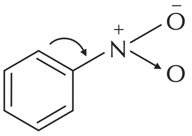
$$CH_3-C\equiv CH + HBr \longrightarrow CH_3-\underset{\underset{Br}{|}}{C}=CH_2 \xrightarrow{H^+} H_3C-\overset{+}{\underset{\underset{Br}{|}}{C}H}-CH_3 \xrightarrow{\text{Rearrangement}} CH_3-\overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{C}}-CH_3$$

2, 2-dibromopropane

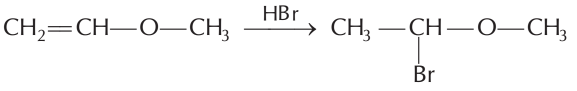
$$CH_3-CH=CHBr \xrightarrow{HBr} CH_3-CH_2-CHBr_2$$

$$CH\equiv CH \xrightarrow{2HBr} CH_3CHBr_2$$

$$CH_3-CH=CH_2 \xrightarrow{HBr} CH_3-CHBr-CH_3$$

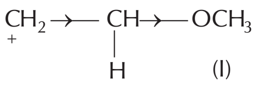
44. 

—NO_2 group withdraw electron from the ring, shows –*M* effect makes ring electron deficient, thus deactivates the ring for electrophilic substitution.

45. 

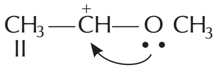
$$CH_2=CH-O-CH_3 \xrightarrow{HBr} CH_3-\underset{\underset{Br}{|}}{C}H-O-CH_3$$

First protonation occurs, two possible intermediates are



$$\overset{+}{C}H_2 \leftarrow \underset{\underset{H}{|}}{CH} \leftarrow OCH_3 \quad (I)$$

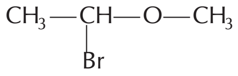
(–*I* effect destabilises carbocation)

and 

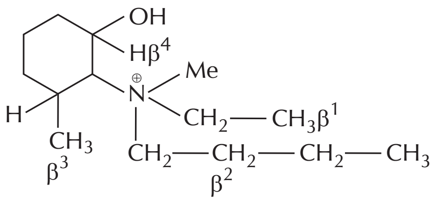
$$CH_3-\overset{+}{C}H-\ddot{O}\ CH_3 \quad II$$

(+ *M* effect stabilises carbocation)

II, is more favourable. Hence, $Br^{\ominus}$ attacks and product is



$$CH_3-\underset{\underset{Br}{|}}{C}H-O-CH_3$$

46. 

There are four β-hydrogens, in this quarternary ammonium salt.

On heating, quarternary ammonium salt gives Hofmann elimination (abstraction of most acidic hydrogen which is β^1).

Hence, major product is $CH_2=CH_2$ (least substituted alkene).

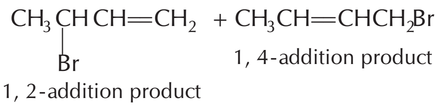
47. (A) 2-methyl pentane $\xrightarrow{Cl_2}$ five types of monochlorinated compounds

(B) 2, 2-dimethylbutane $\xrightarrow{Cl_2}$ three types...

(C) 2, 3-dimethylbutane $\xrightarrow{Cl_2}$ two types...

(D) *n*-hexane $\xrightarrow{Cl_2}$ three types ....

48. $CH_2=CHCH=CH_2 + HBr \longrightarrow$

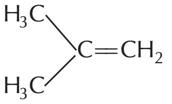


$$\underset{\text{1, 2-addition product}}{CH_3\underset{\underset{Br}{|}}{C}H\,CH=CH_2} + \underset{\text{1, 4-addition product}}{CH_3CH=CHCH_2Br}$$

Addition is through the formation of allylic carbocation.

$$\underset{\substack{(2°\text{ allylic})\\(\text{more stable})}}{CH_2=CH\overset{\oplus}{C}HCH_3} \longleftrightarrow \underset{\substack{(1°\text{ allylic})\\(\text{less stable})}}{CH_3CH=CH\,\overset{\oplus}{C}H_2}$$

Under mild conditions (temperature ≈ – 80° C) **kinetic product** is the **1, 2-addition product** and under vigorous conditions
(temp. ≈ 40° C) **thermodynamic product** is the **1, 4-addition product.**
Thus, 1-bromo-2-butene is the major product under given condition.

49. *iso*-butene  has minimum force of attraction (due to steric hindrance). Thus, minimum boiling point.

50. $$\underset{\text{butene-1}}{CH_2=CH-CH_2CH_3} \xrightarrow[\Delta,\text{ pressure}]{Pd/H_2} \underset{\text{butane}}{CH_3-CH_2-CH_2-CH_3}$$

Other reagents are successful with polar double bonds.

51. $$CH\equiv CH + Na \longrightarrow CH\equiv C^{-}Na^{+} + \frac{1}{2}H_2$$

$$CH\equiv CH + \underset{(\text{ammoniacal})}{AgNO_3} \longrightarrow \underset{\text{white ppt.}}{CH\equiv C^{-}Ag^{+}}$$

$$CH\equiv CH + HCl \longrightarrow CH_2=CH-Cl$$

Usually occurs in the presence of Hg^{2+}

$$CH=CH + NaOH \longrightarrow \text{no reaction}$$

Because of hard acid hard base soft acid soft base (HASB) theory.

$$CH\equiv CH + NaNH_2 \longrightarrow CH\equiv C^{-}Na^{+} \text{ feasible.}$$

16 Environmental Chemistry

JEE Main MILESTONE

- Components of Environment
- Environmental Pollution
- Pollutants
- Atmospheric Pollution
- Tropospheric Pollution
- Water Pollution
- Soil Pollution
- Strategies to Control Environmental Pollution

16.1 Components of Environment

Environment includes three main components, viz.

1. Abiotic or non-living components include atmosphere, hydrosphere and lithosphere.
2. Biotic or living components include plants and animals (including human beings).
3. Energy components include various kinds of energy such as solar energy, thermal energy and nuclear energy.

Anything that environs us such as air, water, soil, sunlight etc., constitutes our environment and the branch of chemistry, which deals with the chemical phenomena happening in the environment is termed as **environmental chemistry.** *This term has come to be regarded as synonymous with environmental pollution by some scientists. However, it must be emphasised that environmental chemistry deals with a wider aspect of knowledge. The problem of pollution is just a small segment of it.*

Atmosphere

Earth is surrounded by a covering of various gases (air), called atmosphere, which extends to a height of about 1600 km above the earth surface. Dry air contains roughly (by volume) nitrogen (78.08%), oxygen (20.95)%, argon (0.93%), carbon dioxide (0.033%) and trace amount of other gases such as Ne (18 ppm), He (5.2 ppm), methane (1.3 ppm), Kr (1 ppm), H_2 (0.5 ppm), CO (0.10 ppm), O_3 (0.02 ppm), SO_2 (0.001 ppm) etc. Thus, **atmosphere is the gaseous component of the earth.** The gaseous covering (or the atmosphere) prevents the harmful radiations, coming from the sun or outer space, to reach on the earth and protects the life on earth.

The thickness of atmosphere is not same at all heights because of the presence of concentric layers of air or regions of different density. *Thus, atmosphere, can further be divided into the following regions*

(a) Troposphere

It is the lower layer of atmosphere which extends up to the height of ~ 10 to ~ 18 km from the sea level. It is a turbulent and dusty zone which contains air (N_2, O_2, CO_2, etc.), much water vapours and clouds. Therefore, this is the region that supports life. This region constitutes about 80% of the total mass of the atmosphere. Temperature of this region decreases with altitude due to decrease in pressure and density of air and it is minimum at about 11 km. This point is called **tropopause** and acts as boundary between the troposphere and the next layer, *i.e.,* stratosphere.

(b) Stratosphere

Above the troposphere is the stratosphere which lies between 18-50 km above sea level. In this region, temperature starts to rise, therefore, tropopause is the point at which temperature inversion occurs. In stratosphere, at about 20 to 40 km, there is a part of relatively high ozone concentration, called the **ozone layer.** Due to such a high concentration of ozone, this region is also known as **ozonosphere.**

Ozone is formed when UV light strikes oxygen molecule and splits it into individual oxygen atoms (O) which combine with undissociated oxygen. Since O_3 is unstable and again splits into O_2 and O, a dynamic equilibrium exists between production and dissociation of ozone molecule.

$$O_2(g) \xrightarrow{\text{UV light}} 2O(g)$$

$$O\,(g) + O_2(g) \underset{}{\overset{\text{UV light}}{\rightleftharpoons}} O_3(g)$$

Thus, this region contains dinitrogen, oxygen, ozone, and little water vapours. Ozone layer absorbs about 99.5% of harmful UV radiations coming from the sun and thus, protects human and other living things from it. The boundary between the mesosphere and stratosphere is called **stratopause.**

(c) Mesosphere

It is the region above stratosphere and extends from 50-85 km. In this region again temperature decreases with height and reaches to −100°C. That's why when any meteors enter in mesosphere, it burns up.

(d) Thermosphere

Above the mesosphere is thermosphere which extends up to 640 km. In this region, although, the temperature can rise to 1500°C, a person would not feel warm because of the extreme low pressure. The international space station orbit is also in this layer.

Caution Point *Mesosphere and thermosphere are collectively called ionosphere as in these, gases are present in their ionised form.*

(e) Exosphere

Above thermosphere, the highest region of atmosphere, known as exosphere (500-1600 km), is present which also contains ionised gases.

Beyond this region, an unbounded area, called **interstellar space** is present.

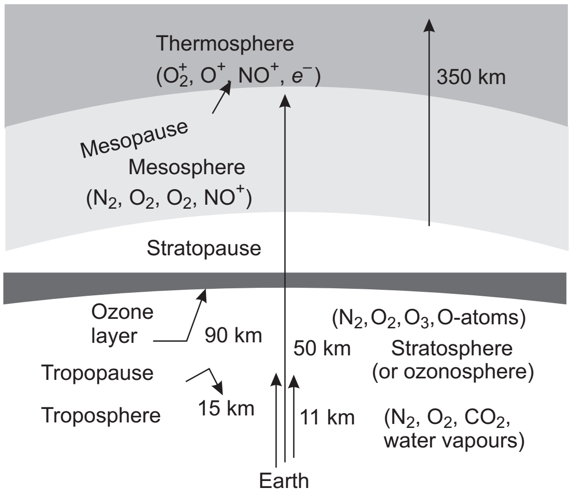


Fig. 16.1 Various regions of the Earth's atmosphere

Hydrosphere and Lithosphere

The liquid parts (the parts that contain water) of environment such as sea, oceans, rivers, lakes etc., constitute **hydrosphere** whereas the solid components of earth such as soil, rocks, mountains etc., constitute **lithosphere.**

Biosphere

It is that part of abiotic components (lithosphere, hydrosphere and atmosphere) where living organisms live and interact with these components.

Check Point 1

1. When any meteors enters in the mesosphere, it burns up. Explain, why?
2. Explain why does the temperature in troposphere decrease with altitude?
3. The composition of atmosphere is different at different heights. Explain.

16.2 Environmental Pollution

The contamination of environment (*i.e.,* air, water and soil) with any undesirable substance, obtained from either a natural source or human activity, which has adverse effect on plants, animals and human beings, is called **environmental pollution.** The biotic and abiotic components that are affected adversely, are known as **receptors or targets.** On the basis of the part of environment (*i.e.,* air, water, soil) affected, pollution may be of the following three types :

(i) Atmospheric pollution (when air gets polluted),
(ii) Water pollution,
(iii) Soil pollution

However, on the basis of nature of pollutants, pollution can be classified into following categories : Thermal pollution, noise pollution, radioactive pollution, smog pollution, plastic pollution, industrial pollution, metal toxicity pollution, acid rain pollution, oil pollution etc.

16.3 Pollutants

The substance that contaminate the environment are referred to as **pollutants.** There are several substances which in normal conditions are not pollutants but when present in excess or at a wrong place, act as pollutants and have harmful effect, *e.g.,* fertilisers act as pollutant for water. Remember that the pollutants that do not occur in nature and are introduced into the environment by human activity are called **contaminants.**

Classification of Pollutants Depending upon their State

On this basis pollutants are classified into following categories

(a) Solid Pollutants

These exist in solid state, *e.g.,* rubbish, ashes, wastes sludges, pesticides, insecticides, chemicals etc. Solid pollutants may be degradable or non-degradable. **Degradable solid pollutants** are those, which are easily decomposed either by microorganisms (biodegradable), *e.g.,* wastes sludges or by any other treatment such as chemical treatment (non-biodegradable), *e.g.,* heat while **non-degradable solid pollutants** are those which do not degrade, *e.g.,* DDT, plastics etc. Soil pollution is mainly caused by solid pollutants.

(b) Liquid Pollutants

These exist in liquid state, *e.g.,* sewage, wastes which contain faecal matter, urine and some bacteria and industrial wastes. These are the main source of water pollution. However, these also cause soil pollution.

(c) Gaseous Pollutants

These exist in gaseous form. Examples of such pollutants are CO, NO, CO_2, SO_3, O_3, NO_2 etc. These are the main source of atmospheric pollution. However, these also cause soil and water pollution.

(d) Invisible Pollutants

Heat, noise and radiations are the examples of such pollutants. These are the main source of thermal, noise and radioactive pollutions.

Classification of Pollutants on the Basis of their Formation

On this basis pollutants are of following two types

(a) Primary Pollutants

These are simple molecules that persist in the environment in the form, they are formed. *e.g.,* oxides of carbon, nitrogen, sulphur such as SO_2, NO_2, CO, hydrocarbons etc.

(b) Secondary Pollutants

These are the products of reactions of primary pollutants. These are more harmful than primary pollutants, *e.g.,* PAN (peroxyacetyl nitrate) which is formed when hydrocarbons react photochemically with oxides of nitrogen, ozone, aldehydes, phenols etc.

16.4 Atmospheric Pollution

Atmospheric pollution is defined as *the presence or addition of some undesirable substances, which have adverse effect on plants and animals including human being, into the atmosphere either due to some natural phenomenon or due to human activity.* Although atmosphere comprises several regions, atmospheric pollution is related to only tropospheric pollution (pollution of air) and stratospheric pollution (pollution of stratosphere, *i.e.,* depletion of ozone layer).

16.5 Tropospheric Pollution

Tropospheric pollution is defined as **the contamination of air by undesirable solid or gaseous particles.** The major sources of tropospheric pollution are of two types

(a) Gaseous air pollutants such as oxides of nitrogen, sulphur, carbon, hydrocarbons, ozone and other oxidants.
(b) Particulate air pollutants such as dust, mist, fumes, smoke.

Major Gaseous Air Pollutants

Major gaseous pollutants along with their sources and harmful effects are as follows

(a) Oxides of Carbon

Carbon forms two oxides, *viz*, carbon monoxide (CO) and carbon dioxide (CO_2). Out of these two oxides, carbon monoxide is most harmful. Under normal conditions, carbon dioxide does not act as air pollutant but when present in large excess, has an adverse effect on our climate.Carbon monoxide is obtained by incomplete combustion of fossil fuels in automobiles, metallurgical operations,forest fire or burning of agricultural waste and volcanic eruption. Cigarette smoke also contains CO. However, about 70% carbon monoxide is obtained only from automobiles.

Carbon monoxide *is highly poisonous to living beings because it has an ability to form more stable carboxyhaemoglobin complex with haemoglobin due to which the delivery of oxygen to the organs and tissues is blocked.* The carboxyhaemoglobin complex is about 200 times more stable than the oxygen haemoglobin complex. If the concentration of carboxy-haemogobin complex, in blood, reaches about 3-4%, the oxygen carrying capacity of blood is reduced greatly which results in headache, nervousness, muscular weakness, weak eyesight and asphyxia. *Microorganisms present in the soil act as a sink for carbon monoxide.*

On exposing the victim (person) suffering from CO poisoning to 2-2.5 atm oxygen, under a high pressure, the CO of carboxyhaemoglobin is substituted by oxygen and transport of oxygen to the different parts of the body starts again.

$$\text{HbCO} + \underset{\text{2-2.5 atm}}{O_2} \xrightleftharpoons{\text{High pressure}} \text{HbO}_2 + \text{CO}$$

$$\text{HbO}_2 \longrightarrow \text{Hb} + \underset{\substack{\text{(goes to the different}\\ \text{body parts)}}}{O_2}$$

Respiration, burning of fossil fuels for energy, decomposition of lime stone for cement manufacturing, volcanic eruptions etc., all p rocesses proceed with the liberation of carbon dioxide into the atmosphere. Thus, a large amount of carbon dioxide is released into the atmosphere which is removed by green plants on account of photosynthesis and in turn they release oxygen and maintain an appropriate level of CO_2 (*i.e.,* 0.03%) in the troposphere (or atmosphere). But deforestation and excessive burning of fossil fuels increase the level of CO_2 and disturb the atmospheric balance. This increased level of CO_2 may be expected to result in fast growing of plant, if climate is warm with adequate rainfall. Excessive concentration of CO_2 in atmosphere also causes headache, mild narcotic effect and global warming.

Caution Point *Ocean acts as sink for* SO_2, CO_2 *and nitrogen oxides and remember that* NO *has greater affinity towards haemoglobin than* CO.

(b) Oxides of Nitrogen

Among the oxides of nitrogen, nitric oxide (NO), a colourless, odourless gas and nitrogen dioxide (NO_2), a brown gas with pungent odour act as tropospheric pollutants. At high altitudes when lightning strikes or thunderstrome, the two major constituents of air, *i.e.,* dinitrogen and dioxygen combine to give these oxides. Other sources of these oxides are combustion of fossil fuels such as coal, oil, gasoline etc., in automobile engines, tobacco smoke, denitrifying bacteria and many industrial processes.

$$N_2(g) + O_2(g) \xrightarrow{1210°\text{C}} 2\,\text{NO}(g)$$

Actually NO, itself, is not a pollutant but it reacts readily with oxygen in the troposphere and with ozone in the stratosphere, to give NO_2.

NO_2 is highly toxic for living tissues. Its higher concentration causes leaf fall and retards the rate of photosynthesis. It is a corrosive oxide and helps in the formation of smog. NO_2 produces irritation in eyes and can injure liver and kidneys. In the presence of oxygen, NO_2 reacts with water or moisture and produces HNO_3 which is an important factor for making rain acidic.

(c) Oxides of Sulphur

SO_2 is the most harmful gaseous pollutant. In atmosphere, it is released by volcanic eruptions. It is also released by the combustion of sulphur containing materials. A part of SO_2, present in the atmosphere, is oxidised to SO_3 by photolytic or catalytic oxidation. Thus, atmospheric SO_2 also contains some SO_3, although the quantity of SO_3 is not high.

SO_2 is highly toxic for both animals and plants. Its very low concentration can cause several respiratory diseases such as bronchitis, asthma, emphysema. It also causes eye and throat irritation and breathlessness. In plants, it reduces the rate of formation of chloroplast and thus, causes chlorosis. SO_2 is highly corrosive and damages buildings, marbles (Taj Mahal) and textiles. In the presence of particulate matter and NO_2 or H_2O_2 (promoter), SO_2 is oxidised to SO_3 which reacts with water to give H_2SO_4. H_2SO_4 remains suspended in the air as droplets or come down in the form of acid rain.

$$2SO_2(g) + O_2(g) \xrightarrow[\text{NO}_2 \text{ or } \text{H}_2\text{O}_2]{\text{Particulate matter}} 2SO_3(g)$$

$$SO_3(g) + H_2O \longrightarrow H_2SO_4$$

Lime stone reacts with H_2SO_4 (formed from SO_2 and SO_3) *and removes oxides of sulphur from atmosphere. Therefore,* $CaCO_3$ *acts as sink for oxides of sulphur.*

(d) Hydrocarbons

These are the compounds of only carbon and hydrogen. These are obtained by the incomplete combustion of fuels in automobile engines and by anaerobic decomposition of organic matter. Out of the hydrocarbons, methane (CH_4) is the most abundant hydrocarbon pollutant. High concentrations of hydrocarbons have carcinogenic effect, *i.e.*, are cancer producing. They cause ageing of plants, breakdown of plant tissues and shedding of leaves. Hydrocarbons react with oxides of nitrogen to form secondary pollutants.

Caution Points

(*i*) *The atmospheric pollution is mainly caused by* CO (≃ 52%) *and the order of other pollutants (to cause atmospheric pollution) is as* SO_2 (18%) > *hydrocarbons* (12%) > *particulates* (9%), *nitrogen oxides* (6%). *A rememberable point here is that spraying of DDT causes all; air, water and soil pollutions.*

(*ii*) *Bhopal gas tragedy* (*on December* 1984) *in which about* 3000 *people were on killed and about* 50000 *are still suffering from respiratory, lung and eye diseases, was due to leakage of methyl isocyanate* (*MIC*) *vapours.*

Consequences of Air Pollution Caused by Gaseous Pollutants

Global warming, caused by more heating of green house (earth's atmosphere and surface) and acid rain are the two important consequences of gaseous air pollutants.

Hot Spot 1

GREEN HOUSE

Effect and Global Warming

Although the chapter is not very important for JEE Main examination, but the question, if asked, may be based on this topic. The question is general and easy.

When sunlight containing UV rays, IR rays and visible rays falls on earth, the UV rays are absorbed by ozone, present in the stratosphere and visible and IR rays (short wavelength) reach on the earth. IR rays, having heating effect, heat up the earth and its various objects. As a result, the earth and its objects also begin to emit IR rays (but of higher wavelength). The CO_2 layer present in the air (atmosphere) traps these IR rays and does not allow them to go out of the earth's atmosphere. This is because CO_2 absorbs only IR rays of longer wavelengths. Consequently, the earth and its atmosphere remains warm. **This heating up of earth and its objects because of the trapping of IR radiations by** CO_2 (mainly) **and other green house gases such as methane, NO,** O_3**, CFCs, water vapour etc., in the atmosphere is called green house effect.** Green house effect is very essential for existence of life because in its absence, the earth would be converted into extremely cold planet.

When concentration of green house gases increases, these trap excess IR rays and increases the temperature of earth too much, i.e., increases the green house effect, which is termed as global warming. Thus, global warming is the main consequence of disturbance of green house effect. Global warming had a drastic effect on climatic conditions. It may cause melting of ice caps and glaciers which result in floods of low lying areas. Moreover global warming also increases the incidence of several infectious diseases such as malaria, sleeping sickness etc.

The name 'green house effect' is come from the fact that at cold places, plants, flowers are grown in a glass covered area, called green house because the glass walls are transparent for incoming radiations but not transparent for outgoing IR radiations. Thus, required temperature is maintained. Similarly, earth atmosphere is also transparent for incoming visible and IR radiations but not for outgoing IR radiations and thus, keeps the earth warmth.

Sample **Problem 1** *What would have happened if the green house gases were totally missing in the earth's atmosphere?* **[NCERT]**

(a) *The plant leaves turn yellow*
(b) *All plants turn yellow*
(c) *No vegetation or life exists*
(d) *Earth becomes warm*

Interpret (c) Carbon dioxide, methane, water vapour, nitrous oxide, CFCs and ozone are green house gases. These gases trap some of the heat radiated by the earth's object near the earth's surface and keep it warm. This is called natural green house effect because it maintains the temperature and makes the earth perfect for life. If there were no green house gases, there would have no vegetation and life on our earth (because the earth would convert into a cold planet).

(b) **Acid Rain**

The pH of normal rain water is 5.6 due to the dissolution of carbon dioxide from atmosphere which furnish H^+ ions to the rain water.

$$H_2O + CO_2 \rightleftharpoons \underset{\text{carbonic acid}}{H_2CO_3}$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

When the pH of rain water drops below 5 *because of the presence of certain acids, it is called acid rain.* The term "acid rain" was putforth by *'Robert Augus'. Oxides of nitrogen and sulphur, released into the atmosphere from thermal power plants, industries and automobiles, are the main sources of acid rain.* These oxides on oxidation followed by hydrolysis (*i.e.,* reaction with water) give sulphuric acid and nitric acid that along with HCl are responsible for the acidity of rain., The oxidation reaction is catalysed by particulate matter present in the polluted atmosphere.

$$2SO_2 + O_2 + 2H_2O \longrightarrow 2H_2SO_4$$

$$4NO_2 + O_2 + 2H_2O \longrightarrow 4HNO_3$$

In acid rain, concentration of these acids follows the order $H_2SO_4 > HNO_3 > HCl$.

Acid rain damages the buildings and other structures made up of lime stone or marble, *i.e.,* $CaCO_3$, *e.g.,* Due to acid rain the marble of a wonderful monument Taj Mahal, situated at Agra, is getting discoloured and lustreless. Acid rain also corrodes metal pipes, as a result of which heavy metals such as Fe, Pb and Cu get leached into the drinking water and make it toxic. The nutrients required for growth and development of plants and trees are dissolved in acid rain, so it is very harmful for agriculture, trees and plants. In human beings and animals, it causes several respiratory diseases. When acid rain water is mixed with river or lakes, it adversely affect the aquatic life.

Some important facts related to acid rain are as follows

1. The most acidic rain with a pH of 1.7 has occurred over West Virginia, USA.
2. The historic marble statue, in Greece and Itlay also have been damaged by acid rain.
3. In order to save Taj Mahal, Government of India announced a plan in early 1995. According to this plan, it was decided to clear the air in the "Taj Trapezium", an area which includes the towns of Agra, Mathura, Firozabad and Bharatpur.

   The main points of this plan are as follows

   (i) Industries lying in the Trapezium would be allowed to use only natural gas or LPG instead of coal or oil. For this purpose a new natural gas pipeline would be laid.
   (ii) Peoples living in these area would be encouraged to use LPG or a low sulphur containing fuel.
   (iii) Vehicles plying in the nearby areas would be encouraged to use low sulphur content fuel.

Control of Pollution Caused by Gaseous Pollutants

The tropospheric pollution, caused by the gaseous air pollutants, can be prevented by following methods

1. Catalytic converters are used in automobile exhaust pipes to prevent formation and release of oxides of nitrogen.These convert oxides of nitrogen to free nitrogen or to a small amount of ammonia.
2. esnareshratoaeFlue gases, obtained from power plants and many industrial units, are made free from NO_2 and SO_2 by treating them with either sulphuric acid or alkaline solutions such as $Ca(OH)_2$, $Mg(OH)_2$. The process is called **scrubbing process.**
3. SO_2 pollution can also be prevented either by desulphurisation of coal or by using natural gas instead of coal for heating purposes, since natural gas does not produce SO_2 on burning.
4. Production of CO and unburnt hydrocarbons from automobiles can be prevented by fitting catalytic converters and tune-ups (for high air-fuel ratio) in automobiles exhaust pipes.
5. CO and hydrocarbons production can also be controlled by using a modified internal combustion engine with an extra combustion chamber where fuel undergoes complete combustion.
6. CO pollution can be completely controlled by using LPG and CNG instead of gasoline, coal etc.
7. Another way to reduce CO pollution is using leaded petrol (the petrol mixed with tetraethyl lead). *The addition of tetraethyllead to the petrol minimise the CO and unburnt hydrocarbon pollution, but it leads to the lead pollution.* (metal pollution).
8. Keeping the vehicle properly tuned for the optimum combustion of fuel is another way to reduce CO and unburnt hydrocarbon pollution.
9. Use of tall chimney in the kitchen can minimise the pollution of air at ground level.
10. The increasing concentration of carbon dioxide can be controlled by growing more plants and using LPG instead of coal and such fuels. In other words, global warming can be minimised by growing more plants and reducing the use of fossil fuels.

Particulate Air Pollutants

Minute solid particles and liquid droplets dispersed in air are called **particulate matter.** Particulate present in the atmosphere may be viable and non-viable. The viable particulates are minute living organisms, such as bacteria, fungi, algae, moulds, etc., that are dispersed into the atmosphere. Some of the fungi, present in air are allergic for human beings and can also cause many plant diseases. The disintegration of large size materials or condensation of small size particles or droplets result in the formation of non-viable particulates. Indeed, **non-viable particulates** are non-living, small size particles or condensed droplets that are dispersed in the atmosphere. Examples of non-viable particulates are flyash, fur, spores, pollen grains, dusts of various kinds, fumes, smoke etc.

On the basis of particle size, the non-viable particulate matter may further be differentiated into two types, *viz*, settleable particulates having particle size larger than $10\,\mu m$ and suspended particulates having particle size less than $10\,\mu m$. While on the basis of nature, non-viable particulates may be classified into following four types

(a) Smoke

These particulates are composed of solid particles or mixture of solid and liquid particles which are formed during the burning of organic matter. Since smoke contains unburnt carbon particles, it pollutes the air. It spoils clothes, blacken the buildings, monuments, causes several diseases of lungs. Examples of smoke are oil smoke, tobacco smoke and carbon smoke. Clouds of smoke over big industries unable the Sun rays to reach every corner of the city and thus, lead several infectious diseases. **A clusture of smoke particles is called soot.**

(b) Dusts

It consist of fine solid particles (> $1\,\mu m$ in diameter) that are produced during some industrial operations such as crushing and grinding of solid materials, *e.g.,* coal, cement, flyash and silica dust (from factories), sand (from sand blasting), saw dust (from wood works) etc. Dust, in the air, causes poor visibility. It deposits on plants leaves and inhibits photosynthesis by blocking stomata. Dust deteriorates the quality of articles, reflects sun rays back and thus causes cooling of the earth. Dust produces allergic reactions and can cause several diseases on the basis of particles present, *e.g.,* **Pneumoconiosis,** a lung disease, is caused due to inhalation of coal dust from coal mining industry. **Silicosis** is caused due to inhalation of free silica or SiO_2 from dust.In this disease, person suffers from chronic cough and pain in chest. Bronchial asthma and lung cancer are also caused by dust. Coal miners usually suffer from black lung disease whereas textile workers suffer from white lung disease due to inhalation of dust of corresponding particles. Asbestosis and byssinosis are caused due to inhalation of asbestos dust and cotton fibres dust respectively.

(c) Fumes

These are condensed vapours present in air. These are generally obtained by condensation of vapours during boiling, distillation, sublimation and other such processes. These are also obtained from metals, metallic oxides and organic solvents. Fumes, when mixed with air, inhaled by the people and cause several dangerous diseases, *e.g.,* inhalation of beryllium compounds causes beryllosis. Similarly, lead particulates are highly poisonous as lead interferes in the development and maturation of RBC. Moreover, it adversely affect the children's brain and causes cancer.

(d) Mists

These are obtained by particles of spray liquids and by condensation of vapours in air, *e.g.,* herbicides and insecticides, while spray travel through air and form mists. Other examples of mists are sulphuric acid mist, nitric acid mist etc.

Hot Spot 2

SMOG

It is also an important topic of the chapter for JEE Main examination, if question is from this chapter. The level of question is easy.

Smog is an important example of air pollution which can be seen in many cities throughout the world. Actually, the word "smog" is obtained by combining two words, *viz.*, smoke and fog.

Smogs are mainly of two types

(a) Classical or London Type Smog

It occurs in cool humid climate when carbon soot particles combine with gaseous oxides of sulphur, present in atmosphere. Since, it was first observed in London (in 1952), it is also called **London smog.** The main source for the formation of this type of smog, is combustion of industrial and household fuels (coal and petroleum). Usually, it is formed in the early morning hours of winter months. However, shortly after sunrise it increases because of the oxidation of SO_2 and subsequent combination with moisture to give sulphuric acid aerosol.

$$2SO_2 + O_2 \longrightarrow 2SO_3 \text{ (oxidation)}$$

$$SO_3 + H_2O \longrightarrow \underset{\substack{\text{aerosol}\\ \text{(increases the smog)}}}{H_2SO_4}$$

Due to the presence of carbon particles and SO_2, it is **reducing in nature.** This smog causes lung and throat irritation and in higher concentrations, it leads to death.

(b) Photochemical or Los Angeles Smog

It occurs in warm, dry and sunny climate, generally during the day time from its components, which are obtained by the action of sunlight on unsaturated hydrocarbons and nitrogen oxides (produced by automobiles and factories). The following reactions take place during the formation of components of photochemical smog.

$$N_2 + O_2 \xrightarrow[\substack{\text{or in petrol and}\\ \text{diesel engines)}}]{\text{(At high altitudes}} 2NO$$

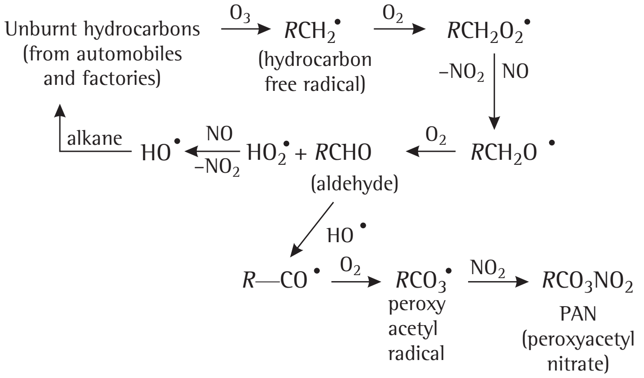
$$\underset{\substack{\text{in high}\\ \text{concentration}}}{2NO} + O_2 \xrightarrow{\text{Sunlight}} 2NO_2$$

$$NO_2 \xrightarrow{h\nu} NO + \underset{\substack{\text{nascent oxygen}\\ \text{(very reactive)}}}{[O]}$$

$$[O] + O_2 \rightleftharpoons \underset{\substack{\text{(reacts rapidly}\\ \text{with NO)}}}{O_3}$$

$$O_3 + NO \longrightarrow \underset{\substack{\text{(brown gas)}\\ \text{(in high concentration}\\ \text{forms haze)}}}{NO_2} + O_2$$

Since, O_3 and NO_2 are strong oxidising agent, they react with unburnt hydrocarbons to give following compounds (secondary pollutants).



(where, R = H, CH_3, C_6H_5)

(If R = H, acrolein and formaldehyde are obtained.)

Due to the presence of high concentration of oxidising agents, photochemical smog is **oxidising in nature.**

Photochemical smog due to the presence of ozone, PAN and nitric oxide, irritates eyes, nose, lungs, causes headache, chest pain etc. It also leads to the cracking of rubber and extensive harm to plant life. It corrodes metals, stones and even painted surfaces.

Its formation can be prevented by controlling the formation and release of primary precursors such as oxides of nitrogen, hydrocarbons etc., by their usual methods. Other method of its prevention is plantation of certain plants such as pyrus, pinus, juniparus and vitis that have an ability to metabolise nitrogen oxide. Spraying of suitable free radical generating compounds also reduce photochemical smog.

Sample **Problem 2** *Photochemical smog occurs in warm, dry and sunny climate. One of the following is not amongst the components of photochemical smog, identify it.*

- (*a*) NO_2
- (*b*) O_3
- (*c*) SO_2
- (*d*) *Unsaturated hydrocarbon*

Interpret (*c*) SO_2 is reducing in nature and not obtained in sunny, dry climate. So, it is not a component of photochemical smog. It is a component of classical smog.

Control of Pollution Caused by Particulates

The particulates, present in the atmosphere, can be removed by following methods.

1. Larger particulate particles from air are removed by using gravity settling chamber.
2. Particulates such as soluble gases and particles are removed by fine spray of water or alkaline fluid, which are called **wet scrubbers.**
3. Cyclone collectors are used to remove the particulates of 5-20 μm. This method is based on centrifugation.
4. Particulate matters are also removed by using bag filters, a porous bag made up of teflon or other polyester.
5. The most effective and efficient method to remove particulates especially aerosol particles, is the use of electrostatic precipitators, a charged plate.
6. A broad strip of vegetation also reduces particulate pollution.

Hot Spot 3

OZONE LAYER DEPLETION
or Stratospheric Pollution

It is more important as compared to other topic of the chapter and questions, if asked, may be generally from this topic. The level of question may be easy to average.

Stratospheric pollution is mainly concerned with **ozone layer depletion.** In stratosphere, there is a region of high concentration of ozone (10 ppm), at a height of 23 km, called **ozone layer.** This layer does not allow the UV rays coming from the sun to reach on the earth. Thus, protects us from harmful effects of UV rays.

Sources of Stratospheric Pollution

In recent years, it has been reported that the ozone layer is getting thin at some places. Thinning of ozone layer has mainly observed over Antarctica and north pole. Depletion of ozone layer is being caused by certain compounds such as chlorofluorocarbon compounds (CFCs), oxides of nitrogen etc., obtained from various human activities.

Nitric oxide is released into upper atmosphere from engine of supersonic transport planes. When it reaches into the stratosphere, it reacts with ozone and causes its depletion.

$$NO + O_3 \longrightarrow NO_2 + O_2$$

$$O_2 \xrightarrow{\text{UV light}} [O] + [O]$$

$$NO_2 + [O] \longrightarrow NO + O_2$$

Since, chlorofluorocarbon compounds, *i.e.,* freons (CFCs) are non-reactive, non-inflammable, non-toxic organic molecules, these are widely used in air conditioners, refrigerators, in electronic industry for cleaning computer parts. Due to very long life time (CF_2Cl_2— 12 : 139 yr and $CFCl_3$ —11 : 77 yr), these compounds ultimately reach the stratosphere where they get broken down by powerful UV radiations and release chlorine free radical. The chlorine free radicals react with ozone and cause its depletion.

$$CF_2Cl_2 \xrightarrow{h\nu} \dot{Cl} + \dot{C}F_2Cl$$

$$CFCl_3 \xrightarrow{h\nu} CFCl_2 + \dot{Cl} \qquad \text{(free radical)}$$

$$\underset{\substack{\text{(chlorine}\\ \text{free radical)}}}{\dot{Cl}} + O_3 \longrightarrow Cl\dot{O} + O_2$$

$$Cl\dot{O} + O \longrightarrow \dot{Cl} + O_2$$

The reaction, once start, continues for a long time. Thus, a single chlorine free radical is able to convert about one lakh ozone molecules into oxygen. Due to this, a massive **ozone hole** has been created in the ozone layer.

Other compounds that are responsible for ozone layer depletion are carbon tetrachloride, halons and methyl chloroform. They react with ozone in the same manner as chlorofluorocarbons.

Caution Point *Because of ozone depletion ability, chlorofluorocarbons (CFCs) are being replaced by hydrofluorocarbons and hydrochlorofluorocarbons (HCFCs).*

Causes of Formation of Ozone Hole over Antarctica

Although the above reactions of depletion of ozone take place all over the stratosphere yet ozone hole has mainly been observed in the stratosphere over Antarctica. This is because, in other parts of the stratosphere, nitrogen dioxide and methane react with chlorine monoxide radicals and chlorine radicals respectively. Thus, these act as a sink for chlorine free radicals and prevent the depletion of ozone.

$$Cl\dot{O} + NO_2 \longrightarrow ClONO_2$$

$$\dot{Cl} + CH_4 \longrightarrow \dot{C}H_3 + HCl$$

Moreover, a unique set of conditions was responsible for the ozone hole over Antarctica. In Antarctica during summer season, there exist nitrogen dioxide and methane which act as sink for chlorine free radicals and prevent much ozone depletion, whereas, in winters, there exist special type of clouds, called polar stratospheric clouds (PSCs) over Antarctica.

These clouds are of two types

(i) Type I clouds that are formed at about −77°C, have some solidified nitric acid trihydrate ($HNO_3 \cdot 3H_2O$).

(ii) Type II clouds that are formed at about −85°C, contains some ice. These clouds convert chlorine nitrate ($ClONO_2$) and hydrochloric acid (HCl) formed in the above reactions, into HOCl and Cl_2.

$$ClONO_2 + H_2O \longrightarrow HOCl + HNO_3$$
$$ClONO_2 + HCl \longrightarrow Cl_2 + HNO_3$$

During spring season, *i.e.,* in the months of September and October, the sunlight returns to the Antarctica and breaks up the clouds and photolysis HOCl and Cl_2.

$$HOCl \xrightarrow{h\nu} \dot{O}H + \dot{C}l$$
$$Cl_2 \xrightarrow{h\nu} 2\,\dot{C}l$$

The chlorine free radicals, thus formed, again start the chain reaction for ozone depletion.

Further, in the stratosphere, polar vortex (a tight whirlpool of wind) is formed due to the presence of PSCs over Antarctica which unables the ozone rich air of the non-polar regions to reach in Antarctica. Consequently the ozone hole remains unfilled. But after spring, the high intensity sunlight breaks down these vortex and ozone rich air from surroundings rushes in and replenishes the ozone hole.

Consequences of Stratospheric Pollution

Due to the depletion of ozone layer, harmful UV radiations reach the earth surface. These radiations can cause skin cancer, sunburn, ageing of skin, cataract or even blindness. These also lead to the harmful mutation of cells in plants, depletion of plants and crops. These decrease the moisture content of soil, thereby increasing the evaporation of surface water.

Sample **Problem 3** *Ozone is a toxic gas and is a strong oxidising agent even then its presence in the stratosphere is very important. What would happen if ozone from this region is completely removed?* **[NCERT Exemplar]**

(*a*) *Skin infection*
(*b*) *Sun burn*
(*c*) *Harmful mutation of cells in plants*
(*d*) *All of the above*

Interpret (*d*) Ozone prevents harmful UV radiations of the Sun from reaching to the earth's surface, thereby it protects life from bad effects of UV radiations. If ozone is removed completely from the stratosphere, the UV rays will reach to the earth and leads to several diseases like sun burn, skin infection etc.

Check Point 2

1. What is the difference between a contaminant and a pollutant?
2. Carbon monoxide gas is more dangerous than carbon dioxide gas, why?
3. Why 'photochemical smog' is so called?
4. How do particulates help in the cloud formation?
5. What would have happened, if the green house gases were totally missing in the earth's atmosphere?

16.6 Water Pollution

The contamination of water by foreign substances such as solid particles, soluble salts, sewage, algae etc., which make it injurious for living organisms and unfit for domestic, agricultural and industrial use, is called **water pollution.** The pollution of water can be checked by one or more of the following parameters : taste of water, its odour, colour presence of oil or grease on its surface. These foreign substance are termed as **'water pollutants'.**

Types of Sources of Water Pollutants

The sources from which these pollutants are obtained and released, are of two types :

(a) Point Sources

These are easily identified sources or places of pollution. These, discharge pollutants directly into the water source. Examples of such sources are factories, power plants, underground coal mines and oil wells situated near the water source. Therefore, the pollutants obtained by these sources can be treated easily before entering in the water source.

(b) Non-point Sources

Such sources cannot be easily identified. These sources are usually scattered and are difficult to monitor, regulate and treat. These sources include run off from field lawns, construction sites, acid rain, storm water drainage etc.

Major Water Pollutants

The major water pollutants are of three types, *i.e.,* pathogens such as bacteria, organic wastes such as leaves, grass, phytoplankton and chemical pollutants such as metals from industrial wastes, petroleum etc.

(a) **Pathogens**

Bacteria and other microorganisms are disease causing agents. These enter into the water bodies from domestic sewage and animal excreta. These are the most serious water pollutants because these are transmitted from one living being to another through water supplies. These cause various water borne diseases such as typhoid, cholera, dysentry, hepatitis, jaundice etc., in human beings. To control pathogen pollution, domestic sewage and animal excreta should not be drained directly to any water body. These should be drained after proper treatment.

(b) **Organic Wastes**

Leaves, grass, sewage, oxygen demanding wastes (from industries and agriculture) etc., are other major water pollutants. Water gets polluted as a consequence of run off of organic wastes. Water gets also polluted by excessive phytoplankton growth. All of these wastes are biodegradable, *i.e.,* degraded by microorganisms. The microbes require oxygen for the decomposition of organic matter, that they get from water.

Water contains some dissolved oxygen (DO) but in limited amount. The concentration of DO in water is very important because, if it is below 5 ppm, the growth of the fishes is inhibited. Generally, in cold water, the concentration of dissolved oxygen (DO) can reach upto 10 ppm (parts per million). The aquatic plants and animals use this dissolved oxygen for respiration.

Thus, organic matter, if present in excess, the microorganisms require a large amount of oxygen. But due to absence of such a large amount, anaerobic bacteria (without using oxygen) begin to decompose organic matter and give foul smelling compounds which are also harmful to human beings. However, aerobic bacteria also decompose these organic matter.

In water of good quality, the optimum value of DO is 5-6 ppm. This also ensures healthy aquatic life in water body. The lower the concentration of DO in a water sample, the more polluted is the water sample.

Degree of Water Pollution Due to Organic Matter

It is measured in terms of biochemical oxygen demand (BOD), mainly and chemical oxygen demand (COD).

1. **Biochemical oxygen demand** (BOD) is defined as the total amount of oxygen in milligrams required by microbes to decompose the organic matter present in 1 L of water sample. Whereas the term BOD_5 refers to the total amount of oxygen required for five days by microbes to decompose the organic matter. Thus,

$$\text{BOD} = \frac{\text{amount of oxygen required (in mg)}}{\text{volume of water sample (in L)}}$$

For clean water, the BOD value is less than 5 ppm while highly polluted water could have a BOD value of 17 ppm or more. The value of BOD_5 can be 100-400 ppm for untreated sewage. To find the BOD value of a water sample, it is first saturated with oxygen and then incubated at 20°C for five days. Oxidation of organic matter takes place and remaining amount of dissolved oxygen is determined. Thus, BOD is obtained by subtraction.

2. **Chemical oxygen demand** (COD) It is the total amount of oxygen in ppm that would be consumed by the pollutants, in a given water sample. For pure water COD value is 4 ppm. For COD determination, the given water sample is treated with a known quantity of oxidising agent such as $K_2Cr_2O_7$ in acidic medium. The reagent oxidises most of the organic matters. The remaining amount of $K_2Cr_2O_7$ is determined by titrating the water sample against a suitable reducing agent such as Mohr's salt. From the amount of $K_2Cr_2O_7$ used, the amount of oxygen used can be obtained (in ppm) by the following equation

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

Due to the presence of organic matter in water, its colour gets brown. This water has an unpleasent odour due to the formation of secondary pollutants such as CH_4, NH_3, H_2S. These waste also produce scum and sludge in water. These lead oxygen dependent aquatic life to die. Sewage also increases the growth of phytoplankton and thus, reduces the amount of DO in water and leads to eutrophication, *a process of enrichment of water by nutrients to support a dense plant population, which affect the fish population and also kills other aquatic animals.*

Organic matter pollution is also controlled by drainning these matter into water body after proper treatment.

Sample **Problem 5** *A large number of fish are suddenly found floating dead on a lake. There is no evidence of toxic dumping but you find an abundance of phytoplankton. Suggest a reason for the fish kill.* **[NCERT]**

(a) *Low BOD* (b) *Low DO*
(c) *Low COD* (d) *None of these*

Interpret (*b*) Large quantities of phosphates and nitrates increases the growth of phytoplankton. These phytoplankton use so much oxygen that it is not enough available for other organisms to use in respiration. Moreover a large population of bacteria decomposes organic matter such as leaves, grass, etc., in water. During this process, they consume the oxygen dissolved in water. Microorganisms may become so abundant that they form a mat covering on the water surface and preventing sunlight from penetrating the surface and thereby preventing photosynthesis. In all these processes concentration of dissolved oxygen in water decreases. When the concentration of dissolved oxygen of water is below 6 ppm, the growth of fish gets inhibited and they cannot survive.

(c) Chemical Pollutants

These include inorganic minerals, heat, chemical compounds, petroleum (oil), pesticides, detergents (surfactants), fertilizers etc. Since, water is an excellent solvent, all these substance dissolve in it and pollute it.

(i) **Fertilizers** They contain phosphates and nitrates. When added to crop fields, a part of these fertilizers is passed down to water bodies by rain water through surface run off. Since, the contaminated water becomes rich in these nutrients, it increases the growth of algae and other aquatic plants, *i.e.,* causes eutrophication which leads to organic loading, lack of dissolved oxygen, death of animals and bad odour of water. The water containing nitrate is unfit for drinking purposes. Moreover, it cannot be purified for drinking. After a long period, these nutrients convert the lakes and slow moving waters in swamps and marshes. Compost should be used instead of fertilizers to control fertilizers pollution.

(ii) **Municipal and industrial waste water** It contains various toxic elements which are very dangerous to humans as our body does not excrete them. If their concentration is quite high, these cause several diseases. Some metals, their sources and harmful effects are tabulated below.

Table 16.1 **Toxic Metals, their Sources and Harmful Effect**

Element	Sources	Harmful effect
Mercury	Pesticides, coal, industrial waste, mining.	(i) Highly toxic in CH_3Hg^- form. (ii) Causes *minamata* (*minimata*) disease which is characterised by diarrhoea, haemolysis, meningitis and death.
Chromium	Metal plating industries.	Carcinogenic, causes gastrointestinal ulcers and nervous system disorder.
Cadmium	Industrial wastes, Ni-Cd batteries.	(i) High blood pressure, kidney malfunctioning, disorder of bone marrow. (ii) *Itai-itai* disease.
Lead	Plumbing, mining, coal gasoline	(i) Anaemia, kidney malfunctioning, nervous disorder. (ii) Interferes with haem synthesis and glucose metabolism.
Zinc	Industrial wastes	Vomiting, cramps, renal damage and toxic to plants.
Arsenic	Chemical wastes, pesticides	Carcinogenic, *i.e.,* cancer producing.
Copper	Industrial waste, leaching process	Not very toxic to animals but toxic to plants and algae.

Caution Point *When polluted water contains acids or alkalies, self purification process is hindered due to the absence of microorganisms because microorganisms are destroyed by acids or alkalies.*

(iii) **Detergents** They contain alkyl benzene sulphonates (ABS), a surfactant (surface active agent) which is non-biodegradable and thus, forms stable foam, stabilise colloidal impurities and create several problems during the treatment of waste water. However, most of the detergents, available now a days, are biodegradable but they can cause other problems. PCBs (polychlorinated biphenyls), a chemical, used as fluids in transformers and capacitors, have been found to be carcinogenic.

(iv) **Oil** It mainly pollutes sea water, when spilled accidently or intentionally into it. Oil may form a thin layer on the surface of water, called oil spill or a thick layer on the surface of sea water, called oil slick. It checks the growth of phytoplanktons and disrupts the entire marine life cycle. The oil film may catch fire and harms to the aquatic life. *Oil pollution greatly affects the flight and swimming capability of sea-birds.*

(v) **Pesticides** When pesticides (such as DDT) is mixed with water, they pollute it and cause several problems such as cerebral haemorrhage, hypertension, softening of brain. However, microorganisms capable of degrading these chlorinated hydrocarbons have been discovered recently. These degrade chlorinated compounds due to secretion of enzyme dehalogenase. Pesticides are generally broad spectrum (used widely) and function as biocides. When persistant pesticides such as DDT passes from lower tropic level to higher one, through food chain, the amount of pesticides per unit weight of organism increase due to their accumulation in fat. This phenomenon is called **biomagnification.**

(vi) **Thermal and Nuclear power plants** The waste water, discharged from **thermal** and **nuclear power plants,** is at a raised temperature which has several adverse effect. The warm water has lower density and viscosity, thus suspended solids settle faster. Moreover, warm water has less DO, lower rate of putrescibility which results in organic loading and replacement of green algae (aerobic) by blue-green algaes (an-aerobic). The rate of evaporation also rises with rise in temperature which results in greater wastage of water in the form of vapours. At high temperature, many animals fail to reproduce, *e.g.,* salmon.

(vii) **Elements** Some elements, when present within prescribed concentration are not harmful but when their concentration exceeds it, these have several adverse effect. Some such elements with their sources, prescribed concentration and adverse effect of higher amount are tabulated below :

Table 16.2 **Prescribed Concentration and Harmful Effects of Different Elements**

Element/ion	Sources	Prescribed concentration		Adverse effect of higher concentration
		by WHO	by EV	
Fluorides (F)	Added externally	1.5 ppm (or 1.5 mg dm^{-3})	1.5 ppm	(i) Converts enamel (hydroxyapatite, $[3Ca_3(PO_4)_2 \cdot Ca(OH)_2]$ to more harder fluorapatile, $[3Ca_3(PO_4)_2 \cdot CaF_2]$. (ii) Concentration (> 2 ppm) causes brown mottling of teeth. (iii) High concentrations (> 10 ppm) are harmful for bones and teeth.
Lead (Pb)	Lead pipes	0.01 ppm	0.01 ppm	Damage kidney, liver and reproductive system.
Sulphate (SO_4^{2-})	Acid rain, industries	500 ppm	250 ppm	Has laxative effect.
Nitrate (NO_3^-)	Fertilizers	50 ppm	50 ppm	Methemoglobinemia (blue baby syndrome).
Other metals :				
(i) Iron (Fe)	—	No guideline	0.2 ppm	
(ii) Manganese (Mn)	—	0.5 ppm	0.05 ppm	
(iii) Copper (Cu)	—	2 ppm	2 ppm	
(iv) Aluminium (Al)	—	0.2 ppm	0.2 ppm	
(v) Zinc (Zn)	—	3 ppm	not given	
(vi) Cadmium (Cd)	—	0.003 ppm	0.005 ppm	
(vii) Sodium (Na)	—	200 ppm	200 ppm	

Sample **Problem 6** *A person was using water supplied by municipality. Due to shortage of water he started using underground water. He felt laxative effect. Its cause is high concentration of* **[NCERT** Exemplar**]**

(*a*) CO_2 (*b*) SO_4^{2-} (*c*) CO_3^{2-} (*d*) S^{2-}

Interpret (*b*) The laxative effect is observed only when the sulphates present in water have concentration greater than 500 ppm. Otherwise at moderate levels it is harmless.

16.7 Soil Pollution

Soil pollution is alteration in soil caused by addition or removal of such substances or factors that deteriorates the quality, texture and mineral content of the soil or that disturbs the biological balance of the organisms in the soil and has a lethal effect on plant growth. The substances or factors are called **soil pollutants.**

Types of Soil Pollution

Soil pollution can be classified into following types

(a) Positive Soil Pollution

Reduction in soil productivity because of the addition of undesirable substances such as fertilizers, pesticides, industrial wastes, air pollutants etc., is termed as positive soil pollution.

(b) Negative Soil Pollution

The reduction in the productivity of soil due to soil erosion and over use is termed as **negative soil pollution.**

(c) Landscape Pollution

If the fertile land gets converted into barren land by dumping wastes such as rubbish, industrial wastes, broken cans, bottles, plastics etc., the pollution is termed as **landscape pollution.**

Sources of Soil Pollution

Major source of soil pollution is indiscriminate use of pesticides and fertilizers. Accumulation of excreta of grazing animals, dumping of urban, industrial and radioactive wastes are some other sources of soil pollution.

(a) Pesticides

The chemical substances, used to control the growth of pests, are called **pesticides**. These are usually insoluble in water and non-biodegradable. However, a few biodegradable pesticides have been synthesised now a days. Being water insoluble, these transfer from lower tropical level to higher one through food chain. Pesticides are basically toxic chemicals but their repeated use make the pest more resistant towards pesticides. These have adverse effect on human health, when reach in the body. Studies have shown that a single pesticide can not elimiate all species of a target pest. Due to this, the number of commercial pesticides is increasing tremendously. Depending upon their target, *i.e.,* insects, weeds, fungi etc. *Pesticides are classified into following classes :*

(i) **Insecticides** are the chemical substances which are used to kill crops destroying insects. A very small amount of such chemicals is toxic to insects. Organochlorine group compounds such as DDT (dichlorodiphenyl trichloro ethane), BHC (benzene hexa chloride), aldrin, dieldrin were widely used as insecticides but because of their high insolubility and persistant nature, their use is being restricted. Now a days, a series of organophosphate and carbamates, which are more biodegradable, are used as insecticides. However, these chemicals are nerve toxic and more harmful to humans.

(ii) **Herbicides** are used to kill weeds. Sodium chlorate ($NaClO_3$) and sodium arsinite (Na_3AsO_3) are used as herbicides. These are also toxic to mammals but are not as persistant as organochlorine compounds. These chemicals take a few months to decompose. Some herbicides cause birth defects. Now a days, organic compounds such as triazines are widely used as herbicides, especially for the corn-fields.

(iii) **Fungicides** are used to stop growth of fungi and to check plant diseases. Fungi, due to the lack of chlorophyll, depend upon other plants for their food and consequently, retard their growth. Organomercury compounds are commonly used as fungicides but their dissociation in soil produces mercury which is highly toxic.

(b) Soil Conditioners

Compounds of some toxic metals such as As, Pb, Hg, Cd etc., called **soil conditioners,** are used for killing the insects and to protect the soil fertility. After the decomposition of these compounds, the obtained metals accumulate in the soil, from where they reach the growing crops and from crops to animals.

Caution Point *Loam soil because of the presence of equal amounts of sand, slit and clay alongwith humus and* 34% *air,* 66%, *water, is best for growing plants.*

(c) Solid Wastes

Solid wastes such as industrial wastes, urban wastes, farm waste, radioactive wastes etc., also cause soil or land pollution.

(d) Soil Salination

Halomorphic soil contains a large concentration of salts. The process by which salt concentration in soil is increased is called **soil salination.** There is a white incrustation over the soil surface after salination, thus soil becomes barren. The sources/processes that lead to soil salination are excessive use of fertilizers, canal water, poor drainage systems, salts blown from rocks/sea, absorption of acidic ions by plants etc. Conductivity meter is used to measure soil salinity.

16.8 Strategies to Control Environmental Pollution

Environmental pollution is mainly controlled either by waste management or by green chemistry.

Waste Management

Management of industrial and household wastes through suitable treatment plays an important role to reduce environmental pollution.

It can be done by the following methods :

(a) Recycling

It is a process in which waste materials can be used as raw materials for manufacturing many useful products again. Therefore, it is the most important technique for waste disposal, *e.g.,* agricultural wastes are used for manufacturing paper, hard board, animal feed etc., used newspapers and magazines for making paper and paper envelopes, organic wastes for making compost or in biogas plants. Plastics and metals are also recycled now.

(b) Digestion

This process involves, the degradation of toxic organic wastes by anaerobic microorganisms, *i.e.,* in the absence of oxygen. In this process, CO_2 and methane are obtained.

$$2(CH_2O) \longrightarrow CO_2 + CH_4$$

Methane is used as fuel.

(c) Incineration

It involves combustion of a substance into its ash at a high temperature ($\approx 1000°C$) and in a plentiful supply of oxygen. Therefore, waste materials can be converted into their ash by incineration and the obtained ash can be used to fill the low lying lands. Exhaust gases must be filtred. It is an important method for the disposal of polychlorinated biphenyls (PCBs) because in presence of high temperature, C—Cl bonds get ruined. The major disadvantage of this process is the production of highly toxic chloro compounds due to incomplete combustion of PCBs.

(d) Dumping

Dumping of sewage sludge into ocean has been widely used in all countries. However, dumping of sludge into land is preferred, now a days. This is because of the presence of compounds of nitrogen and phosphorus in sludge that act as soil fertilizers.

(e) Sewage Treatment

The treatment of sweage involves the following steps

1. Large size materials are filtered off and used to fill low lying land.
2. Then, the residual water is allowed to stand in tanks, by which many solid materials settle down as primary sludge but oil and grease float on the surface from where these are removed.
3. The organic content of residual water are allowed to undergo oxidation by aerobic microorganisms. By this secondary sludge is formed which is mixed with primary sludge and subjected to anaerobic oxidation (by anaerobic microbes).
4. Finally, phosphate is removed from waste water by treating it with lime followed by coagulation, filtration and disinfectant (such as chlorine). The sludge obtained in this process is dried and then may be incinerated, digested or dumped.

Green Chemistry

The concept of green chemistry was introduced in 1990. It is an alternative tool for reducing pollution. Indeed, **green** *chemistry is a branch of chemistry in which chemicals of daily needs are produced by using such reactions or processes that neither use toxic chemicals nor emit such chemicals into the atmosphere*. In this, various reactions are carried out in the presence of mild and environment friendly reagents such as ultraviolet light (photochemistry), sound waves (sonic chemistry), enzymes and microwaves so that harmful chemicals are neither used up nor released.

Applications of Green Chemistry

Some uses of the green chemistry in day to day life are

1. Use of liquefied carbon dioxide with suitable detergents for drycleaning clothes which replaces tetrachloroethene, a pollutant and suspected carcinogen (used earlier for drycleaning).
2. Use of hydrogen peroxide for bleaching clothes, in laundary and paper.
3. Catalytic dehydrogenation of diethanolamine without using formaldehyde and cyanide.
4. Preparation of ethanol from oxidation of ethene in the presence of ionic catalyst.
5. Synthesis of ibuprofen by using smaller quantities of solvents.
6. Replacement of organotins by sea-nine.
7. Replacement of chlorofluorocarbons (CFCs) and used in manufacturing polystyrene foam sheets, by CO_2.

Metathesis is an example that exhibits the importance of application of basic science for human welfare.

Sample **Problem 7** *For which of the following you apply green chemistry?*

I. To control photochemical smog.
II. To avoid use of halogenated solvents in dry cleaning and that. of chlorine in bleaching.
III. To reduce use of synthetic detergents.
IV. To reduce the consumption of petrol and diesel.

The correct choice is/are **[NCERT Exemplar]**

(a) *I and II only*
(b) *II and III only*
(c) *I and III only*
(d) *I, II, III and IV*

Interpret (*d*)

I. Certain plants, e.g., *Pinus*, *Janiparus*, *Quercus*, *Pyrus* and *Vitis* can metabolize nitrogen oxide (NO) and therefore, their plantation could help in reducing photochemical smog.
II. Liquefied CO_2 with a suitable detergent is used for dry cleaning and H_2O_2 (hydrogen peroxide) is used for the purpose of bleaching clothes in the process of laundry which gives better results and makes use of lesser amount of water.
III. Soaps are 100% biodegradable so they should be used in place of detergents. Now a day biodegradable detergents are available. Therefore, they should be used in place of non-biodegradable hard detergents.
IV. CNG (compressed natural gas), should be used as it causes much less pollution. Moreover, electrical vehicles should be used to reduce the consumption of petrol and diesel.

WORKED **OUT**
Examples

Example 1 *Ozone is formed in the upper atmosphere from oxygen by the action of*

(*a*) *thermal radiation from sunlight*
(*b*) *cosmic rays*
(*c*) *ultraviolet rays*
(*d*) *infrared rays*

Solution (*c*) Ozone is formed when UV light strikes oxygen molecules and splits it into individual oxygen atom (O) which combine with undissociated oxyen.

$$O_2(g) \xrightarrow{\text{UV light}} 2O(g)$$

$$O(g) + O_2(g) \overset{\text{UV light}}{\rightleftharpoons} O_3(g)$$

Example 2 SO_2 *and* NO_2 *cause pollution by increasing*

(*a*) *alkalinity* (*b*) *neutrality*
(*c*) *acidity* (*d*) *buffer action*

Solution (*c*) SO_2 and NO_2 when dissolve in water, form H_2SO_4 and HNO_3, (strong acids) respectively.

$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$$

$$2SO_2 + O_2 \xrightarrow{\text{Particulate}} 2SO_3$$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

Thus, they cause the pollution by increasing acidity.

Example 3 *In acid rain, the acid present in highest concentration is*

(*a*) *nitric acid* (*b*) *hydrochloric acid*
(*c*) *sulphuric acid* (*d*) *carbonic acid*

Solution (*c*) In acid rain, the percentage of various acids is as

$$H_2SO_4 > HNO_3 > HCl$$

Example 4 *Which of the following statements is not true?*

(*a*) *London smog is a mixture of smoke and fog*
(*b*) *London smog is oxidising in nature*
(*c*) *Photochemical smog causes irritation in eyes*
(*d*) *Photochemical smog results in the formation of PAN*

Solution (*b*) Smogs either London or photochemical, are the mixture of smoke and fog. London smog is formed in cool humid climate when carbon soot particles combine with gaseous oxides of sulphur. Since in this type of smog, C particles and SO_2 are present, it is reducing in nature. Photochemical smog, on the other hand, occurs in warm, dry and sunny climate. It results in the formation of PAN. Since in photochemical smog, O_3 is present, it irritates the eyes, nose, lungs etc.

Example 5 *Which causes water pollution?*

(*a*) *Smoke-flyash* (*b*) 2,4-*D*
(*c*) *Automobile exhaust* (*d*) *Cars*

Solution (*b*) Pathogenes, organic wastes and chemical pollutants are the sources of water pollution. Hence, 2, 4-D being a chemical pollutant, causes water pollution.

Example 6 *Which one of the following is considered as point source for water pollution?*

(*a*) *Factories* (*b*) *Construction site*
(*c*) *Acid rain* (*d*) *Field lawns*

Solution (*a*) Point source means the sources that can be easily identified. Among the given, factories can be considered as point source for water pollution.

Example 7 *Match Column* I *with Column* II *and select the correct answer using the codes given below.*

Column I (Pollutant)	Column II (Source)
A. Microorganisms	*1. Chemical fertilizers*
B. Plant nutrients	*2. Abandoned coal mines*
C. Sediments	*3. Domestic sewage*
D. Mineral acids	*4. Erosion of soil by strip mining*
	5. Detergents

Codes

	A	B	C	D
(*a*)	2	5	3	1
(*b*)	3	1	4	2
(*c*)	4	2	5	1
(*d*)	1	3	2	4

Solution (*b*) Microorganisms are present in domestic sewage. Chemical fertilizers are also known as plant nutrients. Sediments are obtained by the erosion of soil by strip mining and abandoned coal mines are the source of mineral acids. Thus, the correct match is

A-3, *B*-1, *C*-4, *D*-2.

Start Practice for JEE Main

Round I (Topically Divided Problems)

Components of Environment and General Terms Related to Pollution

1. Which of the following is a living component of atmosphere?

(a) Lithosphere (b) Biosphere
(c) Hydrosphere (d) Troposphere

2. Atmospheric content of CO_2 is

(a) 0.0034% (b) 0.034%
(c) 0.34% (d) 3.4%

3. The gaseous envelope around the earth is known as atmosphere. The lowest layer of this is extended upto 10 km from sea level, this layer is **[NCERT Exemplar]**

(a) stratosphere (b) troposphere
(c) mesosphere (d) hydrosphere

4. Ozone layer is present in

(a) troposphere (b) stratosphere
(c) mesosphere (d) exosphere

5. Region/regions of the atmosphere where temperature decreases with altitude is/are

(a) thermosphere (b) stratosphere
(c) troposphere (d) ozonosphere

6. Which of the following region is the coldest?

(a) Stratosphere (b) Troposphere
(c) Mesosphere (d) Thermosphere

7. The elements present in the core of earth are collectively known as

(a) lithophiles (b) nucleophiles
(c) chaleophiles (d) siderophiles

8. Dinitrogen and dioxygen are main constituents of air but these do not react with each other to form oxides of nitrogen because **[NCERT Exemplar]**

(a) the reaction is endothermic and requires very high temperature
(b) the reaction can be initiated only in the presence of a catalyst
(c) oxides of nitrogen are unstable
(d) N_2 and O_2 are unreactive

9. Pollution is

(a) removal of top soil
(b) release of toxic/undesirable materials in environment
(c) conservation of energy
(d) All of the above

10. Which of the following is a primary pollutant?

(a) CO (b) PAN (c) Aldehydes (d) H_2SO_4

11. The pollutants which come directly in the air from sources are called primary pollutants. Primary pollutants are sometimes converted into secondary pollutants. Which of the following belongs to secondary air pollutants? **[NCERT Exemplar]**

(a) CO
(b) Hydrocarbon
(c) Peroxyacetyl nitrate (PAN)
(d) NO

12. Which of the following is a biodegradable pollutant?

(a) Plastic (b) Sewage
(c) Asbestos (d) Mercury

Gaseous Air Pollution

13. Oxides of sulphur and nitrogen are important pollutants of

(a) water (b) air
(c) soil (d) All of these

14. Gas released during Bhopal gas tragedy was

(a) methyl isocyanate
(b) potassium isothiocyanate
(c) sodium isothiocyanate
(d) ethyl isothiocyanate

15. Which among the given is not a natural source of air pollution?
(a) Automobile exhausts
(b) Vegetation decay
(c) Forest fire
(d) Volcanic eruptions

16. Carbon monoxide, emitted by automobiles, prevents transport of oxygen in the body due to
(a) combining with oxygen to form carbon dioxide
(b) destruction of haemoglobin
(c) preventing reaction between oxygen and haemoglobin
(d) forming stable compound with haemoglobin

17. Taj Mahal is threatened by pollution from
(a) chlorine (b) sulphur dioxide
(c) hydrogen (d) oxygen

18. Most hazardous metal pollutant of automobile exhaust is
(a) mercury (b) lead
(c) cadmium (d) copper

19. Which of the following gases is not a green house gas? **[NCERT Exemplar]**
(a) CO (b) O_3
(c) CH_4 (d) H_2O vapour

20. Acid rains are produced by
(a) excess NO_2 and SO_2 from burning fossil fuels
(b) excess production of NH_3 by industry and coal gas
(c) excess release of carbon monoxide by incomplete combustion
(d) excess formation of CO_2 by combustion and animal respiration

Particulate Pollution

21. Which of the following is a viable particulate?
(a) Algae (b) Smoke
(c) Mist (d) Fumes

22. Pneumoconiosis is caused by inhalation of
(a) coal dust (b) silica dust
(c) cotton fibre dust (d) asbestos dust

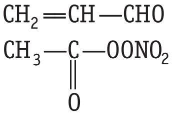
23. White lung cancer is caused by
(a) asbestos (b) silica
(c) paper (d) textiles

24. Oxidation of sulphur dioxide into sulphur trioxide in the absence of a catalyst is a slow process but this oxidation occurs easily in the atmosphere. Which substance here catalyse the reaction? **[NCERT Exemplar]**
(a) Oxygen
(b) Particulate
(c) UV rays
(d) IR rays

25. Photochemical smog always contains
(a) O_3 (b) CO
(c) CO_2 (d) CH_4

26. Which of the following statements is not true about classical smog? **[NCERT Exemplar]**
(a) Its main components are produced by the action of sunlight on emissions of automobiles and factories
(b) Produced in cold and humid climate
(c) It contains compounds of reducing nature
(d) It contains smoke, fog and sulphur dioxide

27. Which of the following statements about photochemical smog is wrong? **[NCERT Exemplar]**
(a) It has high concentration of oxidising agents
(b) It has low concentration of oxidising agents
(c) It can be controlled by controlling the release of NO_2, hydrocarbons, ozone etc
(d) Plantation of some plants like pinus helps in controlling photochemical smog

28. PAN stands for
(a) CH_2O (b) $CH_2{=}CH{-}CHO$
(c) $CH_3CH_2O{-}N{=}O$ (d) 
$CH_3{-}\underset{\underset{O}{\|}}{C}{-}OONO_2$

Stratospheric Pollution

29. Which of the following statements is correct? **[NCERT Exemplar]**
(a) Ozone hole is a hole formed in stratosphere from which ozone oozes out
(b) Ozone hole is a hole formed in the troposphere from which ozone oozes out
(c) Ozone hole is thinning of ozone layer of stratosphere at some places
(d) Ozone hole means vanishing of ozone layer around the earth completely

30. Which of the following statements is wrong? **[NCERT Exemplar]**
(a) Ozone is not responsible for green house effect
(b) Ozone can oxidise sulphur dioxide present in the atmosphere to sulphur trioxide
(c) Ozone hole is thinning of ozone layer present in stratosphere
(d) Ozone is produced in upper stratosphere by the action of UV rays on oxygen

31. Ozone layer of stratosphere requires protection from indiscriminate use of
(a) pesticides
(b) atomic explosions
(c) aerosols and high flying jets
(d) balloons

32. Which of the following is responsible for peeling of ozone umbrella?

(a) PAN (b) Coal burning
(c) CFCs (d) CO_2

33. Chlorofluorocarbons (CFCs) are widely used in air conditioners, refrigerators etc., because of being

(a) highly reactive (b) flammable
(c) non-reactive (d) All of these

34. Result of ozone hole is

(a) green house effect (b) global warming
(c) acid rain (d) UV rays reach the earth

35. Ozone is an important constituent of stratosphere because it

(a) prevents the formation of smog over large cities
(b) removes poisonous gases of the atmosphere by reacting with them
(c) absorbs ultraviolet radiations which is harmful to human life
(d) destroys bacteria which are harmful to human life

36. Ozone hole is maximum over

(a) Europe (b) Antarctica
(c) India (d) Africa

37. Which of the following acts as a sink for chlorine free radicals?

(a) Nitrogen dioxide (b) Methane
(c) Carbon dioxide (d) Both (a) and (b)

38. Some time ago formation of polar stratospheric clouds was reported over Antarctica. What happens when such clouds break up by warmth of sunlight? **[NCERT Exemplar]**

(a) Ozone layer depletion stops
(b) Ozone layer depletion starts
(c) HOCl and Cl_2 are obtained
(d) Both (a) and (c)

Water and Soil Pollution

39. Which of the following statements is false?

(a) The main reason for river water pollution is industrial and domestic sewage discharge
(b) Surface water contains a lot of organic matter, mineral nutrients and radioactive materials
(c) Oil spill in sea water causes heavy damage to fishery
(d) Oil slick in a sea water increases DO value

40. Biochemical Oxygen Demand, (BOD) is a measure of organic material present in water. BOD value less than 5 ppm indicates a water sample to be **[NCERT Exemplar]**

(a) rich in dissolved oxygen
(b) poor in dissolved oxygen
(c) highly polluted
(d) not suitable for aquatic life

41. What does BOD_5 represent?

(a) Biological ozone depletion in five days
(b) Dissolved oxygen left after five days
(c) Dissolved oxygen consumed in five days
(d) Microorganisms killed by ozone in sewage treatment plants in five hours

42. Drawback of DDT as pesticides is that

(a) it is less effective than others
(b) it becomes ineffective after some time
(c) it is a non-degradable substance
(d) it is very costly

43. The sources of dissolved oxygen in water **[NCERT Exemplar]**

(a) photosynthesis
(b) natural aeration
(c) mechanical aeration
(d) All of the above

44. Phosphate pollution is caused by

(a) weathering of phosphate rocks only
(b) agricultural fertilizers only
(c) phosphate rocks and sewage
(d) sewage and agricultural fertilizers

45. Sewage containing organic waste should not be disposed in water bodies because it causes major water pollution. Fishes in such a polluted water die because of **[NCERT Exemplar]**

(a) large number of mosquitoes
(b) increase in the amount of dissolved oxygen
(c) decrease in the amount of dissolved oxygen in water
(d) clogging of gills by mud

46. Negative soil pollution is

(a) reduction in soil productivity due to erosion and over use
(b) reduction in soil productivity due to addition of pesticides and industrial wastes
(c) converting fertile land into barren land by dumping ash, sludge and garbage
(d) None of the above

Strategies to Control Pollution and Green Chemistry

47. Modes of controlling pollution in large cities include

(a) less use of insecticides
(b) proper disposal of organic wastes, sewage and industrial effluents
(c) shifting of factories out of the residential area
(d) All of the above

48. Which one of the following is not an application of green chemistry?
- (a) Replacement of CFCs by CO_2 as blowing agent in the manufacture of polystyrene foam sheets
- (b) Reacting methylamine and phosgene to produce methyl isocyanate
- (c) Replacement of organotins by 'sea-nine' as anti fouling compound in sea marines
- (d) Catalytic dehydrogenation of the diethanol amine without using cyanide and formaldehyde

49. Proper management of disposal of household and industrial wastes can be done by
- (a) recycling the waste material to give useful products again
- (b) burning and incineration of combustible waste
- (c) sewage treatment
- (d) All of the above

50. Green chemistry involves
- (a) production of chemicals of our daily use from green house gases
- (b) such chemical processes in which green plants are used
- (c) those reactions which are of biological origin
- (d) use of non-toxic reagents and solvents to produce environment friendly products

Round II (Mixed Bag)

Only One Correct Option

1. Temperature of troposphere decreases with altitude. This is because of
- (a) high pressure of air
- (b) gases present in air
- (c) lower density of air
- (d) All of these

2. The greatest affinity for haemoglobin is shown by
- (a) NO
- (b) CO
- (c) O_2
- (d) CO_2

3. Which of the following is not regarded as a pollutant?
- (a) NO_2
- (b) CO_2
- (c) O_3
- (d) Hydrocarbons

4. Match the Column I and II and pick the correct matching from the codes given below.

Column I	Column II
(A) Polycyclic aromatic hydrocarbons	1. Global warming
(B) Dioxins	2. Photochemical smog
(C) IR active molecules	3. Carcinogens
(D) Peroxy acetyl nitrate	4. Waste incineration

Codes

	A	B	C	D
(a)	3	4	1	2
(b)	4	3	2	1
(c)	3	4	2	1
(d)	1	2	3	4

5. Ultraviolet light causes
- (a) formation of pyrimidines
- (b) sticky metaphases
- (c) photodynamic action
- (d) destruction of hydrogen bonds between complementary DNA strands

6. Cyclone collector is used for minimising
- (a) radioactive pollution
- (b) air pollution
- (c) noise pollution
- (d) water pollution

7. Which of the following statements is not true?
- (a) Ammonia acts as sink for NO_x
- (b) Limestone acts as sink for SO_x
- (c) The average residence time of NO is one month
- (d) SO_x can be removed from flue gases by passing through a solution of citrate ions

8. Among the following statements which one is incorrect?
- (a) Suspended particulate matter (SPM) is an important pollutant released by diesel vehicles
- (b) Soot particles (size $< 5\ \mu$) cause fibrosis of the lung lining
- (c) H_2SO_4 particulates have size of 500-1000 nm
- (d) Photochemical smog is formed by oxides of sulphur, smoke and dust particles

9. Pick up the correct statement.
- (a) CO plays a major role in photochemical smog
- (b) London smog has an oxidising character whereas Los Angeles smog is reducing in nature
- (c) Classical smog is good for health but photochemical somg not
- (d) Los Angeles smog forms in day time whereas London smog forms in early morning hours

10. Which of the following statements about control of particulate pollution is false?
- (a) Gravity settling chamber removes larger particles from the air
- (b) Cyclone collector removes fine particles in the diameter range 5-20 microns

(c) Wet scrubbers are used to wash away all types of particulates

(d) In electrostatic precipitator, the particulates are made to acquire positive charge which are then attracted by the negative electrode and removed

11. Which of the following statements about polar stratospheric clouds (PSCs) is not correct?

(a) Type I clouds are formed at about −77°C and contain solid $HNO_3 \cdot 3H_2O$

(b) Type II clouds are formed at about −85°C and contains some ice

(c) A tight whirlpool of wind called polar vortex is formed which surrounds Antarctica

(d) PSCs do not react with chlorine nitrate and HCl

12. As it passes into food chain, the concentration of DDT

(a) remains same
(b) decreases
(c) increases
(d) unpredictable

13. For dry cleaning, in the place of tetrachloroethane, liquefied carbon dioxide with suitable detergent is an alternative solvent. What type of harm to the environment will be prevented by stopping use of tetrachloroethane? **[NCERT Exemplar]**

(a) It results in tropospheric pollution

(b) It causes depletion of ozone layer

(c) It causes particulate pollution

(d) Both (a) and (b)

14. Match the activity given in Column I with the type of pollution created by it given in Column II.

	Column I (Activity)		Column II (Effect)
A.	Releasing gases to the atmosphere after burning waste material containing sulphur.	1.	Water pollution
B.	Using carbamates as pesticides.	2.	Photochemical smog, damage to plant life, corrosion to building material, induce breathing problems, water pollution
C.	Using synthetic detergents for washing clothes	3.	Damaging ozone layer
D.	Releasing gases produced by automobiles and factories in the atmosphere.	4.	May cause nerve diseases in human.
E.	Using chlorofluorocarbon compounds for cleaning computer parts.	5.	Classical smog, acid rain, water pollution, induce breathing problems, damage to buildings, corrosion of metals.

[NCERT Exemplar]

Codes

	A	B	C	D	E
(a)	5	4	3	2	1
(b)	5	4	2	1	3
(c)	5	4	1	2	3
(d)	4	5	2	3	1

15. Select the incorrect statement.

(a) Water is considered pure if it has BOD less than 5 ppm

(b) In COD determination, the pollutants resistant to microbial oxidation are not oxidised by oxidising agent like $K_2Cr_2O_7$

(c) The lower the concentration of DO, the more polluted is the water sample

(d) The tolerable limit of lead in drinking water is 50 ppm

16. Which of the following practices will not come under green chemistry? **[NCERT Exemplar]**

(a) If possible, making use of soap made of vegetable oils instead of using synthetic detergents

(b) Using H_2O_2 for bleaching purpose instead of using chlorine based bleaching agents

(c) Using bicycle for travelling small distances instead of using petrol/diesel based vehicles

(d) Using plastic cans for neatly storing substances

More than One Correct Option

17. Non-degradable solid pollutants are

(a) domestic waste

(b) DDT

(c) plastics

(d) cow dung

18. The acids present in acid rain are … . **[NCERT Exemplar]**

(a) peroxyacetylnitrate
(b) H_2CO_3
(c) HNO_3
(d) H_2SO_4

19. The consequences of global warming may be … **[NCERT Exemplar]**

(a) increase in average temperature of the earth

(b) melting of Himalayan Glaciers

(c) increased biochemical oxygen demand

(d) eutrophication

20. Which of the following conditions shows the polluted environment? **[NCERT Exemplar]**

(a) pH of rain water is 5.6

(b) Amount of carbondioxide in the atmosphere is 0.03%

(c) Biochemical oxygen demand 10 ppm

(d) Eutrophication

21. Phosphate containing fertilisers cause water pollution. Addition of such compounds in water bodies causes …… **[NCERT Exemplar]**

(a) enhanced growth of algae
(b) decrease in amount of dissolved oxygen in water
(c) deposition of calcium phosphate
(d) increase in fish population

Assertion and Reason

Directions (Q. Nos. 22 to 27) *Each of these questions contains two statements : Statement* I (*Assertion*) *and Statement* II (*Reason*). *Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes* (*a*), (*b*), (*c*), (*d*) *given below :*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

22. **Statement I** Green house effect was observed in houses used to grow plants and these are made of green glass.

Statement II Green house name has been given because glass houses are made of green glass. **[NCERT Exemplar]**

23. **Statement I** Presently, the global atmosphere is warming up.

Statement II The depletion of stratospheric ozone layer has resulted in increase in ultraviolet radiations reaching the earth.

24. **Statement I** The pH of acid rain is less than 5.6.

Statement II Carbon dioxide present in the atmosphere dissolves in rain water and forms carbonic acid. **[NCERT Exemplar]**

25. **Statement I** Photochemical smog is oxidising in nature.

Statement II Photochemical smog contains NO_2 and O_3, which are formed during the sequence of reactions. **[NCERT Exemplar]**

26. **Statement I** Excessive use of chlorinated synthetic pesticides causes soil and water pollution.

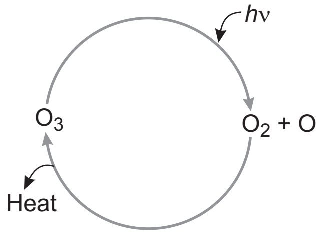
Statement II Such pesticides are non-biodegradable. **[NCERT Exemplar]**

27. **Statement I** If BOD level of water in a reservoir is less than 5 ppm it is highly polluted.

Statement II High biological oxygen demand means low activity of bacteria in water. **[NCERT Exemplar]**

Comprehension Based Questions

Directions (Q. Nos. 28 to 30) When healthy, earth's stratosphere contains a low concentration of ozone (O_3) that absorbs potentially harmful ultraviolet (UV) radiations by the cycle shown :



Chlorofluoro carbon refrigerants, such as freon-12 (CF_2Cl_2), are stable in lower atmosphere, but in the stratosphere, they absorb high energy UV radiation to generate chlorine radicals.

$$CF_2Cl_2 \longrightarrow \dot{C}F_2Cl + \dot{C}l$$

The presence of small number of chlorine radicals appears to lower ozone concentrations dramatically. The following reactions are all known to be exothermic (except the one requiring light) and to have high rate constants.

A. $Cl—O—O—Cl \xrightarrow{h\nu} O_2 + 2Cl^{\bullet}$
B. $Cl—O^{\bullet} + O \longrightarrow O_2 + Cl^{\bullet}$
C. $Cl^{\bullet} + O_3 \longrightarrow Cl—O^{\bullet} + O_2$
D. $2\ Cl—O^{\bullet} \longrightarrow Cl—O—O—Cl$

28. Which of the following reactions is harmful to ozone layer?
(a) A (b) B (c) C (d) D

29. Ozone has the ability to absorb
(a) UV radiations (b) electromagnetic radiations
(c) CFC (d) green house gases

30. Increased UV radiations due to hole in ozone layer
(a) will cause increase in cases of skin diseases
(b) will cause more ice to melt
(c) will cause summer to be more warmer
(d) will cause more rain

Direction (Q. Nos. 31 to 33) Water is one of the most common substances on earth.It covers 72% of the earth's surface. Water is essential for life and its pollution can cause serious problems. The effect of water problems on health can be anything from an upset stomach to severe illness leading to death. Eutrophication is another source of water pollution. It is the process that results when large quantities of phosphates and nitrates are released into aquatic ecosystem. High concentration of phosphates and nitrates causes rapid growth in the populations of bacteria and algae. These microorganisms use so much oxygen that there is not enough oxygen, available for other organisms to use in respiration.

31. Which of the following does not cause water pollution?
(a) Heavy metals such as Cd, Pb, Hg
(b) Detergents
(c) Polychlorobiphenyls
(d) Freons

32. Eutrophication of a lake means, it
(a) is low in nutrients
(b) is high in nutrients
(c) has excess amount of organic matter
(d) has a high temperature

33. Fish die in water bodies polluted by sewage due to
(a) pathogens (b) reduction in oxygen
(c) foul smell (d) None of these

Previous Years' Questions

34. Identify the incorrect statement from the following. [AIEEE 2011]
(a) Oxide of nitrogen in the atmosphere can cause the depletion of ozone layer
(b) Ozone absorbs the intense ultraviolet radiations of the sun
(c) Depletion of ozone layer is because of its chemical reaction with chlorofluoro alkanes
(d) Ozone absorbs infrared radiations

35. Identify the wrong statements in the following. [AIEEE 2008]
(a) Chlorofluoro carbons are responsible for ozone layer depletion
(b) Green house effect is responsible for global warming
(c) Ozone layer does not permit infrared radiation from the sun to reach the earth
(d) Acid rain is mostly because of oxides of nitrogen and sulphur

36. The smog is essentially caused by the presence of [AIEEE 2007]
(a) O_2 and O_3
(b) O_2 and N_2
(c) oxides of sulphur and nitrogen
(d) O_3 and N_2

37. When rain is accompanied by a thunderstorm, the collected rain water will have a pH value [AIEEE 2003]
(a) slightly lower than that of rain water without thunderstorm
(b) slightly higher than that when the thunderstorm is not there
(c) uninfluenced by occurrence of thunderstorm
(d) which depends on the amount of dust in air

Answers

Round I

1. (b)	**2.** (b)	**3.** (b)	**4.** (b)	**5.** (c)	**6.** (c)	**7.** (d)	**8.** (a)	**9.** (b)	**10.** (a)
11. (c)	**12.** (b)	**13.** (b)	**14.** (a)	**15.** (c)	**16.** (d)	**17.** (b)	**18.** (b)	**19.** (a)	**20.** (a)
21. (a)	**22.** (a)	**23.** (d)	**24.** (b)	**25.** (a)	**26.** (a)	**27.** (b)	**28.** (d)	**29.** (c)	**30.** (a)
31. (c)	**32.** (c)	**33.** (c)	**34.** (d)	**35.** (c)	**36.** (b)	**37.** (d)	**38.** (b)	**39.** (d)	**40.** (a)
41. (c)	**42.** (c)	**43.** (d)	**44.** (d)	**45.** (c)	**46.** (a)	**47.** (d)	**48.** (b)	**49.** (d)	**50.** (d)

Round II

1. (c)	**2.** (a)	**3.** (b)	**4.** (a)	**5.** (d)	**6.** (b)	**7.** (c)	**8.** (d)	**9.** (d)	**10.** (d)
11. (d)	**12.** (c)	**13.** (a)	**14.** (c)	**15.** (b)	**16.** (d)	**17.** (b,c)	**18.** (b,c,d)	**19.** (a,b)	**20.** (c,d)
21. (a,b)	**22.** (a)	**23.** (b)	**24.** (b)	**25.** (a)	**26.** (a)	**27.** (d)	**28.** (b)	**29.** (a)	**30.** (a)
31. (d)	**32.** (b)	**33.** (b)	**34.** (d)	**35.** (c)	**36.** (c)	**37.** (a)			

the Guidance

Round I

1. Biosphere is a living component of atmosphere.

3. The gaseous envelope around the earth is known as atmosphere. The lowest layer of this which is extended upto 10 km from sea level, is called troposphere.

4. In stratosphere at about 20 to 40 km, there is a part of relatively high ozone concentration, called the ozone layer.

6. Mesosphere is the coldest region having −100°C temperature.

7. The elements present in the earth's core are collectively called siderophiles. These are found in their native state. These elements generally have low reactivity and exhibit an affinity to form metallic bond, *e.g.,* Pt, Pu, Ru, Pd, Ir, Os etc.

8. Dinitrogen (N_2) and dioxygen (O_2) are main constituents of air but these do not react with each other to form oxides of nitrogen because the reaction of dinitrogen with dioxygen is endothermic and requires very high temperature while in this reaction air does not provide such a high temperature.

11. The pollutants which come directly in the air from sources are known as primary pollutants. SO_2, CO and nitrogen oxide (NO_x) are the example of primary pollutants.

Primary pollutants are sometimes converted into secondary pollutants. Ozone (O_3) and peroxyacetyl nitrate (PAN) belong to the secondary air pollutants.

12. Sewage is a biodegradable pollutant because it is easily decompose by microorganism.

14. Methyl isocyanate (MIC) gas was released during Bhopal gas tragedy.

16. Carbon monoxide is highly toxic to living being because it has an ability to form more stable carboxyhaemoglobin complex with haemoglobin due to which the delivery of oxygen to the organs and tissues is blocked.

19. CO gas is not a green house gas. CH_4, CO_2, N_2O, O_3 and H_2O vapour gases are the green house gases.

22. Pneumoconiosis is caused by inhalation of coal dust.

24. The presence of particulate matter in polluted air catalyses the oxidation of SO_2 to SO_3.

$$2SO_2 + O_2 \xrightarrow{\text{Particulates}} 2SO_3$$

26. Classical smog contains smoke, fog, sulphur dioxide (SO_2). and compounds of reducing nature. It is produced in cold and humid climate. But its main components are not produced by the action of sunlight on emissions of automobiles and factories.

27. Photochemical smog has high concentration of oxidising agents and it can be controlled by controlling the release of NO_2, hydrocarbons, ozone (O_3) etc. Plantation of some plants like pinus helps in controlling photochemical smog..

30. Ozone is responsible for green house effect.

31. Aerosols and high flying jets release nitric oxide into the upper atmosphere which leads to the destruction of ozone layer.

33. Chlorofluorocarbons *i.e.,* freons are non-reactive, non-inflammable, non-toxic organic molecules, that's why these are widely used in air conditioners, refrigerators etc.

36. Ozone hole is maximum over Antarctica.

37. Nitrogen dioxide and methane which act as sink for chlorine free radicals and prevent much ozone depletion.

38. In summer season, nitrogen dioxide and methane react with chlorine monoxide and chlorine atoms forming chlorine sinks, preventing much ozone depletion, whereas in winter, special type of clouds called polar stratospheric clouds are formed over Antarctica. These polar stratospheric clouds provide surface on which chlorine nitrate gets hydrolysed to form hypochlorous acid. It also reacts with hydrogen chloride to give molecular chlorine.

$$Cl\dot{O}(g) + NO_2(g) \longrightarrow ClONO_2(g)$$
$$\dot{Cl}(g) + CH_4(g) \longrightarrow \dot{C}H_3(g) + HCl(g)$$
$$ClONO_2(g) + H_2O(g) \longrightarrow HOCl(g) + HNO_3(g)$$
$$ClONO_2(g) + HCl(g) \longrightarrow Cl_2(g) + HNO_3(g)$$

When sunlight returns to the Antarctica in the spring, the sun's warmth breaks up the clouds and HOCl and Cl_2 are photolysed by sunlight.

$$HOCl(g) \xrightarrow{h\nu} \dot{O}H(g) + \dot{Cl}(g)$$

$$Cl_2(g) \xrightarrow{h\nu} 2\,\dot{Cl}(g)$$

The chlorine radicals thus formed, initiate the chain reaction for ozone depletion.

39. Oil slick causes water pollution, thus it decreases DO value (dissolved oxygen value) of sea water.

40. Biochemical oxygen demand (BOD) is a measure of organic material present in water. BOD value less than 5 ppm indicates a water sample to be rich in dissolved oxygen. For fresh water, the value of BOD is less than 5 ppm while for polluted water the value of BOD is 17 ppm or more than 17 ppm.

41. BOD_5 means dissolved oxygen consumed in five days.

43. Sources of dissolved oxygen in water are (i) photosynthesis (ii) natural aeration and (iii) mechanical aeration.

45. Sewage containing organic waste should not be disposed in water bodies because it causes major water pollution. So, fishes in such a polluted water die because it decrease in the amount of dissolved oxygen in water.

Round II

1. In troposphere, as we move towards the altitude, the density and pressure of air decreases. Due to which temperature also decreases.

2. Nitrous oxide (NO) has the highest affinity towards haemoglobin. However, due to its larger size, it cannot be inhaled.

3. Carbon dioxide, being limiting factor, when present in small amount (*i.e.,* 0.033%), has no adverse effect but when its concentration is slightly higher than 0.033%, it has an adverse effect on our climate. Thus, in normal conditions, CO_2 is not regarded as a pollutant.

4. Polycyclic aromatic hydrocarbons are carcinogens, *i.e.,* cancer producing dioxins are waste incineration, IR active molecules such as CO_2 are related with global warming. PAN (peroxy acetyl nitrate) forms photochemical smog.

5. The hydrogen bonds present between complementary strands of DNA are destructed by UV light.

6. Cyclone collector is used to remove particulate particles, thus it minimises air pollution.

7. The average residence time of NO is 4 days.

8. When climate is warm, dry and sunny, the oxides of nitrogen and unsaturated hydrocarbons are converted in the components such as PAN, formaldehyde which form photochemical smog, by the action of sunlight.

9. Classical or London type smog is formed by the combination of soot particles with oxides of sulphur while climate is cool and humid. Due to presence of soot and oxides of sulphur, it is reducing in nature.

Photochemical smog or Los Angeles smog is obtained from nitrogen oxides when climate is warm, dry and sunny. Due to the presence of O_3 and NO_2 (strong oxidising agents), it is oxidising in nature.

CO does not play any role in the formation of photochemical smog.

10. In electrostatic precipitator, the electrode plate is positively charged. Thus, the particulates acquire negative charge and are attracted by the negative electrode plate.

11. PSCs (polar stratospheric clouds) of type II provide a surface for the conversion of chlorine nitrate ($ClONO_2$) and HCl into HOCl and Cl_2.

$$ClONO_2 + H_2O \xrightarrow{PSCs} HOCl + HNO_3$$
$$ClONO_2 + HCl \longrightarrow Cl_2 + HNO_3$$

12. When a pesticide such as DDT passes from lower tropic level to higher level, through food chain, the amount of pesticide per unit weight of organism increases due to accumulation in fat. This process is called biomagnification.

13. Tetrachloroethane, $Cl_2C{=}CCl_2$ is suspected to be carcinogenic and also contaminates the ground water. This harmful effect will be prevented by using liquefied CO_2 along with suitable detergent.

Note Use of liquefied CO_2 along with detergent will not be completely safe because most of the detergents are non-biodegradable and they cause water pollution. Moreover, liquefied CO_2 will ultimately enter into the atmosphere and contribute to the green house effect.

14. Sulphur dioxide is a component of classical smog, acid rain, water pollution etc., and obtained by burning S.

Carbamates causes nerve diseases in human.

Synthetic detergents cause water pollution. Gases releasing from automobiles and factories contains oxides of N which is a part of photochemical smog.

CFCs are responsible for damaging ozone layer.

15. In COD determination, the pollutants, which are resistant to microbial oxidation, are also oxidised by strong oxidising agents such as $K_2Cr_2O_7$.

16. Using plastic cans for neatly storing substances will not come under green chemistry.

17. Non-degradable solid pollutants are those which do not degrade, *e.g.,* DDT, plastic etc.

18. The acids present in acid rain are H_2CO_3, HNO_3 and H_2SO_4 as the CO_2, SO_2 and NO_2 gases present in the atmosphere dissolve in water to give these acids.

19. The consequences of global warming may be increase in average temperature of the earth and melting of Himalayan Glaciers.

BOD and eutrophication are the result of water pollution.

20. 10 ppm value of biochemical oxygen demand (BOD) and eutrophication show that the environment is polluted.

21. Phosphate containing fertilizers cause water pollution. Addition of such compounds in water bodies causes enhanced growth of algae and hence, results in decreased amount of dissolved oxygen in water. Due to lack of dissolved oxygen, fish population greatly reduces.

22. Green house effect was observed in houses used to grow plants in colder regions. Since the houses were made up of green glasses, these are called green houses.

Note Similar phenomenon is also seen in our environment which keep our earth warm and make life possible on it. This effect is called green house effect.

23. Presently, the global atmosphere is warming up, because the concentration of green house gases increases constantly.

Ozone layer is non-permeable for UV rays, so its depletion resulted in increase in UV radiation reaching the earth.

24. Generally the pH of rain water is 5.6 because of the dissolution of CO_2 from the atmosphere into rain water.

When some other gases, like SO_2, NO_2 etc., also dissolve, the pH goes below 5.6 due to the presence of strong acids like H_2SO_4, HNO_3, etc. This rain now referred as acid rain.

25. Because of the presence of oxidising substance like NO_2, O_3, etc., photochemical smog is oxidising in nature.

26. Pesticides being non-biodegradable result in soil as well as water pollution.

27. If BOD is less than 5 ppm, the water is considered as clear.

High BOD represent less activity of bacteria.

28. Reaction of $ClO^{\bullet}$ with atomic O generates more $Cl^{\bullet}$. These $Cl^{\bullet}$ can continue to destroy ozone by the following reaction.

$$Cl^{\bullet} + O_3 \longrightarrow ClO^{\bullet} + O_2$$

It has been calculated that one molecule of CFC can destroy more than thousand of O_3.

29. Ozone has the ability to absorb harmful UV radiations.

30. UV radiations posses high energy and are harmful to men's life, cause skin cancer.

31. Freons do not cause water pollution.

32. Eutrophication means high concentration of phosphate and nitrates from fertilizer and detergents in aquatic ecosystem.

33. Fish die in water bodies polluted by sewage because of the decrease in the dissolved oxygen in water.

34. $NO + O_3 \longrightarrow NO_2 + O_2$

$O_3 + h\nu \longrightarrow O_2 + O$

$NO_2 + O \longrightarrow NO + O_2$

Net reaction : $2O_3 + h\nu \longrightarrow 3O_2$

Thus, ozone layer is depleted by oxides of nitrogen.

Thus, (a) is corrrect statement.

(b) Ozone layer is a protective layer and absorbs harmful UV rays from the sun.

Thus, (b) is also correct statement.

(c)
$$Cl + O_3 \longrightarrow Cl\dot{O} + O_2$$
$$O_3 + h\nu \longrightarrow \dot{O} + O_2$$
$$Cl\dot{O} + \dot{O} \longrightarrow Cl + \dot{O}_2$$

Net reaction $2O_3 + h\nu \longrightarrow 3O_2$

Thus, ozone layer is also depleted by reaction with freons.

Thus, (c) is also correct statement.

(d) is a incorrect statement as ozone layer is permeable for IR rays.

35. Ozone layer permits the infrared radiation to pass through but does not permit the higher range of ultraviolet radiation to pass through.

36. NO, NO_2, SO_2 and SO_3 are responsible for smog (environmental pollution).

37. During thunderstorm there is formation of NO which changes to NO_2 and ultimately to HNO_3 (acid-rain).

$$N_2 + O_2 \longrightarrow NO \xrightarrow{O_2} NO_2$$
$$\longrightarrow N_2O_5 \xrightarrow{H_2O} HNO_3 \text{ (pH} < 7)$$

PART - II

Chapters from Class 12th Syllabus

1 States of Matter : Solid State

JEE Main MILESTONE

- Solid State
- External Features of Crystals
- Bragg's Law : (Determination of Crystal Structure by X-ray Diffraction)
- Crystal Lattice and Unit Cells
- Packing of Particles in a Solid
- Structures of Ionic Crystals
- Radius Ratio Rules
- Imperfections in Solids
- Electrical Properties of Solids
- Magnetic Properties of Solids
- Dielectric Properties of Solids

1.1 Solid State

A solid is defined as that form of matter which has rigidity and due to which possesses a definite volume and a definite shape. These characteristics are due to the existence of very strong forces of attraction among the constituent species of the solid. Due to these strong forces, the structural units of the solid do not possess any translatory motion but can have only vibrational motion about their mean positions.

Classification of Solids

The solids can be classified into the following two types

(A) Amorphous Solids

The solids which do not have any definite shape geometrically are called amorphous (Morpha = form) solids. Infact these have a random and disordered arrangement of atoms. These solids are also called **supercooled liquids** and are without sharp melting points *i.e.,* these have **short range order** of their constituent atoms like that in the liquids. *e.g.,* glass, rubber, plastics, etc.

Amorphous solids are **isotropic** *i.e.,* have same physical properties in all directions. Actually, here the particles are randomly arranged and disordered due to which all the directions are equivalent, hence all the properties remain same in all the directions.

Amorphous solids soften over a range of temperature and can be moulded and blown into various shapes. On heating they become crystalline at some temperature. Some glass objects from ancient civilisations are found to become milky in appearance because of some crystallisation.

Moreover, solids posses high density and low compressibility as compared to liquids and gases, because of strong intermolecular forces of attraction.

Caution Point *Glass panes fixed to windows or doors of old buildings are invariably found to be slightly thicker at the bottom than at the top. This is because the glass flows down very slowly and makes the bottom portion slightly thicker.*

(B) Crystalline Solids

A crystalline solid is composed of atoms arranged in an orderly repetitive array, *i.e.,* it is a **homogeneous anisotropic substance** having a definite geometrical shape with surfaces that are usually plane with sharp edges. These have sharp melting points.

In many solids, we may not clearly see the shape of crystals because several small or micro-sized crystals are tightly packed together without any specific order. Such a substance which is infact crystalline but is superfine to be seen as crystals is called **micro-crystalline** or **polycrystalline solid** *e.g.,* many metals and alloys. A copper wire have micro-crystalline structure.

Table 1.1 **Distinction between Crystalline and Amorphous Solids**

Property	Crystalline solids	Amorphous solids
Shape	They have definite characteristic geometrical shape.	They have irregular shape.
Melting point	They melt at a sharp and characteristic temperature.	They gradually soften over a range of temperature.
Cleavage property	When cut with a sharp edged tool, they split into two pieces and the newly generated surfaces are plain and smooth.	When cut with a sharp edged tool, they split into two pieces with irregular surfaces.
Anisotropy/ isotropy	Anisotropic in nature	Isotropic in nature
Also called	True solids	Pseudo solids or supercooled liquids
Heat of fusion	They have a definite and characteristic heat of fusion.	They do not have definite heat of fusion.
Order in arrangement of constituents	Long range order.	Short range order.

On the basis of nature of bonding, the crystalline solids have been classified into following four types

(i) Ionic Crystals

These have (+)ve and (–)ve ions as constituent particles which are bonded together by strong electrostatic forces of attraction, *e.g.,* NaCl, KNO_3, etc.

These solids are hard and brittle in nature. They have high melting and boiling points. Since, the ions are not free to move about, they are electrical insulators in the solid state. However, in the molten state or when dissolved in water, the ions become free to move about and they conduct electricity.

(ii) Molecular Crystals

These have molecules as constituent particles which are bonded by van der Waals' forces, *e.g.,* I_2, dry ice (solid CO_2), solid CH_4, ice, etc.

These are further sub divided into the following categories

(a) **Non-polar molecular solids** which comprise of either atoms, *e.g.,* argon and helium or the molecules formed by non-polar covalent bonds *e.g.,* H_2, Cl_2 and I_2. In these solids, the atoms or molecules are held by weak dispersion forces or London forces. They have low melting points and are usually in liquid or gaseous state at room temperature and pressure. These solids are soft and non-conductors of electricity.

(b) **Polar molecular solids** are those in which the molecules are held together by relatively stronger dipole-dipole interactions. These solids are soft and non-conductors of electricity. Their melting points are higher than those of non-polar molecular solids yet most of these are gases or liquids under room temperature and pressure. *e.g.,* solid SO_2, solid NH_3 etc.

(c) **Hydrogen bonded molecular solids** are those in which the molecules contain polar covalent bonds between H and F, O or N atoms. Strong hydrogen bonding binds molecules of such solids like H_2O (ice). They are non-conductors of electricity. Generally they are volatile liquids or soft solids under room temperature and pressure.

(iii) Covalent Crystals

These have atoms as constituent particles (bonded together by covalent bonds), *e.g.,* diamond, graphite, silicon etc. Such solids are very hard and brittle because of the presence of strong and directional covalent bonds which hold the constituents very strongly at their positions. Moreover, melting points of such solids are extremely high, even they may decompose before melting. They are insulator (*i.e.,* do not conduct electricity).

Graphite is soft and conductor of electricity. Its exceptional behaviour is because of the presence of loosely held layers and free electrons.

Free electrons make graphite a good conductor of electricity. Different layers can slide one over the other. This makes graphite a soft solid and a good solid lubricant.

(iv) Metallic Crystals

These have positive metal ions (Kernels) and free electrons as constituent particles (bonded together by metallic bonds), *e.g.,* all metals and alloys. Each metal atom contributes one or more electrons towards this sea of mobile electrons. These free and mobile electrons are responsible for high electrical and thermal conductivity of metals. When an electric field is applied, these electrons flow through the network of positive ions.

Similarly, when heat is supplied to one portion of a metal, the thermal energy is uniformly spread throughout by free electrons. Another important characteristic of metals is their lustre and colour in certain cases. This is also due to the presence of free electrons in them. Metals are highly malleable and ductile.

Sample **Problem 1** *Iodine molecules are held in the crystals lattice by* **[NCERT Exemplar]**

(a) *London force* (b) *dipole-dipole interactions*
(c) *covalent bonds* (d) *coulombic forces*

Interpret (*a*) Iodine is a molecular solids, thus in it the constituent particles, *i.e.,* molecules are held together by weak London forces.

Sample **Problem 2** *Graphite cannot be classified as* **[NCERT Exemplar]**

(a) *conducting solid* (b) *network solid*
(c) *covalent solid* (d) *ionic solid*

Interpret (*d*) Because of the absence of ions, graphite is not an ionic solid. It is a network or covalent solid which has high conductivity due to the presence of free electrons.

Sample **Problem 3** *Which of the following solids is not an electrical conductor?* **[NCERT Exemplar]**

(*A*) Mg(*s*) (*B*) TiO(*s*)
(*C*) $I_2(s)$ (*D*) $H_2O(s)$
(a) *only* (*A*) (b) *only* (*B*)
(c) (*C*) *and* (*D*) (d) (*B*), (*C*) *and* (*D*)

Interpret (*c*) Metallic and ionic solids (in molten state) because of the presence of free electrons and free ions respectively, conduct electricity. Thus, Mg (metallic solid) and TiO are conductor of electricity.

$I_2(s)$ and $H_2O(s)$ are molecular solids and do not have charge carrier like free electrons or ions. That's why these are non-conductor of electricity.

Crystalline and Amorphous Silica

Silica (SiO_2) can be crystalline (quartz) as well as amorphous. *Main differences are given below*

Table 1.2 **Difference between Quartz and Amorphous Silica**

S.N.	Quartz	Amorphous silica
1.	Crystalline.	Light white powder.
2.	All four corners of SiO_4^{4-} tetrahedron are shared by others to give a network solid.	The SiO_4^{4-} tetrahedra are randomly joined giving rise to polymeric chains, sheets or three-dimensional units.
3.	High and sharp melting point (1710°C).	Does not have sharp melting point. On heating softens gradually to liquid.

1.2 External Features of Crystals

The external features of crystals include

1. Faces
2. Forms
3. Edge
4. Solid angle
5. Interfacial angle
6. Zone and zone-axis.

The crystals are bounded by surfaces which are usually planar and arranged in definite pattern. These surfaces are called **faces.** Faces are of two types namely like and unlike faces. The crystals with all similar surfaces is said to have like faces, *e.g.,* alums, fluorspar, etc., while galena crystal has unlike faces, *i.e.,* it has a combination of cubical and octahedral faces.

All the faces corresponding to a crystal are said to constitute a form. The forms may be **simple** (with like faces) or in **combination** (with unlike faces). In a crystal, when two adjacent faces intersect, we get an **edge** and when three or **more** edges intersect, we get a **solid angle.** The angle between the normals to the two intersecting faces is called an **interfacial angle** *i.e.,*

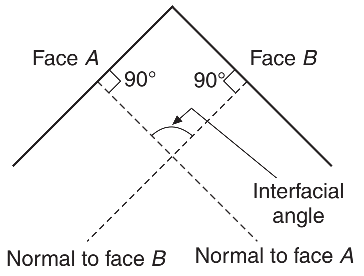


Fig. 1.1 Representation of interfacial angle

The faces, edges and interfacial angles are related as,

$$f + c = e + 2$$

where, f = number of faces
e = number of edges
c = number of interfacial angles

The faces of a crystal occur in sets. These sets are called **zones.** Each zone forms a complete belt around a crystal. A line drawn through the centre of a crystal in a direction parallel to the edges of a zone is known as **zone axis.**

1.3 **Bragg's Law :** (Determination of Crystal Structure by X-ray Diffraction)

The size of the unit cell and arrangement of atoms in a crystal is determined with the help of measurement of diffraction of X-rays by the crystal. W.H. Bragg pointed out that the scattering of X-rays by crystals could be considered as reflection from successive planes of atoms in the crystals.

The process was based upon the principle that a crystal may be considered to be made up of a number of parallel equidistant atomic planes as represented by lines *AB, CD* and *EF* in figure shown below.

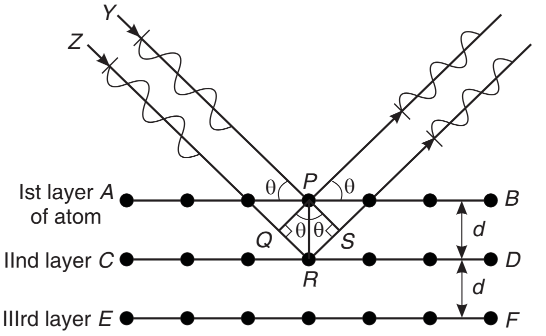


Fig. 1.2 X-ray diffraction by crystal particles

Assume two waves *Y* and *Z* of X-ray beams which are in phase, fall on the surface of the crystal. If ray *Y* gets reflected from the first layer, *i.e., AB* line and ray *Z* is reflected from the second layer of atoms, *i.e., CD* line, then it is evident that as compared to ray *Y*, ray *Z* has to travel a longer distance, equal to *QRS* in order to emerge out of the crystal. If waves *Y* and *Z* are in-phase (for the intensity of the reflected beam to be maximum) after reflection, the difference in distance travelled by the two rays must be equal to the integral multiple of wavelength, *i.e.,* $n\lambda$ (for constructive interference).

Thus, distance $QRS = n\lambda$ ...(i)

It is obvious from the figure that $QR = RS = PR \sin\theta$

$\therefore$ $QRS = 2PR \sin\theta$ ...(ii)

If the distance between the successive atomic planes is *d*, then, $PR = d$. ...(iii)

So, from Eq. (i), (ii), and (iii), we have

$$\boxed{n\lambda = 2d \sin\theta}$$

This is **Bragg's equation.**

Thus, Bragg gave a mathematical equation to establish a relationship between the wavelength of the incident X-ray, the distance between the layers, and the angle of diffraction, where

λ = wavelength of X-ray used

θ = angle between incident X-rays and the plane of the crystal. The diffracted beam makes an angle 2θ.

d = distance between planes of the constituent particles in a crystal.

n = an integer (1, 2, 3, 4, ...) which represents the serial order of diffracted beams.

Applications of Bragg's Law

Bragg diffraction (also referred as Bragg's formulation of X-ray diffraction) is an important application of Bragg's law. The concept of Bragg diffraction applies equally to neutron diffraction and electron diffraction. Electron diffraction provides a basis for studying the structure of crystals and of identifying materials. Metal tend to give a very strong electron diffraction patterns whereas biological specimens generally diffract quite weakly.

In X-ray diffraction, a diffraction pattern is obtained by measuring the intensity of scattered waves as a function of scattering angle. Very strong intensities known as Bragg peaks are obtained in the diffraction pattern when scattered waves satisfy the Bragg's law.

Sample **Problem 4** *The X-ray powder pattern of potassium chloride shows a cone at $\theta = 90°$, using X-rays of wavelength 1.54×10^{-8} cm. What is the spacing between the planes?*

(*a*) 7.5×10^{-5} *cm* (*b*) 7.7×10^{-9} *cm*

(*c*) 3.6×10^{-8} *cm* (*d*) 1.54×10^{-8} *cm*

Interpret (*b*) Using Bragg's equation, we have

$$d = \frac{1.54 \times 10^{-8}}{2 \times \sin 90°} \text{ cm}$$

$$= \frac{1.54 \times 10^{-8}}{2 \times 1} \text{ cm}$$

$$= 7.7 \times 10^{-9} \text{ cm}$$

Sample **Problem 5** *When an electron in an excited* Mo *atom falls from L to K shell, an X-ray is emitted. These X-rays are diffracted at angle of 7.75 by planes with a separation of 2.64 Å. What is the difference in energy between K-shell and L-shell in* Mo *assuming a first order diffraction* (sin 7.75 = 0.1349) ?

(*a*) 36.38×10^{-14} *J* (*b*) 27.88×10^{-16} *J*

(*c*) 45.34×10^{-16} *J* (*d*) 31.46×10^{-15} *J*

Interpret (*b*) Bragg's equation,

$$n\lambda = 2d \sin\theta$$

$$\lambda = \frac{2d \sin\theta}{n}$$

$$= \frac{2 \times 2.64 \times 10^{-10} \times \sin 7.75}{1}$$

$$= 0.7123 \times 10^{-10} \text{ m}$$

Also, we know that

$$E = \frac{hc}{\lambda} = \frac{6.62 \times 10^{-34} \times 3 \times 10^{8}}{0.7123 \times 10^{-10}}$$

$$= 27.88 \times 10^{-16} \text{ J}$$

Check Point 1

1. Why do solids have a definite volume?
2. Why are pseudo solids anisotropic?
3. Why is glass considered a super cooled liquid?
4. Refractive index of solid is observed to have the same value along all directions. Comment on the nature of this solid. Would it show cleavage property?
5. Ionic solids conduct electricity in molten state but not in solid state. Explain.

1.4 Crystal Lattice and Unit Cells

The regular arrangement of the constituent particles of a crystalline solid in the three dimensional space is called the space lattice or crystal lattice.

The smallest portion of the complete space which when repeated again and again in different directions produces the complete space lattice, is called the unit cell.

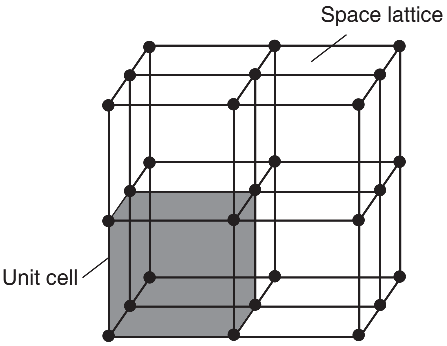
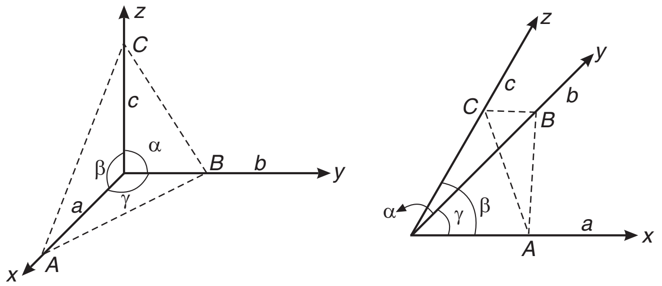


Fig. 1.3 Space lattice and unit cell

Crystal Parameters

The geometry of a crystal can be best described in terms of 3 non-coplanar coordinate axes, called the **crystallographic axes.** These axes namely x, y and z may be mutually at right angles to each other or may be inclined to each other at different angles. As per convention, the angle between y and z-axes is called α, between z and x is called β and between x and y is called γ.



(a) α, β, and γ when perpendicular to each other *i.e.*, $\alpha = \beta = \gamma = 90°$

(b) α, β, γ, when inclined at different angle

Fig. 1.4 Crystallographic axes showing angles

Any face of the crystal may cut into one or more crystallographic axes. The face which cuts all the three axes is called **standard** or **unit plane.** The distances of the points where the standard plane cuts the three axes from the origin are called intercepts. The intercepts a, b and c and axes x, y and z respectively are called crystal parameters. In actual practice, the ratio $a : b : c$ is called the axial ratio and it depends upon the point where all the three axes meet.

On the basis of different possible values of α, β and γ and different axial distances or edge lengths a, b and c following 7 types of three dimensional primitive cells or crystal systems are as follows

Table 1.3 **Seven Crystal Systems and their Unit Cell Parameters**

S.N.	Crystal systems	Bravais lattices	Unit cell parameters		Examples
			Intercepts	Crystal angles	
1.	Cubic	Primitive, Face centred, Body centred	$a = b = c$	$\alpha = \beta = \gamma = 90°$	NaCl, KCl, diamond, copper, zinc blende etc.
2.	Rhombohedral (Trigonal)	Primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	$NaNO_3, CaCO_3$, HgS, etc.
3.	Orthorhombic	Primitive, Face centred, Body centred, End centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Rhombic sulphur, $BaSO_4$ (baryta), $PbCO_3$ etc.
4.	Triclinic (most asymmetric)	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	$K_2Cr_2O_7, H_3BO_3, CuSO_4 \cdot 5H_2O$ etc.
5.	Monoclinic	Primitive, End centred	$a \neq b \neq c$	$\alpha = \gamma = 90°, \beta \neq 90°$	$Na_2SO_4 \cdot 10H_2O, Na_2B_4O_7 \cdot 10H_2O$, monoclinic S etc.
6.	Tetragonal	Primitive, Body centred	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	Cassiterite, white tin, rutile etc.
7.	Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	Mg, beryl, ZnO (zincite) PbI_2, graphite etc.

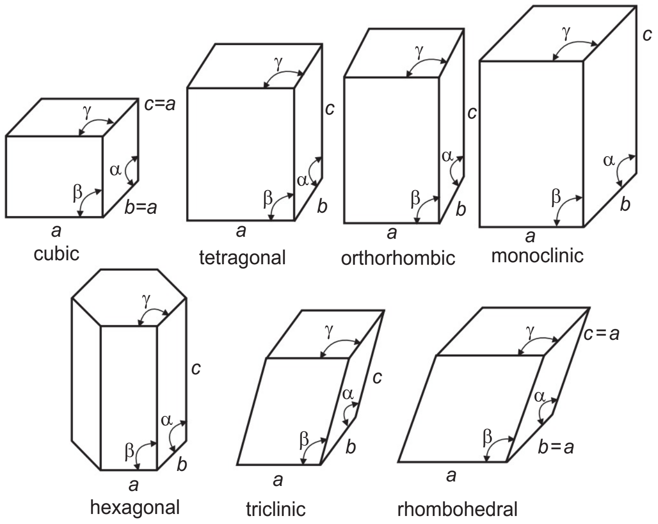


Fig. 1.5 Three dimensional primitive crystal systems

Caution Point *As there are 5 possible two dimensional lattice, similarly there are only 14 possible three dimensional lattices. These are called* Bravais lattices *(after the French mathematician who first described them).*

Sample **Problem 6** *Match box belongs to*

(a) *tetragonal system* (b) *orthorhombic system*
(c) *hexagonal system* (d) *triclinic system*

Interpret (*b*) In match box, all the sides are unequal, *i.e.,*

$$a \neq b \neq c$$

but all the angles are 90°, *i.e.,* $\alpha = \beta = \gamma = 90°$.

Thus, it belongs to orthorhombic crystal system.

Types of Unit Cells

The unit cells are of the following two types

(a) Simple or primitive unit cell

(b) Non-primitive or multiple unit cell.

(a) Simple or Primitive Unit Cell

The **simplest unit cell** has the lattice points at the corners or in other words we can say, when particles are present only at the corners of the unit cell, it is called simplest type. It is denoted by *P*.

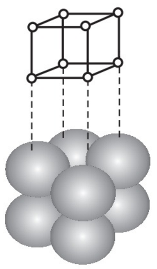


Fig. 1.6 (a) Simple cubic unit cell

(b) Non-primitive or Multiple Unit Cell

When a unit cell contains more than one additional lattice points (additional to those defined in simple unit cell), it is called non-primitive or multiple unit cell. It is further sub-divided into

(i) Face-centred unit cell (*F*)

(ii) End face-centred unit cell (*C*)

(iii) Body-centred unit cell (*I*)

When the particles or lattice points are present at the centre of each face in addition to particles at the corner, the unit cell is called **face centred.**

When in the unit cell, besides the points or particles at the corner of cell, the points or particles are located at the centre of any two parallel faces of the unit cell, it is called **side-centred** or **end face centred unit cell.**

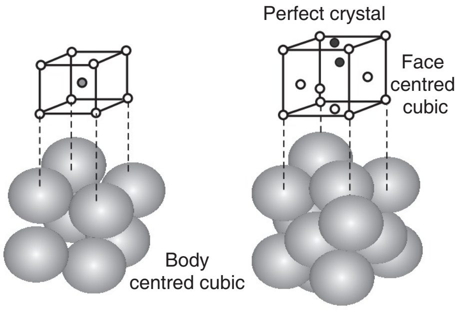


Fig. 1.6 (b) Multiple unit cell types

In a unit cell when, besides the points or particles at the corner there is single particle located at the centre within its body; it is called body centred arrangement and the unit cell is called **body centred unit cell.**

Effective Number of Atoms in a Unit Cell

In a crystal, atoms located at the corner and face center of a unit cell are shared by other cells and only a portion of such an atom actually lies within a given unit cell.

1. A point that lies at the corner of a unit cell is shared among eight unit cells and therefore, only one eighth of each such point lies within the given unit cell.
2. A point along an edge is shared by four unit cells and only one-fourth of it lies within any one cell.
3. A face-centred point is shared by two unit cells and only one half of it is present in a given unit cell.
4. A body-centred point lies entirely within the unit cell and contributes one complete point to the cell. Thus,

Table 1.4 **Contribution of Different Atoms per Unit Cell**

Type of lattice point	Contribution to one unit cell (in Cubic Unit Cell)
Corner	1/8
Edge	1/4
Face centre	1/2
Body centre	1

Calculation of Number of Atoms in Different Unit Cells

In different types of unit cell, the number of atoms per unit cell can be calculated as follows

(a) Primitive or Simple Cubic Unit Cell

From the given figure, it is clear that here eight atoms which are present at 8 corners are shared by 8 unit cells. Hence, contribution of each atom present at the corner $= \frac{1}{8}$

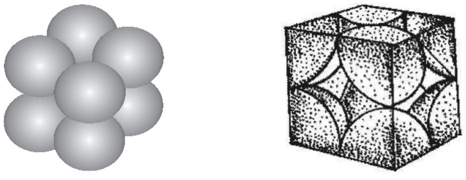


Fig. 1.7 Simple cubic unit cell

Thus, total number of atoms present per unit cell $= 8 \times \frac{1}{8}$

$= 1$ atom

(b) Body Centred Cubic Unit Cell

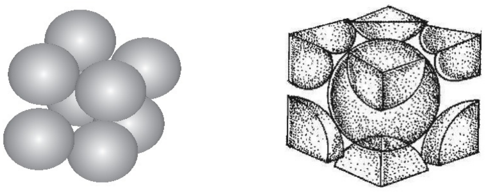


Fig. 1.8 Body centred cubic unit cell

From the above figure, it is clear that this unit cell has 1 complete atom additional to that present in simple cubic unit cell. Hence, the total number of atoms present $= 1 + 1 = 2$ atoms per unit cell.

(c) Face Centred Cubic Unit Cell

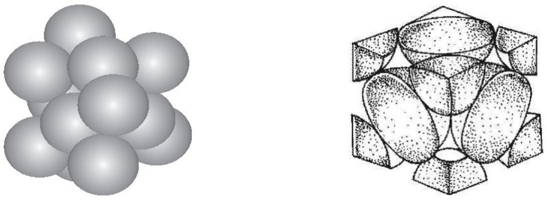


Fig. 1.9 Face centred cubic unit cell

From the above figure it is clear that here

(i) 8 corner atoms $\times \frac{1}{8}$ atoms per unit cell = 1 atom

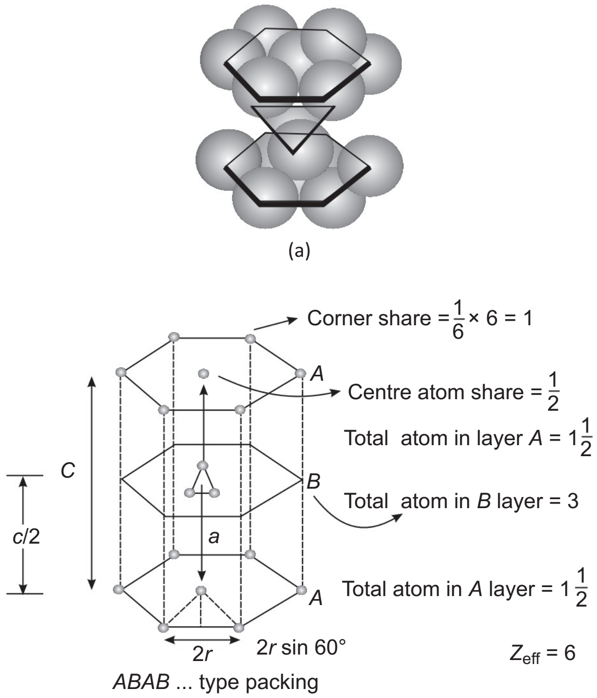
(ii) 6 face atoms (with representation of 1/2 atom per face) per unit cell, thus $6 \times \frac{1}{2} = 3$ atoms

Total atoms present per unit cell = 1 + 3 = 4 atoms

(d) End Face Centred Cubic Unit Cell

Similarly, end face centred cubic unit cell have 1 instead of 3 face atoms present in face centred cubic unit cell. Rest distribution is same (because here only 2 parallel faces have one atom each at the centre of face shared by two unit cells). Thus, the total number of atoms present per unit cell here is $1 + 1 = 2$ atoms per unit cell.

(e) Hexagonal Close Packed Unit Cell



(a)

(b)

Fig. 1.10 Hexagonal close packed unit cell

Three atoms in B layer exclusively belong to this prism (*i.e.,* in the body centre of hexagonal)

In layer A

1. One atom in the centre is shared by two prisms.
2. There are 12 atoms in two A layers and each is shared amongst six prisms of this type $= 12 \times \frac{1}{6} = 2$

   Effective number of atoms in both A layers = 2 + 1 = 3.
3. Effective number of atoms in two A layers + Effective number of atoms in B layer = 3 + 3 = 6

   ∴ Effective number of atoms in hcp = 6

   Alternatively

   Effective number of atoms unit cell $= 12 \times \frac{1}{6}$ (corner) (from both A layer)

   $+ 2 \times \frac{1}{2}$ (in the centre of both A layers)

   + 3 (in the body in layer B) = 6

Table 1.5 **Number of Atoms in Different Unit Cells**

S. No.	Cubic unit cell	n_c	n_f	n_i	Total atoms in unit cell
1.	Simple cubic	8	0	0	1
2.	Body-centred cubic	8	0	1	2
3.	Face centred cubic	8	6	0	4

General Formula for Calculating Number of Atoms

The number of atoms per unit cell can also be determined by the simplest relation

$$Z = \frac{n_c}{8} + \frac{n_f}{2} + \frac{n_i}{1}$$

where, n_c = number of atoms at the corners of the cube

n_f = number of atoms at six faces of the cube

n_i = number of atoms inside the cube

Sample **Problem 7** *A compound formed by elements X and Y has a cubic structure in which X atoms are at the corner of the cube and Y atoms are at the face centres. One atom X is missing from the corner. The formula of the compound is*

(a) X_2Y_4 (b) X_7Y_{24}
(c) $X_{24}Y_7$ (d) X_7Y_3

Interpret (*b*) In a cube there are 8 atoms. Since, one atom *X* is missing from the corner.

The number of *X* atoms at the corners = 7

$$\text{Number of effective } X \text{ atoms} = 7 \text{ corners} \times \frac{1}{8} \text{ per corner atom share}$$

$$= \frac{7}{8} \text{ atom/unit cell}$$

$$\text{Number of effective } Y \text{ atoms} = 6 \text{ faces} \times \frac{1}{2} \text{ per face atom share}$$

$$= 3 \text{ atoms/unit cell}$$

Thus, formula of the compound is $X_{7/8}Y_3$.

Simplifying = X_7Y_{24}.

Sample **Problem 8** *If in the above sample problem, all the atoms are removed from one of the faces of the cube containing atoms at the corners, find the formula of the compound.*

(a) X_7Y_{24} (b) X_6Y_{24} (c) X_3Y_{20} (d) Y_3Y_5

Interpret (c) Atoms removed from one face of the cube, containing all atoms at corners = 4 corners + 1 face-centred atom

= 5 atom/unit cell

Corner atom left = 7 − 4 = 3 atoms at corner

Face-centre atom left = 6 − 1 = 5 atoms at face centre.

Formula of compound

$$Z_{\text{eff }(X)} = \frac{3}{8}, \; Z_{\text{eff }(Y)} = \frac{5}{2}.$$

Formula $X_{3/8}Y_{5/2}$

Simplifying = X_3Y_{20}

1.5 Packing of Particles in a Solid

To understand the packing of particles in a crystal, it is assumed that these particles are hard spheres of identical size. *The number of spheres surrounding a particular sphere is called the coordination number* (CN) *of that sphere i.e.,* in simple words, coordination number is the number of atoms or ions or molecules surrounding a particular atom in a crystal lattice.

Caution Point *In crystals with directional bonds, coordination number is lower than that of crystals with non-directional bonds such as metals and ionic compounds.*

The packing can be seen in one of the following ways

Close Packing in One Dimension

It is the simplest close packing here spheres are placed in a horizontal row, touching each other as shown below

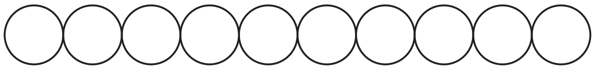


Fig. 1.11 One dimensional packing of spheres

Thus, an edge of crystal is formed.

Here, each sphere is in contact of two other spheres, so its coordination number is 2.

Close Packing in Two Dimensions

When the above written rows combine, two types of combinations are possible

(i) With a horizontal as well as vertical alignment as shown below

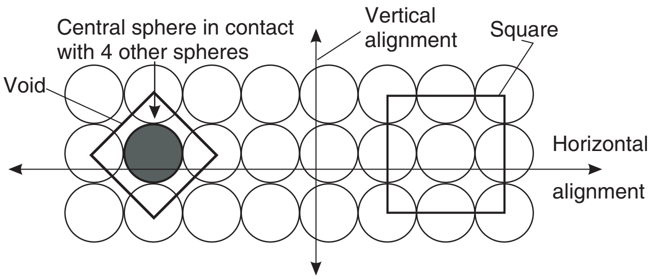


Fig. 1.12 Square close packing of spheres in two dimensions

Here, particles form square and the packing is called **square close packing.** The coordination number of each sphere in such packing is 4. The empty space between the particles in a close packing is called void as seen above.

(ii) With the particles in every next row are placed in the depressions between the particles of first row. The particles of third row will show vertical alignment with the first row as shown below

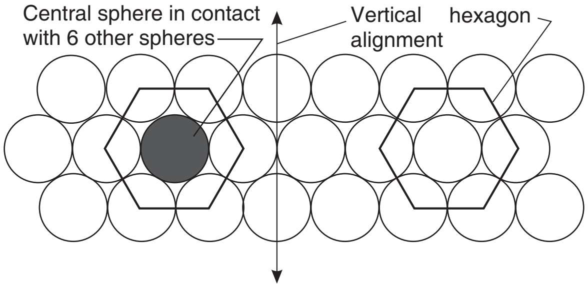


Fig. 1.13 Hexagonal close packing of spheres in two dimensions

Such a packing gives hexagonal pattern, thus called **hexagonal close packing.** Here coordination number is 6.

Caution Point *The hexagonal close packing is more efficient than square close packing as here more space is occupied by spheres.*

Close Packing in Three Dimensions

As among two dimensional packings hexagonal close packing is more efficient, the three dimensional packings are based upon the hexagonal close packing patterns.

Three dimensional close packing from two dimensional square close packed layers, results in the formation of simple cubic lattice.

The two dimensional hexagonal close packing observation shows two types of voids in it as shown below

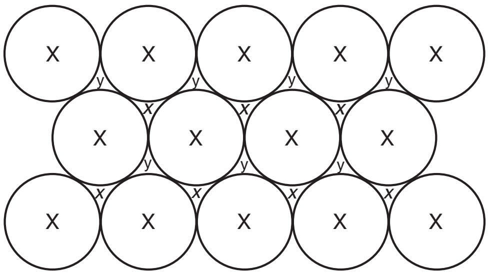


Fig. 1.14 Two dimensional hexagonal close packing

Placing of Second Layer

Keeping both the types of voids in mind, in three dimensional packing, the IInd row of spheres is placed in such a way that its spheres find place above the voids marked x of first row (voids marked y left unoccupied) as shown in the figure

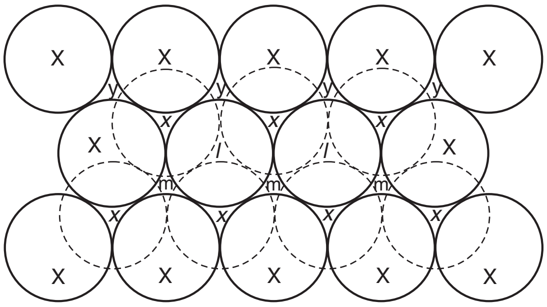


Fig. 1.15 A stack of two layers of close packed spheres and voids

In the second layer, two types of voids are seen again

(i) Those which lie above the spheres of first layer (marked l in above diagram).

(ii) Those which lie above the voids y of first layer (marked m in above diagram).

Placing of Third Layer

There are two possible ways by which the third layer can be placed over the second.

These two ways are as follows

(i) When the third layer is placed in such a way that the spheres cover the l voids of second layer, a three dimensional cubic packing is obtained where the spheres in every 3rd or alternate layer are vertically aligned *i.e.,* 3rd layer is directly above Ist or 4th layer is directly above 2nd. The arrangement is also called as $A\,B\,A\,B$ ...., if we designate first layer as A and second layer as B as seen as below

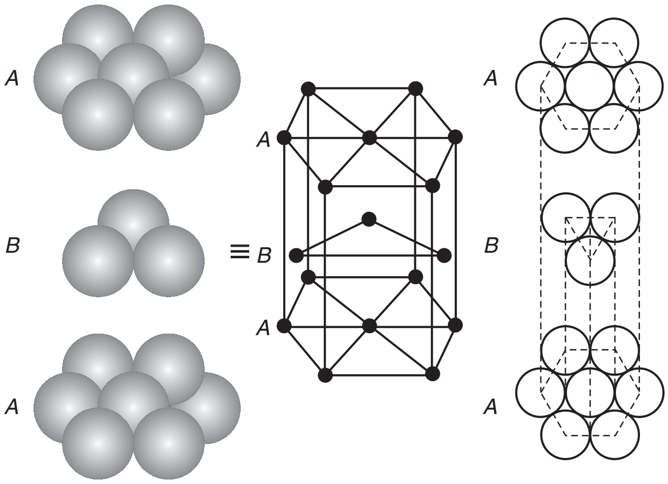


Fig. 1.16 Hexagonal close packing in three dimensions

Such a $A\,B\,A\,B$ ... packing is called **hexagonal close packing** (three dimensional) *e.g.,* Be, Mg crystals, etc.

(ii) Consider the same arrangement described above till 2nd layer, and if a 3rd layer is placed in such a way that spheres cover the void m of second layer, a layer different from A and B described above, is seen. Let us call it as layer C. Continuing further, if the 4th layer is placed over the 3rd layer in such a way that each sphere of it align vertically with the first layer, the packing is called **cubic close packing** with *ABC*, *ABC* ... pattern of layers as shown in the figure

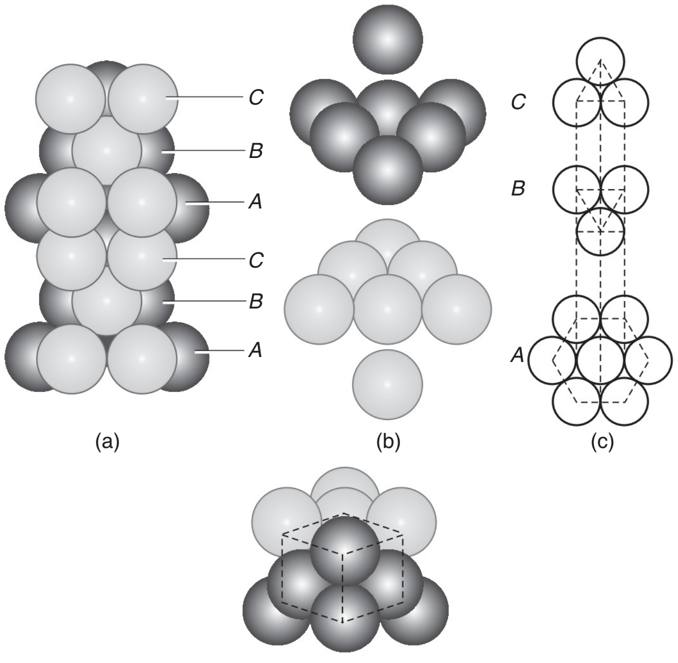


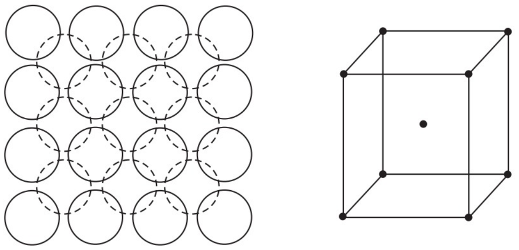
Fig. 1.17 Cubic close packing in three dimensions

The packing is also called face centred cubic packing (fccp). The example of fccp include Fe, Ni, Cu, Ag, Au and Al, etc.

Both the above patterns are almost equally efficient and occupy maximum possible space i.e., about 74% *of the available volume with variable coordination numbers from* 4 *to* 12*, i.e.,* 4, 6, 8 *and* 12.

Body Centred Cubic Close Packing

Body centred cubic (bcc) arrangement is obtained when the spheres of the first layer are opened up and the spheres of second layer are placed at the top of the hollows in the first layer. The spheres of the third layer are placed exactly above the spheres of first layer.



(a) bcc packing of spheres (b) bcc arrangement

Fig. 1.18 Body centred close packing in three dimensions

From the figure, it is clear that each sphere in this arrangement is in contact with 8 spheres, thus, the coordination number is 8. Here, the space occupancy is only 68%. *e.g.,* Li, Na, K, Rb, Cs, etc.

Packing Pattern of Different Metals

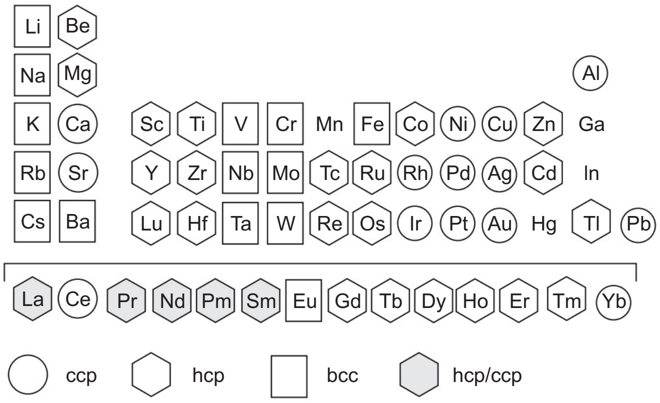


Fig. 1.19 Packing pattern among the metals

Caution Point *The space occupied by hard spheres in fcc and hcp is* 74%*, in bcc it is* 68%*, in simple cubic it is* 52% *and in diamond it is* 34%*. Thus, only fcc and hcp are close packed structures.*

Voids

In closely packed structures, the empty space is called interstitial site or void. The void can be a simple triangular space in the case of two dimensional packing and called the **trigonal void.**

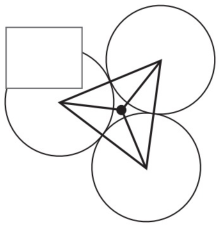


Fig. 1.20 Trigonal void

In three dimensional close packing patterns, the voids can be

(a) Tetrahedral (b) Octahedral

(a) Tetrahedral Void

A tetrahedral void is a simple triangular space surrounded by 4 spheres as shown below

Location and number of tetrahedral voids Number of ions (or atoms) in a close packed structure (fcc or ccp)

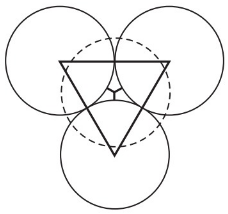


Fig. 1.21 Tetrahedral void

$$= 8 \text{ corner} \times 1/8 \text{ per corner share} + 6 \text{ faces} \times 1/8 \text{ per face share}$$
$$= 1 + 3 = 4/\text{unit cell}$$

2 tetrahedral voids are present on each body diagonal of a cube.

$\therefore$ Number of tetrahedral voids $= 2 \times 4$ body diagonal $= 8/\text{unit cell}$

or the number of tetrahedral voids in a close packed structure $= 8/\text{unit cell}$ or $8/4 = 2/\text{atom}$.

(b) Octahedral Void

An octahedral void is a double triangular void surrounded by 6 spheres as shown below

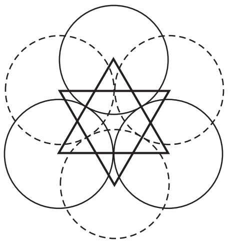


Fig. 1.22 Octahedral void

Location and number of octahedral void Octahedral voids are present on the edge centre of a cube and at body centre of a cube.

$\therefore$ Number of octahedral void $= 12$ edge centre $\times \frac{1}{4}$ per edge centre share $+ 1$ body centre
$$= 3 + 1 = 4/\text{unit cell}$$

Thus, number of octahedral void $= 4/\text{unit cell}$ or
$$\frac{4}{4} = 1/\text{atom}$$

The sum of radius of the atom of host lattice (r_h) and the radius of atom occupying void $(r_{f(t)}$ or $r_{f(0)})$ is given by

For octahedral void, $r_h + r_{f(0)} = \dfrac{a}{2}$

and for tetrahedral void, $r_h + r_{f(t)} = \dfrac{\sqrt{3}a}{4}$

The sizes of above written voids can be seen in increasing order as

Trigonal < Tetrahedral < Octahedral

The actual sizes of the voids can be calculated on the basis of sizes of spheres involved in the formation of solids.

1. The size of trigonal void is 0.115 times of the radius of bigger sphere involved.
2. The size of tetrahedral void is 0.2247 times of the radius of bigger sphere involved.
3. The size of octahedral void is 0.414 times of the radius of bigger sphere involved.

In a closely packed structure containing X spheres (i.e., atoms, molecules or ions), there are 8X trigonal, 2X tetrahedral and X octahedral voids.

Sample Problem 9 *The total number of tetrahedral voids in the face centred unit cell is* **[NCERT Exemplar]**

(*a*) 6 (*b*) 8 (*c*) 10 (*d*) 12

Interpret (*b*) In fcc unit cell.

Number of atoms = 4

$\therefore$ Total number of tetrahedral voids $= 2 \times$ number of atoms $= 2 \times 4 = 8$

Sample Problem 10 *A compound is formed by two elements M and N. The element N forms ccp and atoms of M occupy $\frac{1}{3}$rd of tetrahedral voids. What is the formula of the compound?* **[NCERT]**

(*a*) MN_3 (*b*) M_3N (*c*) M_3N_2 (*d*) M_2N_3

Interpret (*d*) To solve such problems follow the following steps

Step I Find the number of tetrahedral voids as number of tetrahedral voids $= 2 \times$ number of atoms present in the lattice.

Step II Calculate the number of atoms (or ratio) of elements *M* and *N* as a chemical formula represents the number of atoms of different elements present in a compound. Derive the formula.

Suppose atoms of element *N* present in ccp $= x$

Then, number of tetrahedral voids $= 2x$

Since, $\frac{1}{3}$ rd of the tetrahedral voids are occupied by atoms of element *M*.

Therefore, number of atoms of element $M = \dfrac{1}{3} \times 2x = \dfrac{2x}{3}$

Ratio of $M : N = \dfrac{2x}{3} : x = 2 : 3$

Hence, formula of the compound $= M_2N_3$.

Sample Problem 11 *In a crystalline solid, having formula AB_2O_4, oxide ions are arranged in cubic close packed lattice while cations A are present in tetrahedral voids and cations B are present in octahedral voids. The percentage of tetrahedral voids occupied by A is*

(*a*) 50% (*b*) 25%
(*c*) 75% (*d*) 12.5%

Interpret (*d*) In a cubic close packed lattice of oxide ions, there would be two tetrahedral and one octahedral void per oxide ion.

Since, the formula shows the presence of 4 oxide ions, the number of tetrahedral voids is eight and that of octahedral voids is four.

Out of the eight tetrahedral voids one is occupied by *A*.

$\therefore$ Percentage of tetrahedral voids occupied $= \dfrac{1}{8} \times 100 = 12.5\%$

Hot Spot 1

CALCULATIONS Involving Unit Cell Parameters

Questions based on unit cell parameters like radius, edge length, packing efficiency, empty space and density have been frequently seen in JEE Main examination which reveal the importance of the topic for this examination. The questions of this topics are simple formula based and their level may vary from easy to average.

1. Relation Between Radius (r) and Edge Length (a)

(a) **For Simple Cubic Unit Cell**

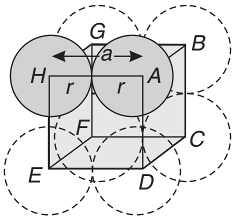


Fig. 1.23 Simple cubic unit cell

$$a = 2r$$

or $a = r_+ + r_-$ (if r_+ and r_- are not equal)

(r_+ radius of cation and r_- radius of anion)

or $\boxed{r = \frac{a}{2}}$

(b) **For Body Centred Cubic Arrangement,**

In ΔEFD,

$$b^2 = a^2 + a^2 = 2a^2$$

$$b = \sqrt{2}a$$

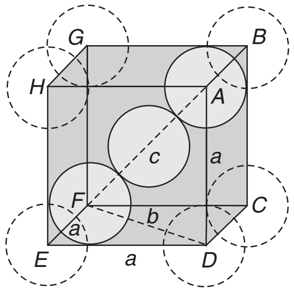


Fig. 1.24 Body centred cubic unit cell

Now in ΔAFD

$$c^2 = a^2 + b^2 = a^2 + 2a^2 = 3a^2$$

$$c = \sqrt{3}a$$

Therefore, $\sqrt{3}a = 4r$ or $\sqrt{3}a = 2r_+ + 2r_-$ (if $r_+ \neq r_-$)

$$a = \frac{4r}{\sqrt{3}}$$

Also we can write, $\boxed{r = \frac{\sqrt{3}}{4}a}$

(c) **For fcc Arrangement**

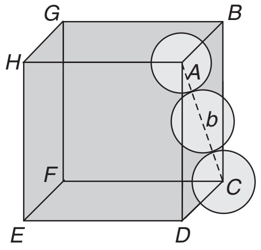


Fig. 1.25 Cubic closed pack unit cell

In ΔABC

$$AC^2 = BC^2 + AB^2$$

$$b^2 = a^2 + a^2 = 2a^2$$

or $b = \sqrt{2}a$

If r is the radius of the sphere,

we find

$$b = 4r = \sqrt{2}a$$

or $2r_+ + 2r_- = \sqrt{2}a$ (if $r_1 \neq r_-$)

or $a = \frac{4r}{\sqrt{2}} = 2\sqrt{2}\,r$

we can also write, $\boxed{r = \frac{a}{2\sqrt{2}}}$

(d) **For hcp Arrangement**

Base area of hexagon $= 6\sqrt{3}r^2$

Height of hexagon $= 4r \times \sqrt{\frac{2}{3}}$

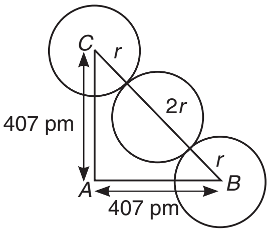
$= 2a \times \sqrt{\frac{2}{3}}$ $(\because\ a = 2r)$

Volume of unit cell of hexagon $= 24\sqrt{2}r^3$

Sample **Problem 12** Ag *metal crystallises in a cubic closest packed arrangement with the edge of the unit cell having a length a* = 407 *pm. The radius of the similar atom is*

(a) 203.5 (b) 176.23
(c) 143.9 (d) 287.7

Interpret (c) $AC^2 + AB^2 = BC^2$



$$a^2 + a^2 = (4r)^2$$

$$r = \frac{a}{\sqrt{8}}$$

$$= \frac{407}{\sqrt{8}}$$

$$= 143.9 \text{ pm}$$

2. Packing Fraction

It is the ratio of total volume of spheres to the volume of the unit cell. In other words, it shows the fraction of volume occupied by spheres.

$$\text{Packing density} = \frac{\text{total volume of spheres}}{\text{volume of the unit cell}}$$

(i) In a **simple cubic unit cell**, packing fraction

$$= \frac{4/3\pi r^3}{8r^3} \times 100 = 52.4\%$$

Here, $\frac{4}{3}\pi r^3$ = volume of one sphere and

for sc,

no. of atoms = 1

$a = 2r$

∴ $a^3 = 8r^3$ = volume of cube (unit cell)

(ii) In **hexagonal close packing** and **face centred cubic** structure, packing fraction $= \frac{16\pi r^3/3}{32 r^3/\sqrt{2}} \times 100 = 74\%$

Here, $\frac{32}{\sqrt{2}} r^3$ = volume of the unit cell

$$\left[\because\ a = \frac{4r}{\sqrt{2}} \text{ and } a^3 = \left(\frac{4r}{\sqrt{2}}\right)^3\right]$$

$\frac{16}{3}\pi r^3$ = total volume of spheres

$$\left[\text{fcc unit cell have 4 particle } \therefore 4 \times \frac{4}{3}\pi r^3\right]$$

(iii) In **body-centred** cubic structure,

$$\text{packing fraction} = \frac{\frac{8}{3}\pi r^3}{\frac{64r^3}{3\sqrt{3}}} \times 100 = 68\%$$

Here, $\frac{64r^3}{3\sqrt{3}}$ = volume of the unit cell

$$\left[\because\ a = \frac{4r}{\sqrt{3}} \text{ and } a^3 = \left(\frac{4r}{\sqrt{3}}\right)^3\right]$$

$\frac{8}{3}\pi r^3$ = total volume of spheres as bcc have two atoms $\left(\therefore 2 \times \frac{4}{3}\pi r^3\right)$

(iv) In hcc, packing fraction $= \frac{6 \times \frac{4}{3}\pi r^3}{24\sqrt{2}\, r^3} = 74\%$

Sample Problem 13 *The percentage of empty space in a body centred cubic arrangement is* **[NCERT Exemplar]**

(a) 74 (b) 68 (c) 32 (d) 26

Interpret (c) In case of body centred cubic arrangement,

$$\text{packing fraction} = \frac{\frac{8}{3}\pi r^3}{\frac{64r^3}{3\sqrt{3}}} \times 100$$

$$= 68\%$$

∴ Fraction of empty space = 100 − 68 = 32%

Sample Problem 14 *The density of solid argon is 1.65 g/mL at −233°C. If the argon atom is assumed to be sphere of radius* 1.54×10^{-8} *cm, what percentage of solid argon is apparently empty space? (At. wt. of* Ar = 40)

(a) 54% (b) 82%

(c) 62% (d) 48%

Interpret (c) Volume of one atom of Ar $= \frac{4}{3}\pi r^3$

Also, number of atoms in 1.65 g per mL $= \frac{1.65}{40} \times 6.023 \times 10^{23}$

∴ Total volume of all the atoms of Ar in solid state

$$= \frac{4}{3}\pi r^3 \times \frac{1.65}{40} \times 6.023 \times 10^{23}$$

$$= \frac{4}{3} \times \frac{22}{7} \times (1.54 \times 10^{-8})^3 \times \frac{1.65}{40} \times 6.023 \times 10^{23}$$

$$= 0.380 \text{ cm}^3$$

Volume of solid Ar = 1 cm^3

$$\therefore \quad \%\text{ empty space} = \frac{1 - 0.381}{1} \times 100 = 62\%$$

3. Density of the Crystal

If we know the type of crystal structure possessed by the cubic crystal, so that the number of particles per unit cell are known and the edge length for it is known by X-ray studies, the density of the crystal can be determined. It is given by the formula

$$d = \frac{Z \times M}{a^3 \times N_A \times 10^{-3}} \text{ g/cm}^3$$

$$d = \frac{Z \times M}{a^3 \times N_A} \text{ kg/cm}^3$$

Here, Z = Number of particles present per unit cell *i.e.,* 1 for simple, 2 for bcc, 4 for fcc

M = Atomic mass of element

a = Edge of the unit cell

N_A = Avogadro number

For ionic crystals, the formula used is same and the difference lies in

1. Z = number of formula units in one unit cell.
2. M = formula mass (molecular mass) of the compound.
3. a = edge which is $2x$ distance between Na$^+$ and Cl$^-$ in NaCl crystal.

Sample **Problem 15** *An element with molar mass* 2.7×10^{-2} *kg mol*$^{-1}$ *forms a cubic unit cell with edge length 405 pm. If its density is* 2.7×10^{3} *kg m*$^{-3}$ *, what is the nature of the cubic unit cell?* **[NCERT Exemplar]**

(*a*) *sc* (*b*) *fcc* (*c*) *bcc* (*d*) *end centred*

Interpret (*b*) To solve out such problems, first calculate the number of atoms present in the unit cell $(Z) = \dfrac{d \times a^3 \times N_A}{M}$ and then find the type of the cubic unit cell as $Z = 1$ for sc, 2 for bcc and 4 for fcc as.

Density $(d) = \dfrac{Z \times M}{a^3 \times N_A}$ so, $Z = \dfrac{d \times a^3 \times N_A}{M}$

Given, $M = 2.7 \times 10^{-2}$ kg mol^{-1}

$a = 405$ pm $= 405 \times 10^{-12}$ m $= 4.05 \times 10^{-10}$ m

$d = 2.7 \times 10^{3}$ kg m^{-3}

$N_A = 6.022 \times 10^{23}$ mol^{-1}

Hence,

$$Z = \frac{(2.7 \times 10^{3}\ \text{kg m}^{-3})\,(4.05 \times 10^{-10}\text{m})^3 \times (6.022 \times 10^{23}\ \text{mol}^{-1})}{(2.7 \times 10^{-2}\ \text{kg mol}^{-1})}$$

$= 3.99 = 4$

Since, there are four atoms per unit cell, the cubic unit cell must be **face-centred**.

Sample **Problem 16** *Niobium crystallises in body-centred cubic structure. If density is* 8.55 *g cm*$^{-3}$ *calculate atomic radius of niobium using its atomic mass* 93 *u.* **[NCERT Exemplar]**

(*a*) 200 *pm* (*b*) 185 *pm*
(*c*) 143 *pm* (*d*) 129 *pm*

Interpret (*c*) Since, we know density, but not radius and radius (*r*) of unit cell is related to *a* for bcc structure as $r = \dfrac{\sqrt{3}\,a}{4}$. So,

We first calculate the edge length of unit cell and then calculate the radius of unit cell

Step I **Calculation of edge length of unit cell** (*a*)

Atomic mass of the element $(M) = 93$ g mol^{-1}

Number of particles in bcc type unit cell $(Z) = 2$

$$\text{Mass of the unit cell} = \frac{Z \times M}{N_A} = \frac{2 \times (93\ \text{g mol}^{-1})}{(6.022 \times 10^{23}\ \text{mol}^{-1})}$$

$= 30.89 \times 10^{-23}$ g

Density of unit cell $(d) = 8.55$ g cm^{-3}

$$\text{Volume of unit cell } (a^3) = \frac{\text{Mass of unit cell}}{\text{Density of unit cell}}$$

$$= \frac{(30.89 \times 10^{-23}\,\text{g})}{(8.55\ \text{g cm}^{-3})}$$

$= 36.16 \times 10^{-24}$ cm^3

Edge length of unit cell $(a) = (36.13 \times 10^{-24}\ \text{cm}^3)^{1/3}$

$= 3.31 \times 10^{-8}$ cm

Step II **Calculation of radius of unit cell** (*r*)

For bcc structure, $r = \dfrac{\sqrt{3}\,a}{4}$

$$= \frac{\sqrt{3} \times (3.31 \times 10^{-8}\ \text{cm})}{4}$$

$= 1.43 \times 10^{-8}$ cm

$= 143$ pm

1.6 Structures of Ionic Crystals

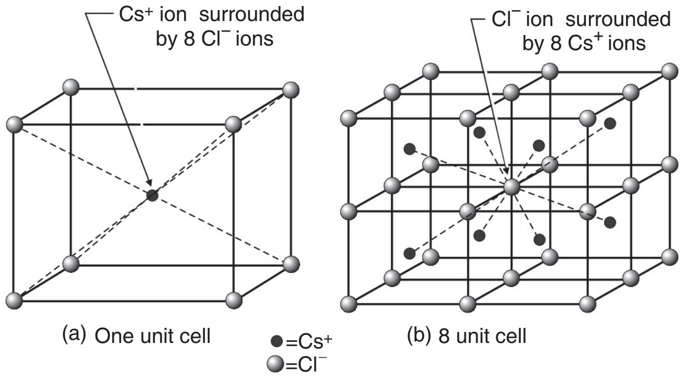
The ionic crystals may be

(i) *AB* type structures,

(ii) AB_2 or A_2B type structures

AB Type Ionic Crystals

The *AB* type structures designate equality in number of cations and the number of anions. The example of this type of structures include NaCl with coordination number 6–6, CsCl with coordination number 8–8 and ZnS with coordination number 4–4.



(a) One unit cell (b) 8 unit cell

Fig. 1.26 Structure of CsCl (8 : 8 coordination)

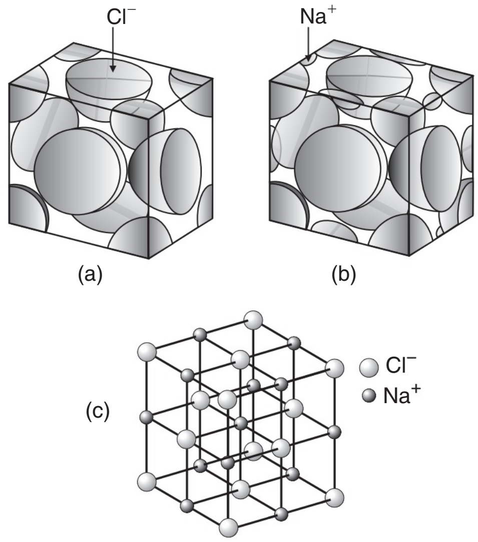


Fig. 1.27 The sodium chloride structure (6 : 6 coordination) : (a) the fcc Cl^- ions array (b) The Na^+ ions enter the voids (c) the resulting two interpenetrating arrays

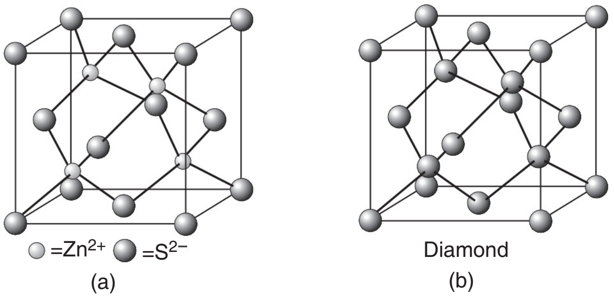
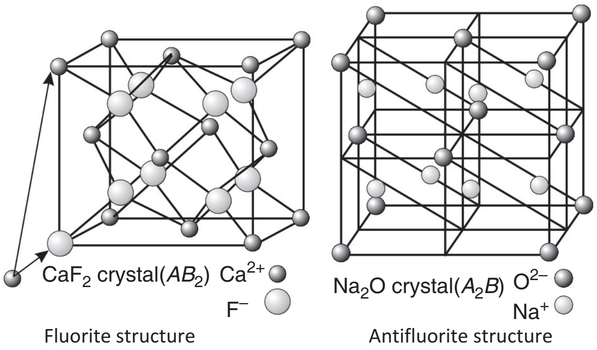


Fig. 1.28 (a) ZnS structure (b) Diamond structure
Both structures are identical (4 : 4 coordination)

AB_2 or A_2B Type Ionic Crystals

The AB_2 or A_2B type of ionic crystals contain the ions in the ratio 1 : 2 or 2 : 1 respectively. *e.g.*, CaF_2 popularly called to have **fluorite structure** with other examples like SrF_2, BaF_2, PbF_2 and $BaCl_2$, etc. The coordination number of Ca^{2+} in CaF_2 is 8 while that of F^- is 4. On the contrary, Na_2O have **antifluorite structure** *i.e.*, here the place of cations is occupied by anions and *vice-versa*.



Fluorite structure Antifluorite structure

Fig. 1.29 Fluorite and antifluorite structure

Caution Point *Pressure and temperature also influence the structure of ionic solids. The structures of chlorides, bromides and iodides of sodium, potassium and rubidium having* 6 : 6 *coordination at normal temperature and pressure. It will change to* 8 : 8 *coordination like* CsCl *structure at high pressure, and reverse takes place at high temperature.*

Sample Problem 17 MgO *has a structure of* NaCl, *the coordination number of* O^{2-} *in* MgO *is*

(*a*) 6 (*b*) 3 (*c*) 12 (*d*) 8

Interpret (*a*) Since MgO have NaCl (rock salt) structure, and in NaCl the coordination number of ions are 6 and 6 respectively. Thus, in MgO, O^{2-} also have coordination number 6.

Remember that in the ionic crystals, the bigger ions (usually anions) form the close packed structure and the smaller ion (usually cation) occupy the voids. *e.g.*,

Table 1.6 **Different Ionic Crystals**

Ionic crystal type	Cations occupy	Anions form
NaCl	All octahedral voids	fcc unit cell
CsCl	Body centre	Simple cubic unit cell
ZnS	Alternate tetrahedral voids	fcc unit cell
CaF_2	Alternate body centre	Simple cubic
Na_2O	All tetrahedral sites	fcc unit cell

Sample Problem 18 *In which of the following structures coordination number for cations and anions in the packed structure will be same?* **[NCERT Exemplar]**

(*a*) Cl^- *ion form fcc lattice and* Na^+ *ions occupy all octahedral voids of the unit cell*

(*b*) Ca^{2+} *ions form fcc lattice and* F^- *ions occupy all the eight tetrahedral voids of the unit cell*

(*c*) O^{2-} *ions form fcc lattice and* Na^+ *ions occupy all the eight tetrahedral voids of the unit cell.*

(*d*) S^{2-} *ions form fcc lattice and* Zn^{2+} *ions go into alternate tetrahedral voids of the unit cell*

Interpret (a) NaCl is 6 : 6 coordinated crystal, thus in it coordination number of cations = coordination number of anion.

Note CaF_2 is 8 : 4, Na_2O is 4 : 8 and ZnS is 4 : 4 coordinated crystals.

Sample Problem 19 *Which of the following is not true about the ionic solids?* **[NCERT Exemplar]**

(*a*) *Bigger ions form the close packed structure*

(*b*) *Smaller ions occupy either the tetrahedral or the octahedral voids depending upon their size*

(*c*) *Occupation of all the voids is not necessary*

(*d*) *The fraction of octahedral or tetrahedral voids occupied depends upon the radii of the ions occupying the voids*

Interpret (*d*) Fraction of voids depends upon the number of constituent particles.

Other given statements are true.

Structure of Diamond

Solids which follow the structure of diamond are called diamond cubic. Diamond has fcc structure with four more atoms that are found to be present in the alternate tetrahedral voids.

So, Z_{eff} of C-atoms in diamond cubic

$$= Z_{\text{eff}} \text{ in fcc unit cell} + Z_{\text{eff}} \text{ in alternate tetrahedral voids}$$

$$= \underbrace{\left[\frac{1}{8}\times 8+\frac{1}{2}\times 6\right]}_{\text{fcc unit cell}} + \underbrace{[1\times 4]}_{\text{Alternate TV's}} = 8$$

The C-atom in tetrahedral voids touches its four surrounding atoms (nearest neighbours), so the coordination number = 4.

The carbon atoms in an fcc lattice do not touch atoms at all. But C-atoms which are present in tetrahedral voids touch the surrounding four atoms. So, the centre-to-centre distance between two C-atoms is

$$2r = \frac{\sqrt{3}}{4}a,$$

where a is the length of the unit cell and r is the radius of C-atom.

Packing Efficiency (PE) of Diamond Cubic (dc)

$$\text{PE} = \frac{Z_{\text{eff}} \times \text{Volume of C-atom}}{a^3} \times 100$$

$$= \frac{8\times\frac{4}{3}\pi r^3 \times 100}{a^3}$$

$$= \frac{8\times\frac{4}{3}\pi\left(\frac{\sqrt{3}}{8}\right)^3 a^3 \times 100}{a^3} \qquad \left(\because r = \frac{\sqrt{3}a}{8}\right)$$

$$= \frac{32}{3}\pi\left(\frac{\sqrt{3}}{8}\right)^3 \times 100 = 34\%$$

Germanium, silicon, and grey tin also crystallize in the same way as diamond does.

Spinel Structures

Spinels are the compounds which have two different cations A^{2+} and B^{3+} and oxide (O^{2-}) as the anion, with the general formula $A^{2+}B_2^{3+}O_4^{2-}$.

Caution Point *Many substances of the type* $(A^{4+}B_2^{2+}O_4^{2-})$ *also have spinel-type structure.*

(a) Normal Spinel Structures

In such structures, O^{2-} anions form the fcc packing and 1/8th of tetrahedral voids are occupied by divalent metal ion A^{2+} and half of the octahedral voids are occupied by trivalent metal ions (B^{3+}).

Let Z_{eff} of O^{2-} anion in fcc packing = 1/atom

Number of tetrahedral void = 2/atom

Number of octahedral void = 1/atom

Therefore,

$$\text{Number of } A^{2+} \text{ ions} = \frac{1}{8}\times\text{tetrahedral void} = \frac{1}{8}\times 2 = \frac{1}{4}$$

$$\text{Number of } B^{3+} \text{ ions} = \frac{1}{2}\times\text{octahedral void} = \frac{1}{2}\times 1 = \frac{1}{2}$$

General formula $A^{2+}_{1/4}B^{3+}_{1/2}O^{2-}_{1}$

On simplifying, we get the formula AB_2O_4.

(b) Inverse Spinel Structures

In such structures, O^{2-} anions form the fcc packing and 1/8th of the tetrahedral voids are occupied by divalent metal ion A^{2+}. Trivalent metal ions B^{3+} are present in $\left(\frac{1}{8}\text{ th tetrahedral void} + \frac{1}{4}\text{ th octahedral void}\right)$

Let Z_{eff} of O^{2-} anion in fcc packing = 1/atom

Number of tetrahedral void = 2/atom

Number of octahedral void = 1/atom

Therefore,

$$\text{Number of } A^{2+} \text{ ions} = \frac{1}{8}\times\text{tetrahedral void} = \frac{1}{8}\times 2 = \frac{1}{4}$$

$$\text{Number of } B^{3+} \text{ ions} = \frac{1}{8}\times\text{tetrahedral void} + \frac{1}{4}\times\text{octahedral void}$$

$$= \frac{1}{8}\times 2 + \frac{1}{4}\times 1$$

$$= \frac{1}{4} + \frac{1}{4} = \frac{2}{4} = \frac{1}{2}$$

So, general formula

$$A^{2+}_{1/4}B^{3+}_{1/2}O^{2-}_{1}$$

Simplifying, formula = AB_2O_4.

Corrundum Structure

In this structure, O^{2-} anions form hcp and cations A^{3+} are present in two-third of the octahedral voids. The general formula of a compound is A_2O_3. Examples are Fe_2O_3, Al_2O_3, Cr_2O_3. From the formula, the ligancy of $(A^{3+} : O^{2-})$ in A_2O_3 is 3 : 2 or 6 : 4.

1.7 Radius Ratio Rules

The structure of many ionic solids can be accounted by considering the relative sizes of the cation and anion, and their relative numbers. By simple calculations, we can work out as how many ions of a given size can be in contact with a smaller ion. Thus, we can predict the coordination number from the relative size of the ions.

The ionic radius ratios (of cation and anion) play a very important role in giving clue to the nature of crystal structure of the ionic substance. This can be clear from the table given below

Table 1.7 **Coordination Number and Shape from Radius Ratio**

S.N.	Limiting radius ratio (r_+/r_-)	Coordination number	Shape	Structure type	Example
1.	Less than 0.225	2 or 3	Linear for 2, triangular planar for 3	same as shape	B_2O_3
2.	0.225 – 0.414	4	Tetrahedral	Sphalerite (ZnS)	CuCl, CuBr, CuI, HgS, BaS
3.	0.414 – 0.732	4 or 6	Square planar for 4 Octahedral for 6	NaCl	MgO, NaBr, CaS, MnO, KBr, CaO, AgCl
4.	0.732 or more	8	Cube	CsCl	CsI, CsBr, TlBr, NH_4Br

Sample Problem 20 *The radius of a divalent cation M^{2+} is 94 pm and that of divalent anion X^{2-} is 146 pm. Thus, $M^{2+}X^{2-}$ has*

(*a*) NaCl *structure* (*b*) *linear structure*
(*c*) CsCl *structure* (*d*) ZnS *structure*

Interpret (*a*) For $M^{2+}X^{2-}$,

$$\frac{r_+}{r_-} = \frac{94}{146} = 0.6438$$

Since, the radius ratio is in between 0.414 to 0.732, it has NaCl structure.

Sample Problem 21 *The structure of* TiCl *is similar to* CsCl. *The radius ratio in* TiCl *is*

(*a*) 0.155 – 0.225
(*b*) 0.225 – 0.414
(*c*) 0.414 – 0.732
(*d*) 0.732 – 1.000

Interpret (*d*) For CsCl structure, the radius ratio is 0.732 – 1.000. Thus, for TiCl, it is also 0.732 – 1.000

Check Point 2

1. The distance between the NaI and LiI is 0.007 nm and that between NaCl and LiCl is 0.03 nm. Suggest why there is such a small difference in internuclear distance between LiI and NaI as compared to that between LiCl and NaCl?
2. Explain in fcc arrangement, there are four atoms per unit cell.
3. Explain why the coordination number for bcc packing is 8?

1.8 Imperfections in Solids

In actual practice, it is difficult to grow a perfect crystal. Even single crystals grown with all care are found to contain many internal irregularities. These irregularities are called **crystal defects** and can be defined as *"Any departure from perfectly ordered arrangement of atoms in a crystal is called imperfection or defect"*. These imperfections not only modify the properties but also sometimes impart new properties to the solids.

If a graph is plotted between Gibb's free energy and defect concentration, Gibb's free energy has a minimum value at non-zero concentration. This shows that defect formation is a spontaneous process.

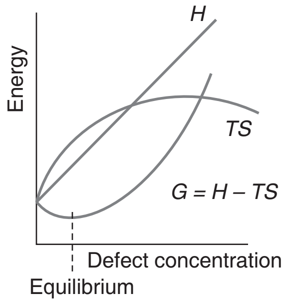


Fig. 1.30 Variation of enthalpy and entropy with defects

In an ionic crystal, the electrons are mostly concentrated around the electronegative component. Some of these electrons have the tendency of thermal release, *i.e.*, the property of losing its position on increase in temperature. These thermally released electrons become mobile resulting in increase in conductivity of solid.

When an electron is thermally removed from its position the electron deficient site thus formed is called a hole. Holes also impart electrical conductivity but their movement is opposite in direction to which the electrons move. The electrons and holes in solids give rise to **electronic imperfections.**

The defect discussed above is/are called point defects as these are found around a point or an atom. These can be categorised into following three types as stoichiometric, non-stoichiometric and impurity defects.

Hot Spot 2

STOICHIOMETRIC Defects

It is also an important topic of the chapter for JEE Main examination. The questions are generally based on Schottky and Frenkel defects.

If imperfection in crystals are such that the ratio between the cations and the anions remain the same as described in its molecular formula, the defect will be called **stoichiometric defects.** They are also called intrinsic or **thermodynamic defects.** Basically these are of two types, vacancy defects and interstitial defects.

(a) Vacancy Defect

When some of the lattice sites are vacant, the crystal is said to have vacancy defect. This results in decrease in density of the substance. This defect can also develop when a substance is heated.

(b) Interstitial Defect

When some constituent particles (atoms or molecules) occupy an **interstitial** site, the crystal is said to have interstitial defect. This defect increases the density of the substance.

Vacancy and interstitial defects as explained above can be shown by non-ionic solids. Ionic solids must always maintain electrical neutrality. Rather than simple vacancy or interstitial defects, they show these defects as **Frenkel and Schottky defects.**

(i) Schottky Defect

In an ionic crystal of A^+B^- type, if equal number of cations and anions are missing from their lattice sites, the defect is called Schottky defect. In this defect electrical neutrality is maintained due to disappearance of similar number of cations and anions (lattice vacancy). It is shown by highly ionic compounds having

(i) high coordination number

(ii) small difference in the size of cations and anions.

e.g., NaCl, KCl, KBr, CsCl, etc.

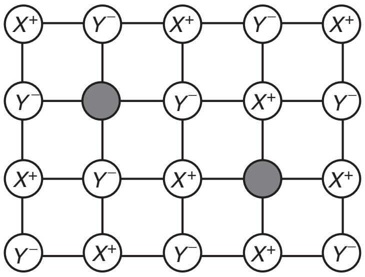


Fig. 1.31 Schottky Defect

Because of the missing of ions from the lattice, this defect results in decrease in density.

(ii) Frenkel Defect

In an ionic crystal, when an ion is missing from its lattice site (causing a hole or vacancy there) and occupies interstitial site, the defect is called Frenkel's defect. It is also called **dislocation defect.** In this defect the electrical neutrality and stoichiometry of the compound is maintained as ion does not leave the crystal completely.

This type of defect is seen in those crystals where the difference in the size of cations and anions is very large and their coordination number is low, *e.g.,* AgCl, AgBr, ZnS, etc., as Zn^{2+} and Ag^+ ions have small size. Due to such a defect the density of the solid remains unchanged because no ion is missing from the lattice.

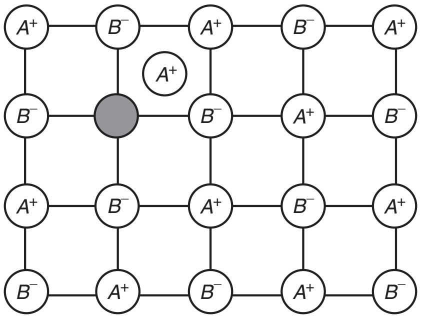


Fig. 1.32 Frenkel defect

Caution Point AgBr *is a compound in which both Schottky and Frenkel defects are found because* AgBr *is highly ionic but there is a great difference in the size of* $Ag^{\oplus}$ *and* $Br^{\ominus}$*.*

Calculation of Number of Schottky/Frenkel Defects

The number (n) of Schottky defects present in an ionic crystal containing N ions at temperature T is given by :

$$n = Ne^{-E/2KT}.$$

where, E is the energy required to create these n Schottky defects and K is the Boltzmann constant $= R/N_A$

$$= 1.38 \times 10^{23} \text{ JK}^{-1}$$

The number (n) of Frenkel defects in an ionic crystal containing N ions and N_i is the number of interstitial sites at a temperature T is given by

$$n = (N/N_i)^{1/2} e^{-E/2KT}$$

where, E is the energy required to create n Frenkel defects.

In NaCl, there are 10^{22} ions and 10^6 Schottky pairs/cm^3 at room temperature, *i.e.,* there is one Schottky pair defect per 10^{16} ions.

Non-Stoichiometric Defects

When the ratio of cations and anions, due to imperfection, differ from that indicated by their molecular formula, the defects are called non-stoichiometric defects. These defects results in either **excess of metal atom** or **excess of non-metal atom.**

(a) Metal Excess Defects

The metal excess may occur in either of the following two ways

(i) **Due to missing of a negative ion from its lattice site,** thus leaving a hole which is occupied by an electron. The electrons thus, trapped in the anion vacancies are called *F*-**centres** (*F* = *Farbe* = German word for colour) as these are responsible for imparting colour to the crystals.

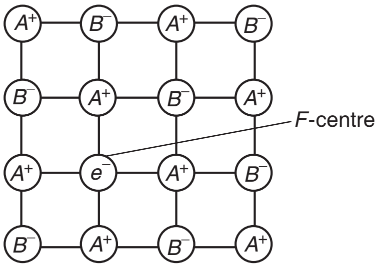


Fig. 1.33 (a) Metal excess defect due to missing of anion

e.g., NaCl when heated in Na vapour atmosphere, the excess Na atom deposit on the surface. Now, $Cl^{\ominus}$ diffuse to the surface where they combine with Na atoms which lose the electrons. The electrons diffuse into the vacant sites created. The electrons absorb some energy from the visible light and re-emit the complimentary yellow colour to NaCl crystal. Excess of Li in LiCl gives a pink colour. Excess of K in KCl make it violet.

This defect is similar to Schottky defect.

(ii) **Due to the presence of extra cations in the interstitial sites.** Here, electrical neutrality is maintained by an electron present in another interstitial site.

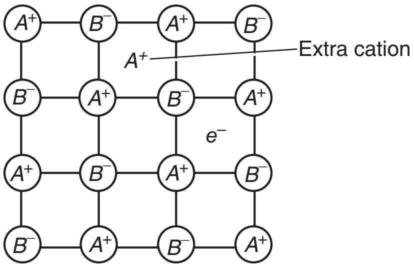


Fig. 1.33 (b) Metal excess defect due to the presence of extra cation

e.g., Zinc oxide is white in colour at room temperature. On heating it loses oxygen and turns yellow.

$$ZnO \xrightarrow{\text{heating}} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

Now, there is excess of zinc in the crystal and its formula becomes $Zn_{1+x}O$. The excess Zn^{2+} ions move to interstitial sites and the electrons to neighbouring interstitial sites.

This defect is similar to Frenkel defect.

(b) Metal Deficiency Defect

Metal deficiency or non-metal excess occurs where the metal shows variable valency *i.e.,* transition metals. The defect usually occur due to missing of a cation from its lattice site and presence of the cation having higher charge at different lattice site thus, balancing the loss as seen above, *e.g.,* FeO, FeS, NiO, etc.

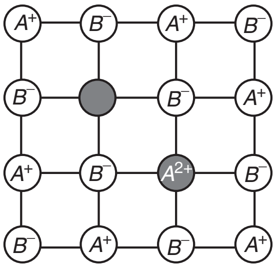


Fig. 1.34 Metal deficiency defect

FeO is mostly found with a composition of $Fe_{0.95}O$. It may actually range from $Fe_{0.93}O$ to $Fe_{0.96}O$. In crystals of FeO some Fe^{2+} cations are missing and the loss of positive charge is made up by the presence of required number of Fe^{3+} ions.

Impurity Defects

Another common method of introducing defects in ionic solids is by adding impurity ions having different charge than host ion. These foreign atoms are present at lattice site in **substitutional solids** and at vacant interstitial sites in **interstitial solids.**

Formation of substitutional solids depends upon the electronic structure of impurity while that of latter on the size of impurity.

The number (n) of defects per cm^3 is given by

$$n = N \times e^{-W/2RT}$$

where, N = number of sites per cm^3

W = work or energy required to produce a defect,
T = absolute temperature
R = gas constant, e = base of natural logarithm

If molten NaCl containing a little amount of $SrCl_2$ is crystallised, some of the sites of Na^+ ions are occupied by Sr^{2+}.

Each Sr^{2+} replaces two Na^+ ions. It occupies the site of one ion and the other site remains vacant. The cationic vacancies thus produced are equal in number to that of

Sr^{2+} ions. Another similar example is the solid solution of $CdCl_2$ and AgCl.

Sample Problem 22 *If* NaCl *is doped with* 10^{-3} *mol% of* $SrCl_2$, *calculate the concentration of cation vacancies* **[NCERT]**

(a) 6.02×10^{18} mol^{-1} (b) 6.02×10^{24} mol^{-1}
(c) 6.02×10^{20} mol^{-1} (d) 6.02×10^{16} mol^{-1}

Interpret (a) Due to addition of $SrCl_2$, each Sr^{2+} ion replaces two Na^+ ions, but occupies only one Na^+ lattice point. This makes one cationic vacancy.

Number of moles of cation vacancies in 100 mol of NaCl $= 10^{-3}$

Number of moles of cation vacancies in 1 mol $= \dfrac{10^{-3}}{100} = 10^{-5}$

Total cationic vacancies $= 10^{-5} \times N_A$

$$= 10^{-5} \times 6.023 \times 10^{23}$$

$$= 6.023 \times 10^{18} \text{ mol}^{-1}$$

Sample Problem 23 *The composition of a sample of wustite is* $Fe_{0.93}O$. *What percentage of the iron is present in the form of* Fe (III)?

(a) 84.95% (b) 45.64%
(c) 15.05% (d) 44.36%

Interpret (c) From the valency of Fe(II) and Fe(III), it is clear that three Fe(II) ions will be replaced by two Fe(III) causing a loss of one iron ion. Total loss of iron from one molecule of FeO $= 1 - 0.93 = 0.07$

Hence, total Fe(III) present in one molecule of

$$FeO = 2 \times 0.07 = 0.14$$

Total number of Fe(II) and Fe(III) present in one molecule of

$$FeO = 0.93$$

Hence, percentage of Fe(III) $= \dfrac{0.14}{0.93} \times 100 = 15.05\%$

Sample Problem 24 *Which of the following point defects are shown by* AgBr(*s*) *crystals?* **[NCERT Exemplar]**

(*A*) *Schottky defect* (*B*) *Frenkel defect*
(*C*) *Metal excess defect* (*D*) *Metal deficiency defect*

(a) (*A*) and (*B*) (b) (*C*) and (*D*)
(c) (*A*) and (*C*) (d) (*B*) and (*D*)

Interpret (a) AgBr crystal exhibits Schottky as well as Frenkel defects because it is ionic in nature and have a large difference in the size of ions.

1.9 Electrical Properties of Solids

Solids are classified into three groups on the basis of conduction power, namely

(i) **Conductors** with conductivity range of the order of $10^7 (\Omega \text{ m})^{-1}$ *e.g.,* metals.

(ii) **Semiconductors** with conductivity range $10^{-6} - 10^{-4} (\Omega \text{ m})^{-1}$ *e.g.,* semi-metals.

(iii) **Insulators** with conductivity range $10^{-10} - 10^{-20} (\Omega \text{ m})^{-1}$, *e.g.,* non-metals.

In most of the solids, conduction is through electrons, however in some ionic solids the conduction is through ions. In metals, conductivity strongly depends upon the number of valence electrons available per atom. The atomic orbitals form molecular orbitals which are so close to each other as to form a **band.**

The conductivity of solids can be better explained on the basis of energy gap present between the conduction band (just higher unoccupied band) and the valence band (Band theory).

Conductors

In conductors, the conduction band is almost overlapping with the valence band, *i.e.,* there is no energy gap present between these two bands or valence band is not completely filled. Then, electrons can flow easily under the influence of electric field, in both the cases.

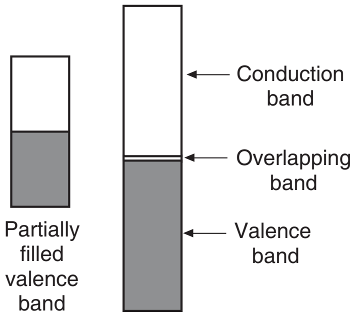


Fig. 1.35 Conductor

Semiconductors

In the case of semiconductors, the gap between valence band and conduction band is small and therefore, some of the electrons may jump from valence band to conduction band and some conductivity is observed. The conductivity here increases with increase in temperature. The reason for such an increase is lowering of energy gap as shown in the figure.

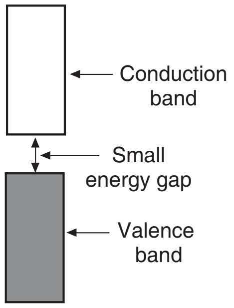


Fig. 1.36 Semiconductor

(a) Intrinsic Semiconductors

Here heat is responsible for ejection of electrons thus, leaving a (+)**ve charge** (positive hole). The crystal can now conduct electricity because on applying the electric field the electrons and holes migrate in opposite directions. This type of conductance is called intrinsic conductance and the semiconductors showing this type of conductivity are called **undoped** or **intrinsic semiconductors**, *e.g.*, Si, Ge, etc.

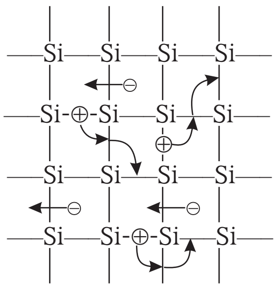


Fig. 1.37 Electrical conduction in an intrinsic semiconductor

(b) Extrinsic Semiconductor

For practical purposes the conductivity of pure Si and Ge is very low at room temperature. In order to increase their conductance, the pure substances are carefully doped (introduced with small amount of impurities in the form of elements of the 13 and 15 group of the Periodic Table). Such conductance is called **extrinsic conductance.** Depending upon the nature of the elements used for doping, the extrinsic semiconductor can be of two types, *viz*, *n*-types semiconductors and *p*-type semiconductors.

The group 15 elements have 1 electron excess to Si or Ge, after forming 4 covalent bonds with group 14 member (Si or Ge). This excess free electron is responsible for electrical conductivity in them. *Group* 14 *elements when doped with group* 15 *elements are called n-type semiconductors*. Here, *n* specifies that negative charge flows in them.

The group 13 elements have 1 electron short to group 14 elements, thus giving rise to electron deficient band or a hole. Here, such holes are responsible for electrical conductivity. Thus, *group* 14 *elements when doped with elements of group* 13 *are called p-type semiconductors*. Here, *p* specifies that conduction is through positive holes in them.

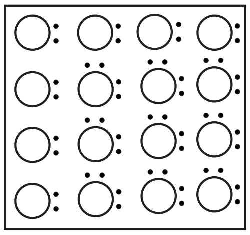


Fig. 1.38 (a) Normal silicon atom

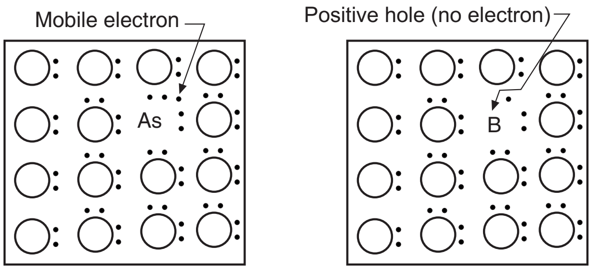


Fig. 1.38 (b) *n* and *p*-type semiconductors

Various combinations of *n*-type and *p*-type semiconductors are used to make electronic components. *e.g.,* diode is a combination of *p* and *n*-type semiconductors and used as rectifier. Transistors which are **pnp** or **npn** sandwich semiconductor, are used to detect or amplify radio or audio signals.

Germanium and silicon, group 14 elements, have a characteristic valence of four and form four bonds as in diamond. A large variety of solid state materials have been prepared by combination of groups 13 and 15 or 12 and 16 to simulate average valence of four as in Ge or Si. Typical compounds of **groups 13–15** are InSb, AlP and GaAs. Gallium arsenide (GaAs) semiconductors have very fast response and have revolutionised the design of semiconductor devices. ZnS, CdS, CdSe and HgTe are examples of **groups 12–16 compounds.** In these compounds, the bonds are not perfectly covalent and the ionic character depends on the electronegativities of the two elements.

Caution Point TiO, CrO_2 *and* ReO_3 *behave like metals. Rhenium oxide,* ReO_3 *is like metallic copper in its conductivity and appearance. Certain other oxides like* VO, VO_2, VO_3 *and* TiO_3 *show metallic or insulating properties depending on temperature*.

Insulators

In case of **insulators,** the energy gap between valence band and conduction band is so large that it cannot even covered up by supplying energy in the form of heat.

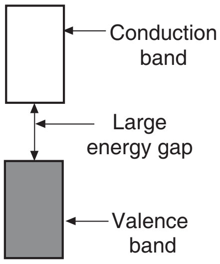


Fig.1.39 Insulators

Sample Problem 25 *To get a n-type semiconductor from silicon, it should be doped with a substance with valence ....*

[NCERT Exemplar]

(*a*) 2	(*b*) 1
(*c*) 3	(*d*) 5

Interpret (*d*) To get a *n*-type semiconductor, Si (tetravalent) should be doped with a pentavalent element (element having five valence electrons) like N, P, As, etc.

Sample Problem 26 *Which of the following oxides behaves as conductor or insulator depending upon temperature?* **[NCERT Exemplar]**

(*a*) TiO	(*b*) SiO_2
(*c*) TiO_3	(*d*) MgO

Interpret (*c*) Oxides like VO, VO_2, VO_3 and TiO_3 exhibit metallic or insulating properties depending on temperature.

1.10 Magnetic Properties of Solids

Every substance has some magnetic properties associated with it. The origin of these properties lies in the electrons. Each electron in an atom behaves like a tiny magnet. Its magnetic moment originates from two types of motions (i) its orbital motion around the nucleus and (ii) its spin around its own axis. Electron being a charged particle and undergoing these motions can be considered as a small loop of current which possesses a magnetic moment. Thus, each electron has a permanent spin and an orbital magnetic moment associated with it. Magnitude of this magnetic moment is very small and is measured in the unit called Bohr magneton, μ_B. It is equal to 9.27×10^{-24} Am^2.

Classification of Substances on the Basis of their Magnetic Properties

On this basis substances can be categorised as

(a) Diamagnetic

These are feebly repelled by magnetic field. These have the characteristic absence of unpaired electrons in them, *i.e.,* their all electrons are paired. *e.g.,* some non-metallic elements (except O_2 and S), inert gases and species with paired electrons *e.g.,* TiO_2, V_2O_5, C_6H_6, NaCl, etc.

(b) Paramagnetic

These are attracted by magnetic field due to the presence of atoms, ions or molecules with unpaired electron in them (*e.g.,* O_2, Cu^{2+}, Fe^{3+} etc). In magnetic field, these tend to orient themselves parallel to the direction of magnetic field. These are used in electronic appliances.

(c) Ferromagnetic

These substances show magnetism even in the absence of magnetic field. Fe, Co, CrO_2 and Ni are 3 elements which show ferromagnetism at room temperature. A spontaneous alignment of magnetic moments in the same direction gives rise to ferromagnetism. The ferromagnetism is not seen above a temperature, called **Curie temperature.**

(d) Antiferromagnetic

These substances have net magnetic moment zero due to compensatory alignment of magnetic moments. *e.g.,* MnO, MnO_2, FeO, NiO, Cr_2O_3, etc.

(e) Ferrimagnetic

They have a net dipole moment due to unequal parallel and antiparallel alignment of magnetic moments. *e.g.,* Fe_3O_4, ferrites of the formula $M^{2+}Fe_2O_4$, where, M = Mg, Cu, Zn, etc.

Caution Point *All ferroelectric crystals are piezoelectric but reverse is not true.*

The details of the above magnetic properties are summarised in the following table.

Table 1.8 **Magnetic Properties of Solids**

S.N.	Properties	Description	Alignment of magnetic dipoles	Examples	Application
1.	Diamagnetic	Feebly repelled by the magnetic fields. Non-metallic elements (except O_2,S) inert gases and species with paired electrons are diamagnetic.	All paired electrons ↑↓ ↑↓ ↑↓	TiO_2, V_2O_5, NaCl, C_6H_6 (benzene)	Insulator
2.	Paramagnetic	Attracted by the magnetic field due to the presence of permanent magnetic dipoles (unpaired electrons). In magnetic field, these tend to orient themselves parallel to the direction of the field and thus, produce magnetism in the substances.	↑↓ ↑ ↑ At least one unpaired electron	O_2, Cu^{2+}, Fe^{3+}, TiO, Ti_2O_3, VO, VO_2, CuO	Electronic appliances
3.	Ferromagnetic	Permanent magnetism even in the absence of magnetic field. Above a temperature, called **Curie temperature,** there is no ferromagnetism.	Dipoles are aligned in the same direction ↑ ↑ ↑ ↑ ↑	Fe, Ni, Co, CrO_2	CrO_2 is used in audio and video tapes
4.	Antiferromagnetic	This arises when net dipole alignment is zero due to equal and opposite alignment.	↑ ↓ ↑ ↓ ↑ ↓	MnO, MnO_2, Mn_2O_3, FeO, Fe_2O_3; NiO, Cr_2O_3, CoO, Co_3O_4	—
5.	Ferrimagnetic	This arises when there is net dipole moment.	↑ ↓ ↓ ↓ ↑ ↓	Fe_3O_4, ferrites	—

Effect of temperature on the magnetic properties is shown by the following graphs

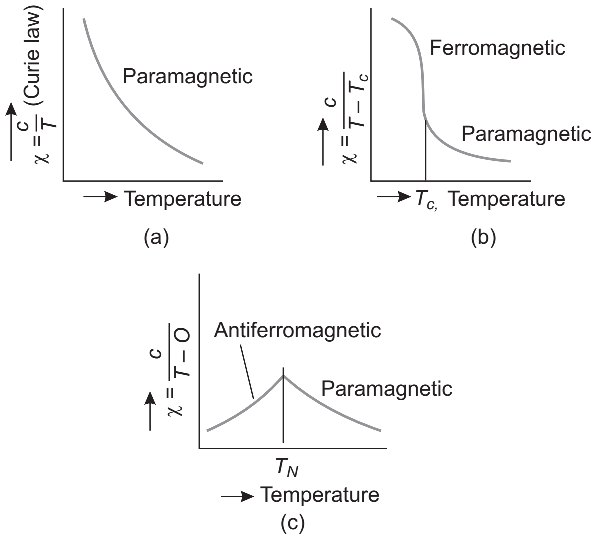


Fig. 1.40 Graphs showing effect of temperature on magnetic properties

1.11 Dielectric Properties of Solids

The dielectric properties are seen in insulators, which, when are placed in an electric field, show generation of dipoles in them due to the pulling of electrons and nuclei of atoms or molecules in opposite directions. These dipoles,

(i) may align themselves in an ordered manner so that there is a net dipole moment in the crystal.

(ii) may align themselves in such a manner that dipole moments may cancel each other.

(iii) It is also possible that there are no dipoles in the crystal but only ions are present.

The crystals where situation (i) is found exhibit **peizoelectricity** or **pressure electricity,** which is the production of electricity by a polar crystal when mechanical stress is applied to it.

Peizoelectric crystals also show development of mechanical stress when electric field is applied to them, thus acting as a mechanical-electrical transducer.

1. Peizoelectric crystals with permanent dipoles are said to have **ferroelectricity** *e.g.*, Rochelle's salt, $BaTiO_3$, KH_2PO_4 etc.
2. Peizoelectric crystals with zero dipole moment have **antiferroelectricity.**
3. Some peizoelectric crystals, when heated produce small electric potential or **pyroelectricity.**

The phenomenon where electricity passes through a material without resistance is called **superconductivity.** The material showing this property is said to be **superconductor.** It was **Kammerlingh Onnes** of Netherlands who first reported the case of Hg as superconductor at a very low temperature of 4.2 K. Afterwards, some metal alloys and certain organic solids have been reported to be superconducting but at very low temperatures. Now a days, superconductors are also reported at comparatively higher temperatures. *e.g.,* : $YBa_2Cu_3O_7$ at 90 K, $Bi_2Ca_2Sr_2Cu_3O_{10}$ at 105 K, and $Tl_2Ca_2Ba_2Cu_3O_{10}$ at 125 K, etc.

Check Point 3

1. Explain why does Schottky defect lower the density of related solids?
2. Frenkel defects are not found in alkali metal halides. Explain why?
3. Impurity doped silicon is a semiconductor. Explain.
4. Which type of defect can arise when a solid is heated?

WORKED OUT Examples

Example 1 *How many number of atoms are there in a cube based unit cell having one atom on each corner and two atoms on each body diagonal of cube?*

(*a*) 4 (*b*) 9 (*c*) 12 (*d*) 14

Solution (*b*) There are four body diagonals. Atoms on the body diagonals are not shared by any other unit cell. Contribution by atoms on corners $= 8 \times \frac{1}{8} = 1$

and contribution by atoms on body diagonal $= 2 \times 4 = 8$

Total number of atoms $= 8 + 1 = 9$

Example 2 *The first order reflection of a beam of X-ray from a given crystal occurs at 5°15′. At what angle will the third-order reflection occur?*

(*a*) 15°55.9′ (*b*) 18°48.9′

(*c*) 20°55.2′ (*d*) None of these

Solution (*a*)

$$n_1\lambda = 2d \sin\theta_1$$

$$n_2\lambda = 2d \sin\theta_2$$

$$\frac{n_1}{n_2} = \frac{\sin\theta_1}{\sin\theta_2}$$

$$\frac{1}{3} = \frac{\sin 5°15'}{\sin\theta_2}$$

$$\therefore \quad \theta_2 = 15°\,55.9'$$

Example 3 *A solid AB has the* NaCl *structure. If radius of cation A^+ is* 120 pm, *the maximum possible value of the radius of the anion B^- is*

(*a*) *240 pm* (*b*) *60 pm* (*c*) *49.6 pm* (*d*) *290 pm*

Solution (*d*) For NaCl crystal,

Radius of cation/radius of anion = 0.414

$$\frac{r_{A^+}}{r_{B^-}} = 0.414$$

$$r_{B^-} = \frac{r_{A^+}}{0.414} = \frac{120}{0.414} = 290 \text{ pm}$$

Example 4 CsCl *crystallises in a cubic lattice that has a* Cl^- *at each corner and* Cs^+ *at the centre of the unit cell. If* $(r_{Cs^+}) = 1.69\,Å$ *and* $(r_{Cl^-}) = 1.81\,Å$, *what is the value of edge length a of the cube?*

(*a*) 4.04 (*b*) 3.50 (*c*) 3.03 (*d*) 1.95

Solution (*a*) The closest Cs^+ to Cl^- distance = sum of ionic radii of Cs^+ and Cl^-

$= 1.69 + 1.81$

$= 3.50$ Å

The distance in one-half of the cubic diagonal $= \frac{a\sqrt{3}}{2}$

$$\frac{a\sqrt{3}}{2} = 3.50 \text{ Å}$$

$$a = 4.04 \text{ Å}$$

Example 5 KCl *crystallises in the same type of lattice as does* NaCl. *Given,* $\frac{r_{Na^+}}{r_{Cl^-}} = 0.5$ *and* $\frac{r_{Na^+}}{r_{K^+}} = 0.7$

The ratio of the side of the unit cell for NaCl *to that for* KCl *is*

(*a*) 1:1.172 (*b*) 1 : 1.143

(*c*) 1 : 1.1413 (*d*) 1 : 1.732

Solution (*b*) NaCl crystallises in the face centred cubic unit cell such that

$$r_{Na^+} + r_{Cl^-} = \frac{a}{2}$$

Given, $\frac{r_{Na^+}}{r_{Cl^-}} = 0.5, \quad \frac{r_{Na^+}}{r_{K^+}} = 0.7$

Thus, we have, $\frac{r_{Na^+} + r_{Cl^-}}{r_{Cl^-}} = 1.5$

$$\frac{r_{K^+}}{r_{Cl^-}} = \frac{r_{K^+}}{r_{Na^+}/0.5} = \frac{0.5}{r_{Na^+}/r_{K^+}} = \frac{0.5}{0.7}$$

Therefore, $\frac{r_{K^+} + r_{Cl^-}}{r_{Na^+} + r_{Cl^-}} = \frac{1.2}{0.7} \times \frac{1}{1.5}$

$$\therefore \quad \frac{a_{KCl/2}}{a_{NaCl/2}} = \frac{1.2}{0.7 \times 1.5} = \frac{a_{KCl}}{a_{NaCl}} = 1.143$$

or $\frac{a_{NaCl}}{a_{KCl}} = 1 : 1.143$

Example 6 *Edge length of M^+X^- (fcc structure) is 7.2 Å. Assuming $M^+ - X^-$ contact along the cell edge, radius of X^- ion is (r_{M^+} = 1.6 Å)*

(*a*) 2.0 Å (*b*) 5.6 Å

(*c*) 2.8 Å (*d*) 3.8 Å

Solution (*a*)
$$2(r_{M^+} + r_{X^-}) = 7.2$$
$$2(1.6 + r_{X^-}) = 7.2$$
$$\therefore \qquad r_{X^-} = 2.0\ \text{Å}$$

Example 7 *Gold (at. wt. 197 g mol^{-1}) crystallises in a cubic closest packed structures (the face-centred cubic) and has a density of 19.3 g/cm^3. Its atomic radius is*

(*a*) 144.17 pm (*b*) 407.8 pm
(*c*) 128.32 pm (*d*) 203.4 pm

Solution (*a*) Density $d = \dfrac{MZ}{a^3 N_A}$
$$a = \sqrt[3]{\frac{197 \times 4}{6.023 \times 10^{23} \times 19.3}}$$
$$a = 407.8 \times 10^{-10}\ \text{cm} = 407.8\ \text{pm}$$
$$r = \frac{407.8}{\sqrt{8}} = 144.18\ \text{pm}$$

Example 8 *Calcium metal crystallises in fcc lattice with edge length 556 pm. Calculate the density (in g cm^{-3}) of metal if it contains 0.2% Schottky defects.*

(*a*) 3.992 (*b*) 1.5455 (*c*) 1.5427 (*d*) 1.4987

Solution (*c*) Due to 0.2% Schottky defect, number of atoms
$$= 4 - \frac{0.2}{100} \times 4 = 3.992$$
$$d = \frac{Z \times M}{a^3 \times N_A} = \frac{40 \times 3.992}{(0.556 \times 10^{-7})^3 \times 6.023 \times 10^{23}}$$
$$= 1.5427\ \text{g cm}^{-3}$$

Example 9 *An element occurs in two crystalline forms α and β. The α-form has an fcc with $a = 3.68$ Å and β- form has a bcc with $a = 2.92$ Å. Calculate the ratio of their densities.*

(*a*) 1 : 1 (*b*) 1 : 2 (*c*) 2 : 1 (*d*) 2 : 3

Solution (*a*) Z_{eff} for fcc = 4, Z_{eff} for bcc = 2
$$\text{Atomic volume of } \alpha\text{-form} = \frac{(3.68 \times 10^{-8})^3 \times N_A}{4}$$
$$\text{Atomic volume of } \beta\text{-form} = \frac{(2.92 \times 10^{-8})^3 \times N_A}{2}$$
(As *Aw* is same, element is same), so the density ratio is
$$\rho_\alpha : \rho_\beta = V_\beta : V_\alpha = \frac{(2.92)^3}{2} : \frac{(3.68)^3}{4}$$
$$= 12.448 : 12.459 = 1 : 1$$

Example 10 *A compound forms hexagonal close-packed structure. What is the total number of voids in 0.5 mole of it?*

(*a*) 3.011×10^{23} (*b*) 6.022×10^{23}
(*c*) 9.033×10^{23} (*d*) 1.802×10^{24}

Solution (*c*) To find total number of voids, we have to calculate the number of octahedral and tetrahedral voids which depend upon the number of atoms in 0.5 mole (*N*), so first calculate the number of atoms in 0.5 mole and then find number of octahedral voids (= *N*),

Number of tetrahedral voids (= 2 *N*) and total voids.

Total number of atoms (*N*) in a closed packed structure (0.5 mol)
$$= 0.5 \times 6.022 \times 10^{23}$$
$$= 3.011 \times 10^{23}$$
Number of octahedral voids $= N = 3.011 \times 10^{23}$

Number of tetrahedral voids $= 2N = 2 \times 3.011 \times 10^{23}$
$$= 6.022 \times 10^{23}$$
$$\text{Total number of voids} = 3.011 \times 10^{23} + 6.022 \times 10^{23}$$
$$= 9.033 \times 10^{23}$$

Start **Practice** *for* JEE Main

Round I (Topically Divided Problems)

Solids and their Classification

1. Which of the following conditions favours the existence of a substance in the solid state? **[NCERT** Exemplar]

(a) High temperature
(b) Low temperature
(c) High thermal energy
(d) Weak cohesive forces

2. Why are solids rigid? **[NCERT]**

(a) Because of large intermolecular forces
(b) Because of vibrating motion
(c) Because of large intermolecular space
(d) All of the above

3. Which of the following is an amorphous solid? **[NCERT** Exemplar]

(a) Graphite (C) (b) Quartz glass (SiO_2)
(c) Chrome alum (d) Silicon carbide (SiC)

4. Which of the following statement is not true about amorphous solids? **[NCERT** Exemplar]

(a) On heating they may become crystalline at certain temperature
(b) They may become crystalline on keeping for long time
(c) Amorphous solids can be moulded by heating
(d) They are anisotropic in nature

5. Which of the following is not a characteristic of a crystalline solid? **[NCERT** Exemplar]

(a) Definite and characteristic heat of fusion
(b) Isotropic nature
(c) A regular periodically repeated pattern of arrangement of constituent particles in the entire crystal
(d) A true solid

6. Which among the following will show anisotropy?

(a) Glass (b) Plastic
(c) Barium chloride (d) Wood

7. Which type of solid crystals will conduct heat and electricity?

(a) Ionic (b) Covalent
(c) Molecular (d) Metallic

8. Solid carbon dioxide is an example of

(a) metallic crystal (b) covalent crystal
(c) molecular crystal (d) ionic crystal

9. Which of the following is not the characteristic of ionic solids? **[NCERT** Exemplar]

(a) Very low value of electrical conductivity in the molten state
(b) Brittle nature
(c) Very strong forces of interactions
(d) Anisotropic nature

10. Which of the following is a network solid? **[NCERT** Exemplar]

(a) SO_2 (Solid) (b) I_2
(c) Diamond (d) H_2O (Ice)

11. Graphite is a good conductor of electricity due to the presence of …… . **[NCERT** Exemplar]

(a) lone pair of electrons (b) free valence electrons
(c) cations (d) anions

Crystal Lattice, Unit Cells and their Parameters

12. How many space lattices are obtainable from the different crystal systems?

(a) 7 (b) 14
(c) 32 (d) 230

13. Monoclinic crystal has dimension

(a) $a \neq b \neq c, \alpha = \gamma = 90^\circ, \beta \neq 90^\circ$
(b) $a = b = c, \alpha = \beta = \gamma = 90^\circ$
(c) $a = b = c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$
(d) $a \neq b = c, \alpha = \beta = \gamma = 120^\circ$

14. The most unsymmetrical crystal system is

(a) hexagonal (b) triclinic

(c) cubic (d) orthorhombic

15. How much portion of an atom located at corner and body centre of a cubic unit cell is part of its neighbouring unit cell respectively? **[NCERT]**

(a) $1, \frac{1}{2}$ (b) $\frac{1}{2}, 1$

(c) $\frac{1}{8}, 1$ (d) $\frac{1}{8}, \frac{1}{2}$

16. The edge lengths (a) of the unit cells in terms of the radius of spheres constituting fcc, bcc and simple cubic unit cell are respectively …… . **[NCERT Exemplar]**

(a) $2\sqrt{2}r, \frac{4r}{\sqrt{3}}, 2r$ (b) $\frac{4r}{\sqrt{3}}, 2\sqrt{2}r, 2r$

(c) $2r, 2\sqrt{2}r, \frac{4r}{\sqrt{3}}$ (d) $2r, \frac{4r}{\sqrt{3}}, 2\sqrt{2}r$

17. If the distance between Na^+ and Cl^- ions in NaCl crystal is 'a' pm what is the length of the cell edge?

(a) $4a$ pm (b) $\frac{a}{4}$ pm

(c) $2a$ pm (d) $\frac{a}{2}$ pm

18. Gold (atomic radius $= 0.144$ nm) crystallises in a face-centred unit cell. What is the length of a side of the cell? **[NCERT Exemplar]**

(a) 0.414 (b) 0.407

(c) 1.414 (d) 1.407

19. The edge of unit cell of fcc Xe crystal is 620 pm. The radius of Xe atom is

(a) 189.37 pm (b) 209.87 pm

(c) 219.25 pm (d) 235.16 pm

20. Calculate the ionic radius of a Cs^+ ion, assuming that the cell edge length for CsCl is 0.4123 nm and that the ionic radius of a Cl^- ion is 0.181 nm.

(a) 0.352 nm (b) 0.116 nm

(c) 0.231 nm (d) 0.176 nm

21. An fcc lattice has a lattice parameter $a = 400$ pm. Calculate the molar volume of the lattice including all the empty space.

(a) 7.6 mL (b) 6.5 mL

(c) 10.8 mL (d) 9.6 mL

22. A metal has bcc structure and the edge length of its unit cell is 3.04 Å. The volume of the unit cell in cm^3 will be

(a) 1.6×10^{21} cm^3 (b) 2.81×10^{-23} cm^3

(c) 6.02×10^{-23} cm^3 (d) 6.6×10^{-24} cm^3

23. Aluminium crystallises in a cubic close-packed structure. Its metallic radius is 125 pm. How many unit cells are there in 1.00 cm^3 of aluminium? **[NCERT Exemplar]**

(a) 4.42×10^{22} (b) 2.36×10^{21}

(c) 2.26×10^{22} (d) 3.92×10^{18}

24. A compound is formed by elements A and B. This crystallises in the cubic structure when atoms A are at the corners of the cube and atoms B are at the centre of the body. The simplest formula of the compound is

(a) AB (b) AB_2

(c) A_2B (d) AB_4

25. X-ray analysis shows that the unit cell length in NaCl is 562.8 pm. Calculate the density you would expect on this basis, $N_A = 6.023 \times 10^{23}$ mol^{-1}.

(a) 0.3216 g cm^{-3} (b) 2.179 g cm^{-3}

(c) 1.859 g cm^{-3} (d) 2.346 g cm^{-3}

Packing in Solids and Bragg's Law

26. For a given crystal, the lattice parameter 'a' is 318 pm. The d-spacing for a (III) plane is

(a) 318 pm (b) 184 pm

(c) 390 pm (d) 225 pm

27. The vacant space in the bcc unit cell is

(a) 23% (b) 26%

(c) 32% (d) None of these

28. The correct order of the packing efficiency in different types of unit cells is **[NCERT Exemplar]**

(a) fcc < bcc < simple cubic

(b) fcc > bcc > simple cubic

(c) fcc < bcc > simple cubic

(d) bcc < fcc > simple cubic

29. What is the coordination number in a square close packed structure in two dimensions? **[NCERT Exemplar]**

(a) 2 (b) 3

(c) 4 (d) 6

30. The arrangement ABC, ABC, ABC …… is referred as

(a) cubic close packing

(b) tetrahedral close packing

(c) octahedral close packing

(d) hexagonal close packing

31. The coordination number of atoms in a cubic-packed structure and in a body-centred cubic structure respectively is **[NCERT Exemplar]**

(a) 6, 8 (b) 8, 6

(c) 12, 6 (d) 12, 8

32. The number of octahedral sites per sphere in a fcc structure is
(a) 1
(b) 2
(c) 4
(d) 8

33. Which of the following statement is not true about the hexagonal close packing? **[NCERT** Exemplar**]**
(a) The coordination number is 12
(b) It has 74% packing efficiency
(c) Tetrahedral voids of the second layer are covered by the spheres of the third layer
(d) In this arrangement spheres of the fourth layer are exactly aligned with those of the first layer

34. A solid is made of two elements X and Z. The atoms Z are in ccp arrangement while the atom X occupy all the tetrahedral sites. What is the formula of the compound?
(a) XZ
(b) XZ_2
(c) X_2Z
(d) X_2Z_3

35. An alloy of Cu, Ag and Au is found to have Cu forming the simple cubic close packed lattice. If the Ag atoms occupy the face centres and Au is present at the body centre, the formula of the alloy will be
(a) Cu_4Ag_4Au
(b) $CuAg_3Au$
(c) CuAgCu
(d) Cu_4Ag_2Au

36. Bragg's law is given by the equation
(a) $n\lambda = 2\,\theta \sin\theta$
(b) $n\lambda = 2d \sin\theta$
(c) $2n\lambda = d \sin\theta$
(d) $n\frac{\theta}{2} = \frac{d}{2} \sin\theta$

37. The number of equidistance oppositely charged ions in a sodium chloride crystal is
(a) 2
(b) 4
(c) 6
(d) 8

38. In which of the following crystals alternate tetrahedral voids are occupied?
(a) NaCl
(b) CaF_2
(c) Na_2O
(d) ZnS

39. Which of the following statements is not true about NaCl structure?
(a) Cl^- ions are in fcc arrangement
(b) Na^+ ions has coordination number 4
(c) Cl^- ions has coordination number 6
(d) Each cell contains 4 NaCl molecules

40. The structure of Na_2O crystal is
(a) NaCl type
(b) CsCl type
(c) ZnS type
(d) antifluorite type

41. In A^+B^- ionic compound, radii of A^+ and B^- ions are 180 pm and 187 pm respectively. The crystal structure of this compound will be
(a) NaCl type
(b) CsCl type
(c) ZnS type
(d) similar to diamond

42. In the calcium fluoride structure, the coordination number of the cation and anion are respectively
(a) 4, 4
(b) 6, 6
(c) 4, 8
(d) 8, 4

43. Iron oxide crystallises in a hexagonal close-packed array of oxide ions with two out of every three octahedral holes occupied by iron ions. Derive the formula of the iron oxide. **[NCERT** Exemplar**]**
(a) FeO
(b) Fe_2O_3
(c) Fe_3O_4
(d) All are possible

44. Potassium fluoride has NaCl type structure. What is the distance between K^+ and F^- ions if cell edge is a cm?
(a) $\frac{a}{2}$ cm
(b) $\frac{a}{4}$ cm
(c) $2a$ cm
(d) $4a$ cm

45. For cubic coordination, the value of radius ratio is
(a) 0.000 – 0.225
(b) 0.225 – 0.414
(c) 0.414 – 0.732
(d) 0.732 – 1.000

46. If the radius ratio is in the range of 0.414 – 0.732, then the coordination number will be
(a) 2
(b) 4
(c) 6
(d) 8

47. The maximum radius of sphere that can be fitted in the octahedral hole of cubical closed packing of sphere of radius r is
(a) $0.732\,r$
(b) $0.414\,r$
(c) $0.225\,r$
(d) $0.155\,r$

48. The ratio of cationic radius to anionic radius in an ionic crystal is greater than 0.732. Its coordination number is
(a) 1
(b) 4
(c) 6
(d) 8

49. If the value of ionic radius ratio $\left(\frac{r_c}{r_a}\right)$ is 0.52 in an ionic compound, the geometrical arrangement of ions in crystal is
(a) planar
(b) pyramidal
(c) tetrahedral
(d) octahedral

Imperfections in Solids

50. Which defect causes decrease in the density of crystal?
(a) Frenkel
(b) Schottky
(c) Interstitial
(d) F-centre

51. Schottky defect is observed in crystals when **[NCERT Exemplar]**

(a) some cations move from their lattice site to interstitial sites
(b) equal number of cations and anions are missing from the lattice
(c) some lattice sites are occupied by electrons
(d) some impurity is present in the lattice

52. Which of the following defects is also known as dislocation defect? **[NCERT Exemplar]**

(a) Frenkel defect
(b) Schottky defect
(c) Non-stoichiometric defect
(d) None of the above

53. Which one of the following has Frenkel defect?

(a) NaCl (b) AgBr
(c) Graphite (d) Diamond

54. Cations are present in the interstitial sites in **[NCERT Exemplar]**

(a) Frenkel defect (b) Schottky defect
(c) Vacancy defect (d) Metal deficiency defect

55. Which kind of defects are introduced by doping? **[NCERT Exemplar]**

(a) Dislocation defect (b) Schottky defect
(c) Frenkel defects (d) Electronic defects

56. The correct statement regarding *F*-centre is

(a) electron are held in the voids of crystals
(b) *F*-centre produces colour to the crystals
(c) conductivity of the crystal increases due to *F*-centre
(d) All of the above

57. What type of defect can arise when a solid is heated? **[NCERT Exemplar]**

(a) Interstitial defect (b) Vacancy defect
(c) Impurity defect (d) None of these

58. The flame colours of metal ions are due to

(a) Schottky defect (b) Frenkel defect
(c) metal excess defect (d) metal deficiency defect

59. An example of a non-stoichiometric compound is

(a) PbO (b) NiO_2
(c) Al_2O_3 (d) Fe_3O_4

60. In AgBr crystal, the ion size lies in the order $\text{Ag}^+ << \text{Br}^-$. The AgBr crystal should have the following characteristics

(a) defect less (perfect) crystal
(b) Schottky defect
(c) Frenkel defect
(d) Both Schottky and Frenkel defect

Properties of Solids

61. Silicon doped with electron-rich impurity forms **[NCERT Exemplar]**

(a) *p*-type semiconductor
(b) *n*-type semiconductor
(c) intrinsic semiconductor
(d) insulator

62. Which of the following is true about the charge acquired by *p*-type semiconductors? **[NCERT Exemplar]**

(a) Positive
(b) Neutral
(c) Negative
(d) Depends on concentration of *p* impurity

63. A ferromagnetic substance becomes a permanent magnet when it is placed in a magnetic field because **[NCERT Exemplar]**

(a) all the domains get oriented in the direction of magnetic field
(b) all the domains get oriented in the direction opposite to the direction of magnetic field
(c) domains get oriented randomly
(d) domains are not affected by magnetic field

64. Which of the following arrangements shows schematic alignment of magnetic moments of antiferromagnetic substances? **[NCERT Exemplar]**

(a) ↑ ↑ ↑ ↑ ↑ ↑
(b) ↓ ↓ ↓ ↓ ↓ ↓
(c) ↑ ↑ ↓ ↑ ↑ ↓
(d) ↑ ↓ ↑ ↓ ↑ ↓

65. Which of the following statements is not true? **[NCERT Exemplar]**

(a) Paramagnetic substances are weakly attracted by magnetic field
(b) Ferromagnetic substances cannot be magnetised permanently
(c) The domains in antiferromagnetic substances are oppositely oriented with respect to each other
(d) Pairing of electrons cancels their magnetic moment in the diamagnetic substances

66. Which of the following is ferroelectric compound?

(a) $BaTiO_3$ (b) Pb_2O_3
(c) $PbZrO_3$ (d) $K_4[Fe(CN)_6]$

67. Which one of the following metal oxides is antiferromagnetic in nature?

(a) MnO_2 (b) VO_2
(c) TiO_2 (d) CrO_2

68. Which of the following oxides shows electrical properties like metals? **[NCERT Exemplar]**
(a) SiO_2 (b) MgO
(c) $SO_2(s)$ (d) CrO_2

69. Piezoelectric crystals are used in
(a) TV (b) radio
(c) freeze (d) record player

70. Which of the following represents correct order of conductivity in solids? **[NCERT Exemplar]**
(a) $\kappa_{\text{metals}} >> \kappa_{\text{insulators}} < \kappa_{\text{semiconductors}}$
(b) $\kappa_{\text{metals}} << \kappa_{\text{insulators}} < \kappa_{\text{semiconductors}}$
(c) $\kappa_{\text{metals}} ; \kappa_{\text{semiconductors}} > \kappa_{\text{insulators}} = \text{zero}$
(d) $\kappa_{\text{metals}} < \kappa_{\text{seminconductors}} > \kappa_{\text{insulators}} \neq \text{zero}$

Round II (Mixed Bag)

Only One Correct Option

1. Amorphous substances show
(i) short and long range order
(ii) short range order
(iii) long range order
(iv) have no sharp melting point
(a) (i) and (iii) are correct
(b) (i) and (ii) are correct
(c) (ii) and (iii) are correct
(d) (ii) and (iv) are correct

2. The following is not a function of an impurity present in a crystal
(a) establishing thermal equilibrium
(b) having tendency to diffuse
(c) contributing to scattering
(d) introducing new electronic energy levels

3. The incorrect statement in the following is
(a) the ionic crystal of AgBr has Schottky defect
(b) the coordination number of Na^+ ion in NaCl is 4
(c) in ionic compounds having Frenkel defect, the ratio $\frac{r_+}{r_-}$ is high
(d) the unit cell having crystal parameters, $a = b \neq c$, $\alpha = \beta = 90°$, $\gamma = 120°$ is hexagonal

4. The number of atoms in 100 g of an fcc crystal with density, $d = 10 \text{ g/cm}^3$ and cell edge equal to 100 pm, is equal to
(a) 1×10^{25} (b) 2×10^{25}
(c) 3×10^{25} (d) 4×10^{25}

5. The pyknometric density of sodium chloride crystal is $2.165 \times 10^3 \text{ kg m}^{-3}$, while its X-rays density is $2.178 \times 10^3 \text{ kg m}^{-3}$. The fraction of unoccupied sites in sodium chloride crystal is
(a) 5.96 (b) 5.96×10^{-1}
(c) 5.96×10^{-2} (d) 5.96×10^{-3}

6. When a certain crystal was studied by the Bragg technique using X-rays of wavelength 229 pm, an X-ray reflection was observed at an angle of 23° 20′. What is the corresponding interplanar spacing? $[\sin(23°20') = 0.396]$
(a) 375.6 pm (b) 256.5 pm
(c) 289.2 pm (d) 315.4 pm

7. An element occurring in the bcc structure has 12.08×10^{23} unit cells. The total number of atoms of the element in these cells will be
(a) 6.04×10^{23} (b) 12.08×10^{23}
(c) 24.16×10^{23} (d) 36.18×10^{23}

8. In a solid '*AB*' having the NaCl structure, '*A*' atoms occupy the corners of the cubic unit cell. If all the face-centred atoms along one of the axes are removed then the resultant stoichiometry of the solid is
(a) AB_2 (b) A_2B
(c) A_3B_4 (d) A_4B_3

9. The number of unit cells in 58.5 g of NaCl is nearly
(a) 0.5×10^{24} (b) 1.5×10^{23}
(c) 3×10^{22} (d) 6×10^{20}

10. Ferrous oxide has a cubic structure and each edge of the unit cell is 5.0 Å. Assuming density of the oxide as 4.0 g cm^{-3} the number of Fe^{2+} and O^{2-} ions present in each unit cell will be
(a) two Fe^{2+} and four O^{2-}
(b) three Fe^{2+} and three O^{2-}
(c) four Fe^{2+} and two O^{2-}
(d) four Fe^{2+} and four O^{2-}

11. A solid has a structure in which 'W' atoms are located at the corners of a cubic lattice 'O' atoms at the centre of edges and Na atoms at the centre of the cube. The formula for the compound is
(a) Na_2WO_3 (b) Na_2WO_2
(c) $NaWO_2$ (d) $NaWO_3$

12. A metallic element has a cubic lattice. Each edge of the unit cell is 2 Å. The density of the metal is 2 g cm^{-3}. The unit cells in 200 g of the metal are

(a) 1×10^{25} (b) 1×10^{24}

(c) 1×10^{22} (d) 1×10^{20}

13. If the pressure on a NaCl structure is increased, then its coordination number will

(a) increase (b) decrease

(c) either (a) or (b) (d) remain the same

14. In orthorhombic lattice, the value of a, b and c are respectively 4.2 Å, 8.6 Å and 8.3 Å. Given the molecular mass of the solute is 155 g mol^{-1} and its density is 3.3 g/cc, the number of formula units per unit cell is

(a) 2 (b) 3

(c) 4 (d) 6

15. Analysis shows that nickel oxide has the formula $Ni_{0.98}O_{1.00}$. What fraction of nickel exist as Ni^{2+}? **[NCERT Exemplar]**

(a) 4% (b) 95%

(c) 98% (d) 90%

16. A sample of ferrous oxide has actual formula $Fe_{0.93}O_{4.00}$. What type of non-stoichiometric defect is present in this sample? **[NCERT Exemplar]**

(a) Schottky defect

(b) Frenkel defect

(c) Metal deficiency defect

(d) Metal excess defect

17. Match the type of packing given in Column I with the items given in Column II.

Column I	Column II
A. Square close packing in two dimensions	1. Triangular voids
B. Hexagonal close packing in two dimensions	2. Pattern of spheres is repeated in every fourth layer
C. Hexagonal close packing in three dimensions	3. Coordination number 4
D. Cubic close packing in three dimensions	4. Pattern of sphere is repeated in alternate layers

[NCERT Exemplar]

Codes

	A	B	C	D
(a)	3	1	4	2
(b)	1	2	3	4
(c)	3	2	1	4
(d)	4	3	2	1

18. Match the items given in Column I with the items given in Column II.

Column I	Column II
A. Mg in solid state	1. *p*-type semiconductor
B. $MgCl_2$ in molten state	2. *n*-type semiconductor
C. Silicon with phosphorus	3. Electrolytic conductors
D. Germanium with boron	4. Electronic conductors

[NCERT Exemplar]

Codes

	A	B	C	D		A	B	C	D
(a)	4	3	2	1	(b)	4	3	1	2
(c)	3	4	2	1	(d)	3	4	1	2

19. Match the type of unit cell given in Column I with the features given in Column II.

Column I	Column II
A. Primitive cubic unit cell	1. Each of the three perpendicular edges compulsorily have the different edge length, *i.e.*, $a \neq b \neq c$.
B. Body centred cubic unit cell	2. Number of atoms per unit cell is one.
C. Face centred cubic unit cell	3. Each of the three perpendicular edges compulsorily have the same edge length, *i.e.*, $a = b = c$
D. End centred orthorhombic unit cell	4. In addition to the contribution from the corner atoms the number of atoms present in a unit cell is one.
	5. In addition to the contribution from the corner atoms the number of atoms present in a unit cell is three.

[NCERT Exemplar]

Codes

	A	B	C	D		A	B	C	D
(a)	1	3	2	5	(b)	2	4	3	1
(c)	2	4	5	1	(d)	1	2	3	5

More than One Correct Option

20. An excess of potassium ions makes KCl crystals to appear violet or lilac in colour since **[NCERT Exemplar]**

(a) some of the anionic sites are occupied by an unpaired electron

(b) some of the anionic sites are occupied by a pair of electrons

(c) there are vacancies at some anionic sites

(d) *F*-centres are created which impart colour to the crystals

21. Under the influence of electric field, which of the following statements is true about the movement of electrons and holes in a p-type semiconductor? **[NCERT** Exemplar**]**

(a) Electron will move towards the positively charged plate through electron holes
(b) Holes will appear to be moving towards the negatively charged plate
(c) Both electrons and holes appear to move towards the positively charged plate
(d) Movement of electrons is not related to the movement of holes

22. For the spinel structure ($MgAl_2O_4$), the correct statement is/are

(a) 50% octahedral voids are occupied by ions
(b) Al^{3+} is equally distributed in tetrahedral voids and octahedral voids
(c) oxide ions occupy ccp lattice
(d) 12.5% tetrahedral voids are occupied by ions

23. For which of the following cases, answer is 4?

(a) Coordination number of Zn^{2+} in zinc blende
(b) Number of body diagonal planes in a cube
(c) Formula units in rock salt structure
(d) Formula units in CsCl structure

24. Which of the following statements are true about metals? **[NCERT** Exemplar**]**

(a) Valence band overlaps with conduction band
(b) The gap between valence band and conduction band is negligible
(c) The gap between valence band and conduction band cannot be determined
(d) Valence band may remain partially filled

Assertion and Reason

Directions (Q. Nos. 25 to 29) *Each of these questions contains two statements : Statement* I *(Assertion) and Statement* II *(Reason). Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c), (d) given below*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

25. **Statement I** Crystalline solids are anisotropic.

Statement II Crystalline solids are not as closely packed as amorphous solids.

26. **Statement I** Total number of octahedral voids present in the unit cell of cubic close packing including the one that is present at the body centre, is four.

Statement II Besides the body centre there is one octahedral void present at the centre of each of the six faces of the unit cell and each of which is shared between two adjacent unit cells. **[NCERT** Exemplar**]**

27. **Statement I** The packing efficiency is maximum for the fcc structure.

Statement II The coordination number is 12 in fcc structures. **[NCERT** Exemplar**]**

28. **Statement I** Semiconductors are solids with conductivities in the intermediate range from $10^{-6} - 10^{4}$ ohm^{-1} m^{-1}.

Statement II Intermediate conductivity in semiconductor is due to partially filled valence band. **[NCERT** Exemplar**]**

29. **Statement I** The conductivity of semiconductors increases with increase in temperature.

Statement II Semiconductors conduct electricity due to the presence of ions.

Comprehension Based Questions

Directions (Q. Nos. 30 to 32) In a unit cell, atoms (A) are present at all corner lattices, (B) are present at alternate faces and all edge centres. Atom (C) are present at face centres left from (B) and one at each body diagonal at distance of 1/4th of body diagonal from corner.

30. Formula of the given solid is

(a) $A_3B_8C_7$
(b) AB_4C_6
(c) $A_6B_4C_8$
(d) $A_2B_9C_{11}$

31. A tetrad axis is passed from the given unit cell and all the atoms touching the axis are removed. The possible formula of the compound left is

(a) AB_3C_6 and AB_4C_5
(b) $A_3B_6C_7$ and $A_3B_6C_5$
(c) $A_4B_5C_8$ and $A_4B_5C_7$
(d) AB_2C and ABC_2

32. Total fraction of voids occupied are

(a) 0.58
(b) 0.25
(c) 0.48
(d) 0.86

Directions (Q. Nos. 33 to 35) In hexagonal systems of crystals, a frequently encountered arrangement of atoms is described as a hexagonal prism. Here, the top and bottom of the cell are regular hexagons and three atoms are sandwitched in between them. A space filling model of this structure, called hexagonal closed packed (HCP), is constituted of a sphere on a flat surface surrounded in the same plane by six identical spheres as closed as possible.

Three spheres are then placed over the first layer so that they touch each other and represent the second layer. Each one of these sphere touches three spheres of the bottom layer. Finally, the second layer is covered with a third layer that is identical to the bottom layer in relative position. Assume radius of every sphere to be 'r'.

33. The number of atoms in the HCP unit cell is

(a) 4 (b) 6
(c) 12 (d) 17

34. The volume of this HCP unit is

(a) $24\sqrt{2}r^3$ (b) $16\sqrt{2}r^3$
(c) $12\sqrt{2}r^3$ (d) $\frac{64}{3\sqrt{3}}r^3$

35. The empty space in this HCP unit cell is

(a) 74% (b) 47.6%
(c) 32% (d) 26%

Previous Years' Questions

36. In a face centred cubic lattice, atom A occupies the corner positions and atom B occupies the face centre positions. If one atom of B is missing from one of the face centred points, the formula of the compound is **[AIEEE 2011]**

(a) A_2B (b) AB_2 (c) A_2B_2 (d) A_2B_5

37. Copper crystallises in fcc lattice with a unit cell edge of 361 pm. The radius of copper atom is **[AIEEE 2011, 2009]**

(a) 181 pm (b) 108 pm (c) 128 pm (d) 157 pm

38. The edge length of a face centred cubic cell of an ionic substance is 508 pm. If the radius of the cation is 110 pm, the radius of the anion is **[AIEEE 2010]**

(a) 288 pm (b) 398 pm
(c) 618 pm (d) 144 pm

39. Percentage of free space in cubic close packed structure and in body centred packed structure are respectively **[AIEEE 2010]**

(a) 30% and 26% (b) 26% and 32%
(c) 32% and 48% (d) 48% and 26%

40. In a compound, atoms of element Y form ccp lattice and those of element X occupy 2/3rd of tetrahedral voids. The formula of the compound will be **[AIEEE 2008]**

(a) X_4Y_3 (b) X_2Y_3 (c) X_2Y (d) X_3Y_4

41. Total volume of atoms present in a face-centred cubic unit cell of a metal is (r is atomic radius) **[AIEEE 2006]**

(a) $\frac{20}{3}\pi r^3$ (b) $\frac{24}{3}\pi r^3$
(c) $\frac{12}{3}\pi r^3$ (d) $\frac{16}{3}\pi r^3$

42. An ionic compound has a unit cell consisting of A ions at the corners of a cube and B ions on the centres of the faces of the cube. The empirical formula for this compound would be **[AIEEE 2005]**

(a) A_3B (b) AB_3
(c) A_2B (d) AB

43. What type of crystal defect is indicated in the diagram shown below ? **[AIEEE 2004]**

Na^+ Cl^- Na^+ Cl^- Na^+ Cl^-
Cl^- Cl^- Na^+ Na^+
Na^+ Cl^- Cl^-, Na^+ Cl^-
Cl^- Na^+ Cl^- Na^+ Na^+

(a) Frenkel defect
(b) Schottky defect
(c) Interstitial defect
(d) Frenkel and Schottky defects

44. How many unit cells are present in a cube shaped ideal crystal of NaCl of mass 1.00 g?

[Atomic mass : Na = 23, Cl = 35.5] **[AIEEE 2003]**

(a) 2.57×10^{21}
(b) 5.14×10^{21}
(c) 1.28×10^{21}
(d) 1.71×10^{21}

45. Number of atoms in the unit cell of Na (bcc type crystal) and Mg (fcc type crystal) are, respectively **[AIEEE 2002]**

(a) 4, 4 (b) 4, 2
(c) 2, 4 (d) 1, 1

Answers

Round I

1. (b)	**2.** (a)	**3.** (b)	**4.** (d)	**5.** (b)	**6.** (c)	**7.** (d)	**8.** (c)	**9.** (a)	**10.** (c)
11. (b)	**12.** (b)	**13.** (a)	**14.** (b)	**15.** (c)	**16.** (a)	**17.** (c)	**18.** (b)	**19.** (c)	**20.** (d)
21. (d)	**22.** (b)	**23.** (c)	**24.** (a)	**25.** (b)	**26.** (b)	**27.** (c)	**28.** (b)	**29.** (c)	**30.** (a)
31. (d)	**32.** (a)	**33.** (d)	**34.** (c)	**35.** (b)	**36.** (b)	**37.** (c)	**38.** (d)	**39.** (b)	**40.** (d)
41. (b)	**42.** (d)	**43.** (b)	**44.** (a)	**45.** (d)	**46.** (c)	**47.** (b)	**48.** (d)	**49.** (d)	**50.** (b)
51. (b)	**52.** (a)	**53.** (b)	**54.** (a)	**55.** (d)	**56.** (d)	**57.** (b)	**58.** (c)	**59.** (d)	**60.** (d)
61. (b)	**62.** (b)	**63.** (a)	**64.** (d)	**65.** (b)	**66.** (a)	**67.** (a)	**68.** (d)	**69.** (d)	**70.** (a)

Round II

1. (d)	**2.** (a)	**3.** (b)	**4.** (d)	**5.** (d)	**6.** (c)	**7.** (c)	**8.** (c)	**9.** (b)	**10.** (d)
11. (d)	**12.** (a)	**13.** (a)	**14.** (c)	**15.** (b)	**16.** (c)	**17.** (a)	**18.** (a)	**19.** (c)	**20.** (a,d)
21. (a,b)	**22.** (a,c,d)	**23.** (a,c)	**24.** (a,b,d)	**25.** (c)	**26.** (c)	**27.** (b)	**28.** (c)	**29.** (c)	**30.** (b)
31. (a)	**32.** (a)	**33.** (b)	**34.** (a)	**35.** (d)	**36.** (d)	**37.** (c)	**38.** (d)	**39.** (b)	**40.** (a)
41. (d)	**42.** (b)	**43.** (b)	**44.** (a)	**45.** (c)					

the Guidance

Round I

1. At low temperature, molecular motion are slow, thus constituents are close together. Moreover, strong cohesive forces also holds the constituents together. These two conditions shows the existence of a substance in solid state.

2. In solid state the constituent particles are not free to move. They can only oscillate about their mean positions due to strong attraction forces between the particles. That is why solids have a closely packed arrangement and rigid structure.

3. Quartz glass is an amorphous solid because in it short range order of constituents is found.

4. Amorphous solids are isotropic in nature. These can be moulded by heating. Moreover, they become crystalline on standing for a long time or on heating.

5. Crystalline solids are anisotropic in nature, *i.e.,* have different properties in different directions.

6. Crystalline solids such as NaCl, $BaCl_2$ etc., will show anisotropy.

7. Metallic crystals are good conductor of heat and current due to the presence of free electrons in them.

9. Ionic solids are hard and brittle because of the presence of very strong forces of attraction. Because of highly ordered arrangement of particles, these are anisotropic in nature. In molten state or in aqueous solution, these are good conductor of electricity because of the presence of free ions.

10. In diamond, the constituent atoms are held together by strong covalent bonds. It is a giant molecule. Thus, classified as network solid.

Note *SO_2, H_2O and I_2 are examples of molecular solids.*

11. In graphite each C atom is sp^2 hybridised. One electron of each C atom remains free and make graphite, a good conductor of electricity.

15. (i) A point lying at the **corner** of a unit cell is shared equally by eight unit cells and therefore, only one-eighth $\left(\frac{1}{8}\right)$ of each such point belongs to the given unit cell.

(ii) **A body centred point** belongs entirely to **one** unit cell since, it is not shared by any other unit cell.

17. Length of the edge of NaCl unit cell,

$$= 2 \times \text{distance between } Na^+ \text{ and } Cl^-$$

$$= 2 \times a = 2a \text{ pm}$$

18. For a face-centred cubic unit cell (fcc),

$$\text{Edge length } (a) = 2\sqrt{2}\, r$$

$$= 2 \times 1.4142 \times 0.144 \text{ nm}$$

$$= 0.407 \text{ nm}$$

19. $r = \frac{a}{2\sqrt{2}} = \frac{620}{2\sqrt{2}} = 219.25$ pm.

20. CsCl has a bcc lattice. So, $d_{\text{body}} = a\sqrt{3}$

or $\quad d_{\text{body}} = \sqrt{3} \times 0.4123 \text{ nm} = 0.7141 \text{ nm}$

The sum of the ionic radii of Cs^+ and Cl^- ions is half of this distance *i.e.,*

$$r_{Cs^+} + r_{Cl^-} = \frac{d_{\text{body}}}{2} = \frac{0.7141}{2} \text{ nm} = 0.3571 \text{ nm}$$

Ionic radius of $Cs^+ = 0.3571 - 0.181 = 0.1761 \text{nm}$

21. Volume $= a^3 = (400 \times 10^{-10} \text{ cm})^3 = 64 \times 10^{-24} \text{ cm}^3$

$$V_{\text{total}} = VN_A = 64 \times 10^{-24} \times 6.02 \times 10^{23} = 38.4$$

Molar volume $= \frac{1}{4} \times V_{\text{total}} = \frac{38.4}{4} = 9.6$ mL

22. Volume of unit cell $(V) = a^3$.

$$\therefore \quad = (3.04 \times 10^{-8} \text{ cm})^3$$
$$= 2.81 \times 10^{-23} \text{ cm}^3$$

23. For an fcc unit cell, $r = \frac{a}{2\sqrt{2}}$ [Given, $r = 125$ pm]

$$a = 2\sqrt{2} \times r = 2 \times 1.414 \times 125$$
$$= 353.5 \text{ pm} \simeq 354 \text{ pm}$$

Volume of unit cell $= a^3 = (353.5 \times 10^{-10} \text{cm})^3$

$$= 442 \times 10^{-25} \text{ cm}^3$$

Number of unit cell $= \frac{1.00 \text{ cm}^3}{442 \times 10^{-25} \text{ cm}^3}$

$$= 2.26 \times 10^{22} \text{ unit cells}$$

24. *A* atoms are at eight corners of the cube. Therefore, the number of *A* atoms in the unit cell $= \frac{8}{8} = 1$,

Atoms *B* per unit cell = 1.

Hence, the formula is *AB*.

25. Density, $d = \frac{ZM}{a^3 N_A} = \frac{4(58.5) \text{ g mol}^{-1}}{(5.628 \times 10^{-8} \text{ cm})^3 (6.023 \times 10^{23} \text{ mol}^{-1})}$

$$= 2.179 \text{ g cm}^{-3}$$

26.

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

$$d_{(111)} = \frac{a}{\sqrt{(1)^2 + (1)^2 + (1)^2}} = \frac{a}{\sqrt{3}}$$

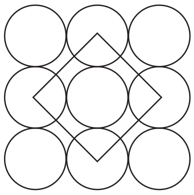
$$d_{(111)} = \frac{318}{\sqrt{3}} = 184 \text{ pm}$$

27. In bcc structure 68% of the available volume is occupied by spheres. Thus, vacant space is 32%.

28. Packing efficiency,
for sc unit cell = 5%
for bcc unit cell = 68%
for fcc unit cell = 74%

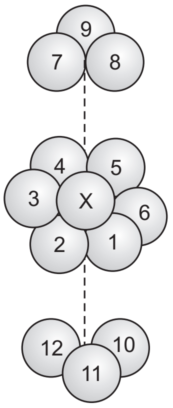
Thus, the order of packing efficiency is fcc > bcc > sc

29. Square close packing in two dimension can be shown as

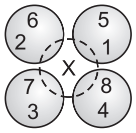


Thus, coordination number is 4 as each atom is sorrounded by four other atoms.

31.



ccp structure



bcc structure

(a) 12 (as each atom is attached with 12 other atoms.)

(b) 8 (because each atom is attached with 8 other atoms.)

32. Number of octahedral sites = Number of sphere in the packing.

∴ Number of octahedral sites per sphere = 1.

33. In hexagonal close packing, it is the third layer, spheres of which are exactly aligned with those of the first layer. Other given statements are true.

34. Tetrahedral sites are double comparable to number of atom then ratio of *X* and *Z* respectively 2 : 1, since formula of the compound X_2Z.

35. Cu atoms are at eight corners of the cube. Therefore, the number of Cu atoms in the unit cell $= \frac{8}{8} = 1$.

Ag atoms are at the face-centre of six faces. Therefore, its share in the unit cell $= \frac{6}{2} = 3$.

Au atoms are at the body centre, so the number of Au atoms = 1

∴ The formula of the alloy is $CuAg_3Au$.

40. Na_2O has antifluorite (A_2B) type structure.

41. $\frac{r_+}{r_-} = \frac{180}{187} = 0.962$, which lies in the range of 0.732 – 1.000, hence, coordination number is 8, *i.e.,* the structure is CsCl type.

43. There is one octahedral hole for each atom in hexagonal close packed arrangement. If the number of oxide ions (O^{2-}) per unit cell is 1, then the number of Fe^{3+} ions $= 2/3 \times$ octahedral holes $= 2/3 \times 1 = 2/3$. Thus, the formula of the compound $= Fe_{2/3}\ O_1$ or Fe_2O_3.

44. Distance between K^+ and $F^- = \frac{1}{2} \times$ length of the edge.

45. For body centred cubic arrangement coordination number is 8 and radius ratio $\left(\frac{r_+}{r_-}\right)$ is $0.732 - 1.000$.

46. The radius ratio for coordination number 4, 6 and 8 lies in between the ranges 0.225 – 0.414, 0.414 – 0.732 and 0.732 – 1.000 respectively.

48. When radius ratio is in between 0.732 – 1.000, then coordination number is 8 and the structural arrangement is body centred cubic.

49. The value of ionic radius ratio is 0.52 which is in between 0.414 – 0.732, then the geometrical arrangement of ions in crystal is octahedral.

50. More is the Schottky defect in crystal, more is the decrease in density.

51. Schottky defect is observed when equal number of cations and anions are missing from their lattice sites.

52. Frenkel defect, which is a stoichiometric defect, is also known as dislocation defect because in it some of the ions dislocated from their position and occupy interstitial spaces.

53. AgBr exhibits Frenkel defect due to large difference in the size of Ag^+ and Br^- ions.

54. In Frenkel defect, the smaller ions, which is generally the cation, leave its place and occupy the interstitial site. That's why this defect is also called interstitial defect.

55. Doping introduces electronic defects as it results in the formation of holes or free electrons.

56. All the given statements are correct about *F*-centres.

57. When a solid is heated, a vacancy is created in the crystal. On heating, some of the lattice sites are vacant and the density of the solid decreases as the number of ions per unit volume decreases.

58. In metal excess defect when holes created by missing of anions are occupied by electrons, these sites are called *F*-centres and are responsible for the colour of the crystal.

59. Fe_3O_4 is a non-stoichiometric compound because in it, the ratio of the cations to the anions becomes different from that indicated by the chemical formula.

61. When Si is doped with an electron rich impurity, the resulting crystal have an extra electron, which makes the crystal conducting. Since an electron (negative charge) is responsible for the conductivity of crystal, it is called *n*-type semiconductor.

62. In case of *p*-type semiconductors, holes are created but the crystal as a whole remains neutral.

63. In the presence of magnetic field, all the domains of a ferromagnetic substance get oriented in the direction of magnetic field. That's why it becomes a permanent magnet.

64. The domains of antiferromagnetic substance are oppositely oriented and cancel out each other's magnetic moment, thus, it is represented as

$$\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$$

65. Ferromagnetic substances can be magnetised permanently. Other given statements are true.

66. The dipoles in certain solids are spontaneously aligned in a particular direction, even in the absence of electric field. Such substances are called ferroelectric substances. Barium titanate ($BaTiO_3$) and potassium hydrogen phosphate (KH_2PO_4) are ferroelectric solids.

68. TiO, CrO_2 and ReO_3 behave as metal, thus, shows electrical properties similar to metals.

70. Conductivity of metals are much higher than the semiconductors and insulators. Insulators are non-conductor of electricity.

Thus, the order of conductivities of solids is

$$\kappa_{metals} >> \kappa_{insulator} < \kappa_{semiconductors}.$$

Round II

1. Amorphous solids have short range order and no sharp melting point.

2. Addition of impurity does not establish equilibrium.

3. Coordination number of Na^+ in NaCl is 6.

4. $$M = \frac{\rho \times a^3 \times N_A \times 10^{-30}}{Z}$$

$$= \frac{10 \times (100)^3 \times 6.02 \times 10^{23} \times 10^{-30}}{4} = 1.505$$

$\therefore$ Number of atoms in 100 g $= \frac{6.02 \times 10^{23}}{1.505} \times 100$

$$= 4 \times 10^{25}$$

5. Difference $= 2.178 \times 10^3 - 2.165 \times 10^3$

$$= 0.013 \times 10^3$$

Fraction unoccupied $= \frac{0.013 \times 10^3}{2.178 \times 10^3}$

$$= 5.96 \times 10^{-3}$$

6. Given that, $\lambda = 229$ pm and $\theta = 23°20'$

Substituting these values in the Bragg's equation, we have

$$d_{hkl} = \frac{\lambda}{2\sin\theta} = \frac{229\text{ pm}}{2\sin(23°20')}$$

$$= \frac{229\text{ pm}}{2\times 0.396} = 289.2\text{ pm}$$

7. There are two atoms in a bcc unit cell.

So, number of atoms in 12.08×10^{23} unit cells

$$= 2\times 12.08\times10^{23}$$

$$= 24.16\times10^{23}\text{ atoms}$$

8. There are 6 *A* atoms on the face centres. Removing face centred atoms along one of the axes means removal of 2 *A* atoms.

Now, number of *A* atoms per unit cell

$$= \underset{\text{(corners)}}{8\times\frac{1}{8}} + \underset{\text{(face-centred)}}{4\times\frac{1}{2}} = 3$$

Number of *B*-atoms per unit cell

$$= \underset{\text{(edge centred)}}{12\times\frac{1}{4}} + \underset{\text{(body centred)}}{1} = 4$$

Hence, the resultant stoichiometry is A_3B_4.

9. 58.5 g NaCl = 1 mol NaCl = 6.023×10^{23} NaCl units.

One unit cell contains 4 NaCl units.

Hence, number of unit cell present

$$= \frac{6.023\times10^{23}}{4} = 1.5\times10^{23}$$

10. Let the units of ferrous oxide in a unit cell = *n*.

Molecular weight of ferrous oxide (FeO)

$$= 56 + 16 = 72\text{ g mol}^{-1}$$

$$\text{Weight of } n \text{ units} = \frac{72\times n}{6.023\times10^{23}}$$

Volume of one unit = (length of corner)^3

$$= (5\text{ Å})^3 = 125\times10^{-24}\text{ cm}^3$$

$$\text{Density} = \frac{\text{wt. of cell}}{\text{volume}}$$

$$\therefore \quad 4.09 = \frac{72\times n}{6.023\times10^{23}\times125\times10^{-24}}$$

$$\text{Hence,} \quad n = \frac{3079.2\times10^{-1}}{72} = 42.7\times10^{-1}$$

$$= 4.27 \approx 4$$

11. In a unit cell, W atoms at the corner $= \frac{1}{8}\times 8 = 1$

O atoms at the centre of edges $= \frac{1}{4}\times 12 = 3$

Na atoms at the centre of the cube = 1

W : O : Na = 1 : 3 : 1

Hence, formula = $NaWO_3$

12. Edge length of the unit cell = 2 Å = 2×10^{-8} cm

$$\text{Volume of the unit cell} = (2\times10^{-8})^3\text{ cm}^3$$

$$= 8\times10^{-24}\text{ cm}^3$$

$$\text{Mass of unit cell} = \text{volume}\times\text{density}$$

$$= 8\times10^{-24}\times2.5\text{ g}$$

No. of unit cells in 200 g of the metal

$$\frac{\text{mass of metal}}{\text{mass of unit cell}} = \frac{200}{8\times10^{-24}\times2.5} = 1\times10^{25}$$

13.

$$\underset{\text{(6 : 6 coordination no.)}}{\text{NaCl structure}} \underset{760\text{ K}}{\overset{\text{High pressure}}{\rightleftharpoons}} \underset{\text{(8 : 8 coordination no.)}}{\text{CsCl structure}}$$

14. $Z = \frac{a^3\times N_A\times\rho}{M}$

$$= \frac{4.2\times8.6\times8.3\times10^{-24}\times6.023\times10^{23}\times3.3}{155}$$

$$= 3.84 \approx 4$$

15. The ratio of Ni and O atoms in pure nickel oxide (NiO) = 1 : 1

Let *x* be the number of Ni (II) atoms replaced by Ni (III) atoms in the oxide.

$\therefore$ Number of Ni (II) atoms present = $(0.98 - x)$

Since, the oxide is neutral in nature,

Total charge on Ni atoms = Charge on oxygen atoms

$$2(0.98 - x) + 3x = 2$$

$$1.96 - 2x + 3x = 2$$

$$x = 2 - 1.96 = 0.04$$

% of Ni (III) atoms in nickel oxide

$$= \frac{\text{Number of Ni (III) atoms}}{\text{Total number of Ni atoms}}\times100$$

$$= \frac{0.04}{0.98}\times100 = 4.01\%$$

% of Ni (II) atoms in nickel oxide = 100 − 4.01

= 95.99%

16. Metal deficiency defect is present in the sample because iron is less in amount than that required for stoichiometric composition.

17. Coordination number is 4 in square close packing in two dimensions.

Two dimensional hexagonal close packing contains triangular voids.

Three dimensional hexagonal close packing have *ABAB* .... arrangement whereas, ccp have *ABCABC* ...... type arrangement.

18. Mg in solid state is an electronic conductor as electrons are responsible for its conductivity. $MgCl_2$ in molten state is an electrolytic conductor as ions are responsible for its conductivity. Si with P is a *n*-type semiconductor and Ge with B is a *p*-type semiconductor.

19. For primitive unit cell number of atoms $= 1$

For bcc, number of atoms $= 1 + 1 = 2$

For fcc, number of atoms $= 1 + 3 = 4$

For end centred orthorhombic unit cell $a \neq b \neq c$

20. The colour of KCl is violet or lilac because of the presence of unpaired electrons, called the *F*-centre, at some of the anionic sites.

21. In *p*-type semiconductors, holes move towards the positively charged plate and electrons towards the negatively charged plate.

22. For spinel structure, O^{2-} ions from ccp arrangement.

$\therefore$ Number of O^{2-} ions = 4.

Numbr of tetrahedral void $= 8$,

Number of octahedral void = 4

$$\text{Number of } Mg^{2+} \text{ ions} = \frac{1}{8} \times \text{tetrahedral void} = \frac{1}{8} \times 8 = 1$$

$$\text{Number of } Al^{3+} \text{ ions} = \frac{1}{2} \times \text{tetrahedral void} = \frac{1}{2} \times 4 = 2$$

So, 50% octahedral voids are occupied and 1/8th, *i.e.*, 12.5% tetrahedral voids are occupied.

23. (a) CN of Zn^{2+} ion in ZnS = 4.

(b) Number of body diagonal planes in a cube $= 6$.

(c) Formula unit in rock salt structure = 4.

(d) Formula unit in CsCl structure $= 1$.

24. In metals valence bond overlaps with the conduction band, thus the gap between these two in negligible. In these, the valence band may also remain partially filled.

25. Crystalline solids possess the properties of rigidity. They are anisotropic and undergo a clean cleavage. The constituent particles are arranged in a definite and orderly pattern through the entire three dimensional space.

26. Statement II is wrong.

27. Both the statements are correct.

28. Intermediate conductivity of semiconductors is due to small energy gap between valence band and conduction band.

29. Semiconductors conduct electricity not due to presence of ions but due to presence of defects.

30. Number of *A* atoms $= 8 \text{ (corner)} \times \frac{1}{8} \text{ (per corner share)} = 1$

$$\text{Number of } B \text{ atoms} = 2 \text{ (alternate face)} \times \frac{1}{2} \text{ (face centre share)}$$
$$+ 12 \text{ (edge)} \times \frac{1}{4} \text{ (edge centre share)}$$
$$= 1 + 3 = 4$$

$$\text{Number of } C \text{ atoms} = 4 \text{ (face centres left from B)} \times \frac{1}{2} \text{ (face centre share)}$$
$$+ 1 \text{ (at body diagonal)} \times 4 \text{ (body diagonal)}$$
$$= 2 + 4 = 6$$

Formula AB_4C_6.

31. ***Case I*** If the tetrad axis passes through the face centres where *B* lies, then

$$\text{Number of } B \text{ atoms} = 4 - \left(\frac{1}{2} \times 2\right) = 3$$

The formula of the compound left is AB_3C_6.

Case II If the tetrad axis passes through the face centres where C lies, then

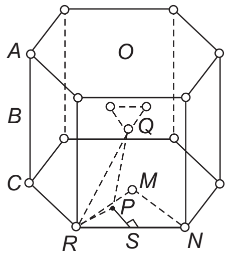
$$\text{Number of C atoms} = 6 - \left(\frac{1}{2} \times 2\right) = 5$$

The formula of the compound left is AB_4C_5.

32. There are 8 effective tetrahedral voids, out of which 4 are occupied (one at each body diagonal) and 4 effective octahedral voids such that one is not filled (body centre). So, out of 12 (8 tetrahedral voids + 4 octahedral voids), only 7 are filled (4 tetrahedral voids + 3 octahedral voids).

$$\text{Therefore, fraction of void occupied} = \frac{7}{12} = 0.58$$

33.



In hcp unit cell

$$\text{Contribution of atoms from corner} = \frac{1}{6}$$

$$\text{Contribution from face centre} = \frac{1}{2}$$

$$\Rightarrow \text{Total number of atoms per unit cell} = 12 \times \frac{1}{6} + 2 \times \frac{1}{2} + 3 = 6$$

34. In close packed arrangement, side of the base $= 2r$

$$\Rightarrow \quad RS = r$$

Also *MNR* is equilateral triangle, $\angle PRS = 30°$

$$\text{In triangle } PRS, \cos 30° = \frac{RS}{PR} = \frac{\sqrt{3}}{2}$$

$$\Rightarrow \quad PR = \frac{2}{\sqrt{3}} RS = \frac{2}{\sqrt{3}} r$$

In right angle triangle $PQR : PQ = \sqrt{QR^2 - PR^2} = 2\sqrt{\frac{2}{3}}\,r$

$\Rightarrow$ Height of hexagon $= 2PQ = 4\sqrt{\frac{2}{3}}\,r$

$\Rightarrow$ Volume = area of base × height $= 6\,\frac{\sqrt{3}}{4}(2r)^2 \times 4\sqrt{\frac{2}{3}}\,r$

$$= 24\sqrt{2}r^3$$

35. Packing fraction $= \dfrac{\text{volume occupied by atoms}}{\text{volume of unit cell}}$

$$= 6 \times \frac{4}{3}\pi r^3 \times \frac{1}{24\sqrt{2}r^3} = 0.74$$

$\Rightarrow$ Fraction of empty space $= 1 - 0.74 = 0.26 = 26\%$

36. Number of atoms (A) per unit cell $= 8 \times \frac{1}{8} = 1$

Number of atoms (B) per unit cell $= (6-1) \times \frac{1}{2} = \frac{5}{2}$

(one atom B is missing)

Thus, formula is $A_1B_{5/2} = A_2B_5$

37. Copper crystallises in fcc lattice.

If r = radius

a = edge length

then $r = \dfrac{a}{2\sqrt{2}} = \dfrac{361}{2\sqrt{2}}$ pm

$= 127.633$ pm ≈ 128 pm

38. For fcc arrangement

$$2(r^+ + r^-) = \text{edge length}$$

$$2(110 + r^-) = 508$$

So, $r^- = 144$ pm

39. Packing fraction of ccp $= \dfrac{\pi}{3\sqrt{2}} = 0.74 \Rightarrow 74\%$

% free space in ccp $= 26\%$

Packing fraction of bcc $= \dfrac{\pi\sqrt{3}}{8} = 0.68 = 68\%$

% free space in bcc $= 32\%$

40. Suppose atoms of element Y in ccp $= 100$

Number of tetrahedral voids $= 2 \times 100$

Number of atoms of element

$$X = \frac{2}{3} \times 200 = \frac{400}{3}$$

$$\frac{X}{Y} = \frac{400}{300}$$

Formula $= X_4Y_3$

41. Total number of atoms in face centred cubic unit cell = 4

At corner $= 8 \times \frac{1}{8} = 1$

On faces $= 6 \times \frac{1}{2} = 3$

Total = 4

Total volume $= 4 \times \dfrac{4\pi r^3}{3}$

$$= \frac{16}{3}\pi r^3$$

42. Unit cell consists of A ions at the corners. Thus, number of ions of the type $A = \frac{8}{8} = 1$

Unit cell consists of B ions at the centre of the six faces.

Thus, number of ions of the type $B = \frac{6}{2} = 3$

[Each corner is shared by 8 cubes and each face is shared by 2 faces]

Thus, formula is AB_3.

43. When equal number of cations and anions (such that charges are equal) are missing ($1Na^+$, $1Cl^-$ /1 Fe^{2+}, $2Cl^-$) then it is a case of Schottky defect.

44. Mass of one unit cell (m) = volume × density

$$= a^3 \times d = a^3 \times \frac{Mz}{N_0a^3} = \frac{Mz}{N_0}$$

$$m = \frac{58.5 \times 4}{6.02 \times 10^{23}}\ \text{g}$$

$\therefore$ Number of unit cells in 1g $= \dfrac{1}{m}$

$$= \frac{6.02 \times 10^{23}}{58.5 \times 4}$$

$$= 2.57 \times 10^{21}$$

45. In Na unit cell (body centred cubic)

8 (corner atoms) $\times \frac{1}{8} = 1$

Atoms placed inside the unit cell = 1

Total atoms = 2 .

In Mg unit cell (face centred cubic)

8 (corner atoms) $\times \frac{1}{8} = 1$

6 (face atoms) $\times \frac{1}{2} = 3$

Total atoms = 4.

2 Solutions

JEE Main MILESTONE

- Types of Solutions
- Solubility
- Concentration of Solution
- Vapour Pressure of Solutions and Raoult's Law
- Ideal Solutions
- Non-Ideal or Real Solutions
- Colligative Properties
- Abnormal Colligative Properties : van't Hoff Factor

2.1 Types of Solutions

In case of binary solutions, each component may be solid, liquid or in gaseous state and on this basis different types of solutions are summarised, in the following Table.

Table 2.1 **Different Types of Solutions**

Types of solution	Solute	Solvent	Common example
Gaseous solutions	Gas	Gas	Mixture of oxygen and nitrogen gases
	Liquid	Gas	Chloroform mixed with nitrogen gas
	Solid	Gas	Camphor in nitrogen gas
Liquid solutions	Gas	Liquid	Oxygen dissolved in water
	Liquid	Liquid	Ethanol dissolved in water
	Solid	Liquid	Glucose dissolved in water
Solid solutions	Gas	Solid	Solution of hydrogen in palladium
	Liquid	Solid	Amalgam of mercury with sodium
	Solid	Solid	Copper dissolved in gold

Solution is a homogeneous mixture of two or more substances on molecular level. A solution of two substances is called a ***binary solution.*** *The substances forming the solution are called* ***components*** *of the solutions. As a generalisation, the component present in smaller amount is called* ***solute*** *and the other present in larger amount is called* ***solvent.***

Caution Point *A solution in which water is the solvent is called an* ***aqueous solution.*** *The solutions in which solid is present in larger proportion are called solid solutions. Amalgam is a solution of liquid in solid. Alloys are solution of a solid is another solid.*

2.2 Solubility

The maximum amount of a solute that can be dissolved in a given amount of solvent (generally 100 g) at a given temperature is termed as **solubility** at that temperature.

Solubility of Gas in Liquid

All gases are soluble in water as well as in other liquids to a greater or lesser extent.

The solubility of a gas in liquids depends upon the following factors

(a) Nature of the Gas

The gases which can be easily liquified, are more soluble in common solvents, *e.g.*, CO_2 is more soluble than H_2 and O_2 in water.

(b) Nature of the Solvent

The gases which are capable of forming ions in aqueous solutions are much more soluble in water than in other solvents, *e.g.*, gases like HCl and NH_3 are highly soluble in water but not in organic solvents in which they do not ionise.

(c) Temperature

The solubility of most gases in liquids decreases with increase of temperature. When a solution of a gas is heated, the gas is usually expelled. However, some gases are more soluble at higher temperature than at lower.

(d) Pressure

The solubility of a gas in liquid is also influenced by pressure. The relation between the solubility and pressure is given by **Henry's law.** According to this law

$$m \propto p \text{ or } m = K_H p \qquad \text{...(i)}$$

where, m = mass of the gas dissolved per unit volume of a solvent

p = pressure of the gas at equilibrium with the solution

K_H = Henry's constant

Thus, Henry's law can also be stated as, the pressure of a gas over a solution in which the gas is dissolved is equal to the amount fraction of the dissolved gas multiplied by Henry's constant.

Different gases have different K_H values at the same temperature. This suggests that K_H is a function of the nature of the gas. Table 2.2 gives K_H values of some common gases at specified temperature.

Table 2.2 **Values of Henry's law Constant** (K_H) **for Some Selected Gases in Water**

Gas	Temp (K)	K_H (k bar)	Gas	Temp (K)	K_H (k bar)
He	293	144.97	Argon	298	40.3
H_2	293	69.16	CO_2	298	1.67
N_2	293	76.48	HCHO	298	1.83×10^{-5}
N_2	303	88.84	CH_4	298	0.413
O_2	293	34.86	Vinyl chloride	298	0.611
O_2	303	46.82	$(CH_2{=}CH{-}Cl)$		

It is obvious from Eq. (i) that *higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid*. It can be seen from Table 2.2 that the K_H value for both N_2 and O_2 increases with increase of temperature indicating that *the solubility of gases decreases with increase of temperature*. It is due to this reason that aquatic species are more comfortable in cold water rather than in warm water.

Sample Problem 1 *The partial pressure of ethane over a solution containing 6.56×10^{-3} g of ethane is 1 bar. If the solution contains 5.00×10^{-2} g of ethane, then what shall be the partial pressure of gas?* **[NCERT]**

(a) 4.2 bar (b) 7.6 bar
(c) 8.9 bar (d) 9.8 bar

Interpret (*b*) According to Henry's law,

Mass of the gas (m) dissolved in solution $\propto$ Partial pressure (p) (At constant temperature)

$$\therefore \quad (6.56 \times 10^{-3} \text{ g}) \propto 1 \text{ bar}$$

$$(5.00 \times 10^{-2} \text{ g}) \propto p$$

$$\text{or} \quad p = \frac{(5.0 \times 10^{-2} \text{ g})}{(6.56 \times 10^{-3} \text{ g})} \times (1 \text{ bar})$$

$$= 7.62 \text{ bar}$$

Sample Problem 2 H_2S*, a toxic gas with rotten egg like smell, is used for the qualitative analysis. If the solubility of* H_2S *in water at STP is* 0.195 *m, calculate Henry's law constant.* **[NCERT]**

(a) 152 bar (b) 100 bar
(c) 200 bar (d) 282 bar

Interpret (*d*) Since molality is given and molality is the moles present in 1000 g of water so first we find the moles of H_2S, if molality is 0.195 m and then calculate the moles of water n_{H_2O} as we know from molality its mass is 1000 g.

Now, we calculate the mole fraction of H_2S using the formula,

$$X_{H_2S} = \frac{n_{H_2S}}{n_{H_2S} + n_{H_2O}} \text{ from which we can easily}$$

calculate Henry's law constant.

Calculation of mole fraction of H_2S 0.195 m means that 0.195 mole of H_2S are dissolved in 1000 g of water.

Number of moles of water in 1000 g, (n_{H_2O})

$$= \frac{(1000\text{ g})}{(18\text{ g mol}^{-1})} = 55.55\text{ mol}$$

$$\text{Mole fraction } H_2S\ (x_{H_2S}) = \frac{n_{H_2S}}{n_{H_2S} + n_{H_2O}}$$

$$= \frac{(0.195\text{ mol})}{(0.195 + 55.55)\text{ mol}}$$

$$= \frac{(0.195\text{ mol})}{(55.745\text{ mol})} = 0.0035$$

Calculation of Henry's Law Constant

According to Henry's law

$$x_{H_2S} = \frac{\text{partial pressure of } H_2S}{K_H \text{ for } H_2S} \text{ at STP}$$

$$K_H \text{ for } H_2S = \frac{\text{partial pressure of } H_2S}{x_{H_2S}}$$

$$= \frac{(0.987\text{ bar})}{(0.0035)} = 282\text{ bar}$$

Solubility of Liquid in Liquid

A liquid may or may not be soluble in another liquid. Depending upon the relative solubility of a liquid in another, the following three cases are possible

(a) Miscible

When two substances dissolve in each other, they are said to be completely miscible, *e.g.,* water and alcohol, benzene and toluene.

(b) Immiscible

Two chemically different liquids such as water and oil, water and mercury, do not dissolve in each other and are said to be completely immiscible.

(c) Partially Miscible

Certain liquids like water and phenol, water and ether, which dissolve only to a limited extent are known as partially miscible.

Caution Point *In general "like dissolves like" e.g., water and* NaCl *both being ionic are completely miscible. Similarly, benzene and chloroform being covalent are miscible.*

Solubility of Solid in Liquid

On the basis of solubility of solid (solute) in a liquid (solvent), solution may be of the following types

(a) Unsaturated Solution

A solution in which more solute can be dissolved without raising temperature is called an *unsaturated solution*.

(b) Saturated Solution

A solution in which no solute can be dissolved further at a given temperature is called a saturated solution.

(c) Supersaturated Solution

When the solution contains more solute than would be necessary to saturate it then it is termed as supersaturated solution. Supersaturated solutions are not in equilibrium with the solid substance. Thus, if a small crystal of solute (say sodium thiosulphate) is added to its supersaturated solution, the excess immediately crystallises out, which is usually quite fast (and dramatic too).

Check Point 1

1. Explain how can you increase the solubility of a gas in liquid?
2. State the condition in which an electrolyte can dissolve in water.
3. What happens when a crystal of solute is introduced into a supersaturated solution of the solute?
4. What happens when a saturated solution is heated?
5. Why true solutions are homogeneous in nature?

2.3 Concentration of Solution

The **concentration** of a solution is defined as the relative amount of a solute present in a solution . It is generally expressed as the amount of solute present in a unit volume of solution. Solutions with relatively low concentration are called **dilute solutions,** while those with relatively high concentration are called **concentrated solutions.**

Various expression for the concentrations of solutions can be summarised as

Per cent by Weight or Mass Per cent

It is the amount of solute present in 100 g of the solution.

$$\text{Per cent by weight } (w/W) = \frac{\text{weight of solute (in g)}}{\text{weight of solution (in g)}} \times 100$$

Per cent by Volume

The volume of solute (in mL) present in 100 mL of the solution is called **volume per cent.**

$$\text{Per cent by volume } (v/V) = \frac{\text{volume of solute (in mL)}}{\text{volume of solution (in mL)}} \times 100$$

Mole Fraction (χ)

It is the ratio of the number of moles of one component (*i.e.,* solute or solvent) to the total number of moles of solute and solvent (*i.e.,* moles of solution).

$$\chi_{\text{solute}} = \frac{\text{moles of solute}}{\text{moles of solute + moles of solvent}}$$

$$\chi_{\text{solvent}} = \frac{\text{moles of solvent}}{\text{moles of solute + moles of solvent}}$$

$$\chi_{\text{solute}} + \chi_{\text{solvent}} = 1$$

Sample Problem 3 *The mole fraction of benzene in a solution containing* 30% *by mass in carbon tetrachloride is* **[NCERT]**

(*a*) 0.46 (*b*) 0.54 (*c*) 0.64 (*d*) 0.45

Interpret (*a*) For 100 g of the solution, mass of benzene = 30 g

Mass of carbon tetrachloride = 100 − 30 = 70 g

$$\text{Molar mass of benzene } (C_6H_6) = (12 \times 6) + (6 \times 1)$$
$$= 72 + 6 = 78 \text{ g mol}^{-1}$$

$$\text{Moles of benzene, } n_{C_6H_6} = \frac{\text{Mass}}{\text{Molar mass}} = \frac{30}{78} = 0.385 \text{ mol}$$

Molar mass of carbon tetrachloride

$$(CCl_4) = 12 + (35.5 \times 4)$$
$$= 12 + 142.0 = 154 \text{ g mol}^{-1}$$

$$\text{Moles of } CCl_4, n_{CCl_4} = \frac{70 \text{ g}}{(154 \text{ g mol}^{-1})} = 0.454 \text{ mol}$$

$$\text{Mole fraction of benzene, } \chi_{C_6H_6} = \frac{n_{C_6H_6}}{n_{C_6H_6} + n_{CCl_4}}$$
$$= \frac{0.385 \text{ mol}}{(0.385 + 0.454) \text{ mol}} = 0.459$$

Parts Per Million (ppm)

When the amount of solute (in g) is present in one million mL (1 million = 10^6) per mL of solution, the concentration of the solution is expressed in **ppm.**

$$\text{ppm} = \frac{\text{weight of solute (in g)}}{\text{total volume of solution (in mL)}} \times 10^6$$

In case of gases, ppm refers to volumes rather than masses, *i.e.,* 1 ppm means 1 cm^3 of gaseous components is present in 1000 L.

Strength or Concentration in Gram Per Litre

It represents the number of grams present in 1 L of solution.

$$\text{Strength of solution} = \frac{\text{mass of solute (g)}}{\text{volume of solution (in L)}}$$

Molarity (M)

It is the number of moles of solute present in one litre of the solution.

$$\text{Molarity } (M) = \frac{\text{number of moles of solute}}{\text{volume of solution (in L)}}$$
$$= \frac{\text{mass of solute (in g)}}{\text{mol. wt. of solute} \times \text{volume of solution (in L)}}$$
$$= \frac{\text{number of millimoles of solute}}{\text{volume of solution (in mL)}}$$
$$= \frac{\text{per cent of solute} \times 10}{\text{molecular weight of solute}}$$
$$= \frac{\text{weight \% of solute} \times \text{sp. gravity of the solution} \times 10}{\text{molecular weight of the solute}}$$

Molarity varies with temperature due to accompanied change in volume of the solution.

Unit of molarity = g-mol/L

Relation between molarity and strength in g/L

$$\text{Molarity } (M) = \frac{\text{weight of solute (in g)}}{\text{molecular weight of solute} \times \text{volume of solution (in L)}}$$

$$\text{Molarity } (M) = \frac{\text{strength in g / L}}{\text{molecular weight of solute}}$$

Relation between molarity (M) *and mole fraction of the solute* (χ)

$$\chi = \frac{MM_1}{M(M_1 - M_2) + d}$$

where, d = density of the solution
M_1 = molar mass of solvent
M_2 = molar mass of solute
M = molarity of solution

Dilution Law

If molarity and volume of solution are changed from M_1, V_1 to M_2, V_2 then

$$M_1V_1 = M_2V_2 \quad \text{(Molarity equation)}$$

If n_1 moles of reactant '1' react with n_2 moles of reactant '2' then

$$\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$$

If two solutions of the same solute are mixed then molarity of the resulting solution,

$$M = \frac{M_1V_1 + M_2V_2}{V_1 + V_2}$$

Volume of water added to get a solution of molarity M_2 from V_1 mL of molarity M_1 is

$$V_2 - V_1 = \left(\frac{M_1 - M_2}{M_2}\right) V_1$$

Sample Problem 4 *Calculate the molarity of* KI *if the density of* 20% *(mass/mass) aqueous* KI *is* 1.202 g mL^{-1}. **[NCERT]**

(*a*) 0.04 *M* (*b*) 1.25 *M* (*c*) 0.25 *M* (*d*) 1.45 *M*

Interpret (*d*) Since density is given, so first we calculate volume and then molarity.

$$\begin{aligned}
\text{Weight of the solution} &= 100\ \text{g}\\
\text{Density of the solution} &= 1.202\ \text{g mL}^{-1}\\
\text{Volume of the solution} &= \frac{\text{weight of solution}}{\text{density}}\\
&= \frac{(100\ \text{g})}{(1.202\ \text{g mL}^{-1})}\\
&= 83.19\ \text{mL} = 0.083\ \text{L}\\
\text{Molarity of the solution } (M) &= \frac{\text{number of gram moles of KI}}{\text{volume of solution in litres}}\\
&= \frac{(20\ \text{g})/(166\ \text{g mol}^{-1})}{(0.083\ \text{L})}\\
&= 1.45\ \text{mol L}^{-1} = 1.45\ \text{M}
\end{aligned}$$

Alternate Method

$$\begin{aligned}
\text{Molarity} &= \frac{\%\ \text{by mass} \times \text{density} \times 10}{\text{molar mass of KI}}\\
&= \frac{20 \times 1.202 \times 10}{166} = 1.45\ \text{M}
\end{aligned}$$

Molality (*m*)

It is the number of moles of the solute dissolved in 1000 g of the solvent.

$$\begin{aligned}
\text{Molality } (m) &= \frac{\text{number of moles of solute}}{\text{mass of solvent (in g)}} \times 1000\\
&= \frac{\text{mass of solute (in g)} \times 1000}{\text{molecular weight of solute} \times \text{mass of solvent (in g)}}\\
&= \frac{10 \times \text{solubility}}{\text{molecular weight of solute}}
\end{aligned}$$

Molality is independent of temperature.

Unit of molality = g moles/kg of solvent.

Relation between molality and weight percentage of solute (x)

$$= \frac{1000 \times \text{weight \% of solute } (\chi)}{(100 - x) \times \text{molecular weight of solute}}$$

Relation between molality (m) *and mole fraction of the solute* (χ)

$$\chi = \frac{mM_1}{1 + mM_1}$$

where, M_1 = molecular mass of the solvent

Relation between molality (m) *and molarity* (M)

$$\text{Molality } (m) = \frac{M}{d - MM_2} \quad (\text{If } d \text{ in kg/L and } M_2 \text{ in kg/mol})$$

$$\text{Molality } (m) = \frac{M}{1000d - MM_2} \times 1000$$

(If d in g/L and M_2 in g/mol)

$$\text{Molarity } (M) = \frac{m \times d}{1 + \dfrac{m \times M_2}{1000}}$$

where, M_2 = molar mass of the solute

d = density of the solution.

Sample Problem 5 *If the density of some lake water is* 1.25 g mL^{-1} *and contains* 92 g *of* Na$^+$ *ions per kg of water, calculate the molality of* Na$^+$ *ions in the lake.* **[NCERT]**

(*a*) 2 *m* (*b*) 4 *m* (*c*) 8 *m* (*d*) 10 *m*

Interpret (*b*) Molality of Na$^+$ ions (m)

$$\begin{aligned}
&= \frac{\text{number of moles Na}^+ \text{ ions}}{\text{mass of water in kg}}\\
&= \frac{(92\ \text{g})/(23\ \text{g mol}^{-1})}{(1\ \text{kg})}\\
&= 4\ \text{mol kg}^{-1} \text{ or } 4\ \text{m}
\end{aligned}$$

Sample Problem 6 *A solution of glucose in water is labelled as* 10% *w/ w. What should be the molality of the solution, if the density of solution is* 1.2 g mL^{-1}? **[NCERT]**

(*a*) 0.45 (*b*) 0.62

(*c*) 0.82 (*d*) 0.19

Interpret (*b*) 10% means

$$\begin{aligned}
W_B &= \text{Mass of glucose} = 10\ \text{g}\\
&\quad\ \text{Mass of solution} = 100\ \text{g}\\
W_A &= \text{Mass of water (solvent)}\\
&= 100 - 10 = 90\ \text{g} = 0.09\ \text{kg}\\
M_B &= \text{Molar mass of glucose } (C_6H_{12}O_6)\\
&= (12 \times 6) + (1 \times 12) + (16 \times 6)\\
&= 72 + 12 + 96 = 180\ \text{g mol}^{-1}
\end{aligned}$$

$$\begin{aligned}
\text{Molality of solution } (m) &= \frac{W_B/M_B}{W_A} = \frac{(10\ \text{g})/(180\ \text{g mol}^{-1})}{(0.09\ \text{kg})}\\
&= \frac{(10\ \text{g})}{(180\ \text{g mol}^{-1}) \times (0.09\ \text{kg})}\\
&= 0.617\ \text{mol kg}^{-1} \text{ or } 0.617\ \text{m}
\end{aligned}$$

Sample Problem 7 *An 'm' molal solution of a compound in benzene has mole fraction of solute equal to* 0.2. *The value of 'm' is*

(*a*) 0.018 (*b*) 0.14

(*c*) 0.040 (*d*) 0.0032

Interpret (*d*) Mole fraction of solute is given by

$$\chi = \frac{mM_1}{1 + mM_1}$$

where, M_1 = molecular mass of the solvent, *i.e.*, benzene = 78

$$0.2 = \frac{m \times 78}{1 + m \times 78}$$

$$0.2 + 0.2 \times 78\, m = 78\, m$$

or $$(78 - 15.6)\, m = 0.2$$

or $$62.4\, m = 0.2$$

or, $$m = \frac{0.2}{62.4} = 0.0032$$

Normality (N)

Normality is the number of gram equivalents of substance dissolved per litre of the solution.

$$\text{Normality } (N) = \frac{\text{number of g-equivalent of solute}}{\text{volume of solution (in L)}}$$

$$= \frac{\text{mass of solute (in g)}}{\text{equivalent weight} \times \text{volume (in L)}}$$

$$N = \frac{\text{mass of solute } (w) \text{ (in g)}}{\text{equivalent weight } (E) \times \text{volume } (V) \text{ (in mL)}} \times 1000$$

or $$N = \frac{w \times 1000}{E \times V}$$

or $$w = \frac{NEV}{1000} = \frac{\text{per cent of solute}}{\text{equivalent weight of the solute}} \times 10$$

$$\text{Again, Normality } (N) = \frac{\text{per cent of solute}}{\text{equivalent weight of the solute}} \times 10$$

$$= \frac{\text{weight per cent of solute} \times \text{sp. gravity of the solution} \times 10}{\text{equivalent weight of the solute}}$$

Relation between normality and strength in g/L

$$\text{Normality } (N) = \frac{\text{mass of solute (in g)}}{\text{equivalent weight} \times \text{volume (in L)}}$$

$$= \frac{\text{strength in g / L}}{\text{equivalent weight}}$$

Relation between normality and molarity

$$\text{Normality} = \frac{\text{number of g-equivalents of solute}}{\text{volume of solution (in L)}}$$

and, $$\text{Molarity} = \frac{\text{number of moles of solute}}{\text{volume of solution (in L)}}$$

$$\therefore \quad \frac{\text{Normality}}{\text{Molarity}} = \frac{\text{number of g-equivalent of solute}}{\text{number of moles of solute}}$$

$$= \frac{\text{molecular weight}}{\text{equivalent weight}}$$

$$\Rightarrow \textit{normality} \times \textit{equivalent weight} = \textit{molarity} \times \textit{molecular weight}$$

For an acid, $$\frac{\text{molecular weight}}{\text{equivalent weight}} = \text{basicity}$$

$$\therefore \quad \text{Normality of an acid} = \text{molarity} \times \text{basicity}$$

For a base, $$\frac{\text{molecular weight}}{\text{equivalent weight}} = \text{acidity}$$

$$\therefore \quad \text{Normality of a base} = \text{molarity} \times \text{acidity}$$

Relation between normality and percentage of solute

$$N = \frac{x \times d \times 10}{E}$$

where, x = % of the solute by mass

d = density of solution in g/mL

E = equivalent mass of solute

Dilution Law

If normality and volume of solution are changed from N_1, V_1 to N_2, V_2 then

$$N_1V_1 = N_2V_2 \quad \text{(Normality equation)}$$

If n_1 moles of reactant '1' react with n_2 moles of reactant '2', then

$$\frac{N_1V_1}{n_1} = \frac{N_2V_2}{n_2}$$

If two solutions of the same solute are mixed then normality of the resulting solution,

$$N = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$$

Volume of water added to get a solution of normality N_2 from V_1 mL of normality N_1 is

$$V_2 - V_1 = \left(\frac{N_1 - N_2}{N_2}\right) V_1$$

Normality changes with temperature since it involves volume.

When a solution is diluted x times, its normality also decreased by x times.

Unit of normality = gram equivalents per litre.

Sample Problem 8 *The amount of* H_2SO_4 *in* 150 *mL of* $\frac{N}{7}$ H_2SO_4 *is*

(*a*) 15 g
(*b*) 2.10 g
(*c*) 1.05 g
(*d*) 51.45 g

Interpret (*c*) $$w = \frac{NEV}{1000} = \frac{1}{7} \times \frac{49 \times 150}{1000}$$

($\because$ Eq. weight of H_2SO_4 = 49)

$$= 1.05 \text{ g}$$

Sample Problem 9 *What will be the normality of a solution obtained by mixing* 0.45 *N and* 0.60 *N* NaOH *in the ratio* 2 : 1 *by volume ?*

(a) 0.15 *N* (b) 0.8 *N* (c) 0.5 *N* (d) 0.45 *N*

Interpret (c) g-equivalents $= 0.45 \times 2V + 0.60 \times V$

Total volume $= 2V + V = 3V$

$\Rightarrow$ g-equivalents of NaOH solution obtained $= N \times 3V$

$$\therefore \quad N \times 3V = 0.45 \times 2V + 0.6V$$

$$3NV = 0.9V + 0.6V$$

$$N = \frac{1.5V}{3V} = \frac{1}{2} = 0.5$$

Formality (*F*)

This is the concentration unit for ionic compounds which dissolve in a polar solvent to give pair of ions. This represents number of gram-formula weight of the substance dissolved per litre of the solution. It is almost the same as molarity. It describes the solute that is mixed in a liquid rather than the solute present in solution after the dissolution process.

$$\text{Formality} = \frac{\text{moles of substance added to solution}}{\text{volume of solution (in L)}}$$

If formula weight is equal to molecular weight, formality and molarity will be same.

Formality is also dependent on temperature.

Demal (*D*)

It is equal to molar concentration at 0°C, *i.e.,* 1D represents one mole of the solute present in one litre of the solution at 0°C.

Caution Point *Normality and molarity changes with temperature because they involve volumes while molarity, mole fraction and mass fraction do not change with temperature because they involve weights.*

Check Point 2

1. In which mode of expression, the concentration of the solution remains independent of temperature and why?
2. What is the difference between molality and molarity?
3. What is the difference between normality and formality?
4. Why molarity is affected by changes in temperature?
5. At same temperature, oxygen in found to be more soluble in water as compared to hydrogen. Which of these have higher K_H value and why?

2.4 Vapour Pressure of Solutions and Raoult's Law

The pressure exerted by the vapours of a solvent while in equilibrium with pure solvent, at a given temperature, is called vapour pressure.

Factors Affecting Vapour Pressure

Vapour pressure gets affected by following factors.

(a) Purity of the Liquid

Pure liquid always has a vapour pressure higher than its solution.

(b) Nature of the Liquid

Liquids which have weak intermolecular forces are volatile and have greater vapour pressure.

(c) Temperature

The vapour pressure of a liquid increases with increase in temperature. This is because on increasing the temperature the kinetic energy of molecules increases that results into the fact that more molecules of the liquid can go into vapour phase.

(d) Effect of Adding Solute

When a liquid contains a solute, some of the solvent molecules are replaced by the solute particles on the liquid surface and therefore, the available surface area for the escape of solvent molecule decreases.

Due to the less available area on the surface of liquid for escape, rate of evaporation and hence, the rate of condensation both lowers.

The vapour pressure of liquid in solution is known as its **partial vapour pressure** and is less than the vapour pressure of the pure liquid at the same temperature.

If p° be the vapour pressure of pure liquid and p_s be that of liquid in solution then lowering of vapour pressure of the liquid $= p^\circ - p_s$

$$\therefore \quad \text{Relative lowering in pressure} = \frac{p^\circ - p_s}{p^\circ}$$

Hot Spot 1

RAOULT'S Law

Questions based on Raoult's law have been frequently asked in the JEE Main examination, so it is an important topic for the examinations. The nature of questions is numerical type and their level vary from moderate to difficult.

Raoult's law states, "For a solution of two miscible liquids, the vapour pressure of each liquid in the solution is less than the respective vapour pressure of the pure liquid and at the equilibrium, partial vapour pressure of the liquid is directly proportional to its mole fraction in solution."

For a solution containing two liquids *A* and *B*, the partial vapour pressure of liquid *A* is

$$p_A \propto \chi_A \quad \text{or} \quad p_A = k\chi_A$$

where, $\chi_A = \dfrac{n_A}{(n_A + n_B)}$ = the **mole fraction of liquid *A***

The proportionality constant *k* is obtained by considering the pure liquid when $\chi_A = 1$, then $k = p_A{}^\circ$, (the vapour pressure of pure liquid), hence,

$$p_A = p_A{}^\circ\, \chi_A$$

Similarly, $$p_B = p_B^\circ\, \chi_B$$

According to **Dalton's law of partial pressure,** the total pressure (p_{total}) over the solution phase in the container will be the sum of the partial pressures of the components of the solution and is given as

$$p_{\text{total}} = p_A + p_B$$

Substituting the values of p_A and p_B, we get

$$\begin{aligned} p_{\text{total}} &= \chi_A p_A^\circ + \chi_B p_B^\circ \\ &= (1 - \chi_B)p_A^\circ + \chi_B p_B^\circ \\ &= p_A^\circ + (p_B^\circ - p_A^\circ)\chi_B \end{aligned}$$

Following conclusions can be drawn from the equation

(i) Total vapour pressure over the solution can be related to the mole fraction of any one component.

(ii) Total vapour pressure over the solution varies linearly with the mole fraction of component *B*.

(iii) Depending on the vapour pressures of the pure components *A* and *B*, total vapour pressure over the solution decreases or increases with the increase of the mole fraction of component.

The composition of vapour phase in equilibrium with the solution is determined by the partial pressures of the components. If y_1 and y_2 are the mole fractions of the component 1 and 2 respectively in the vapour phase then, using Dalton's law of partial pressures :

$$p_1 = y_1\, p_{\text{total}}$$

$$p_2 = y_2\, p_{\text{total}}$$

In general

$$p_i = y_i\, p_{\text{total}}$$

Raoult's Law as a Special Case of Henry's Law

According to Raoult's law, the vapour pressure of a volatile component in a given solution is given by $p_i = x_i\, p_i^\circ$. In the solution of a gas in a liquid, one of the components is so volatile that it exists as a gas and we have already seen that its solubility is given by Henry's law which states that

$$p = K_{\text{H}} x$$

If we compare the equations for Raoult's law and Henry's law, it can be seen that the partial presssure of the volatile component or gas is directly proportional to its mole fraction in the solution. Only the proportionality constant K_{H} differs from p_i°, Thus, Raoult's law becomes a special case of Henry's law in which K_{H} becomes equal to p_i°.

Sample **Problem 10** *At 40°C, the vapour pressure in torr, of methyl alcohol-ethyl alcohol solution is represented by the equation.* $p = 119X_A + 135$ *where* X_A *is mole fraction of methyl alcohol, then the value of* $\lim\limits_{X_A \to 1} \dfrac{p_A}{X_A}$ *is*

(*a*) *254 torr* (*b*) *135 torr*
(*c*) *119 torr* (*d*) *140 torr*

Interpret (*a*) $p = 119X_A + 135$;

$$\lim_{X_A \to 1} \frac{p_A}{X_A} = 119 + 135 = 254 \text{ torr}$$

Sample **Problem 11** *The vapour pressure of a pure liquid A is 40 mm* Hg *at 310 K. The vapour pressure of this liquid in a solution with liquid B is 32 mm* Hg. *Calculate the mole fraction of A in the solution if it obeys the Raoult's law.*

(*a*) 0.5 (*b*) 0.6 (*c*) 0.7 (*d*) 0.8

Interpret (*d*) Vapour pressure of pure *A* = 40 mm Hg

Vapour pressure of *A* in solution = 32 mm Hg

According to Raoult's law

$$p_A = p_A^\circ \chi_A$$

or $$\chi_A = \frac{p_A}{p_A^\circ} = \frac{32 \text{ mm Hg}}{40 \text{ mm Hg}} = 0.8$$

Sample **Problem 12** *Heptane and octane form an ideal solution. At 373 K, the vapour pressure of the two liquid components are 105.2 kPa and 46.8 kPa respectively. What* *will be the vapour pressure of a mixture of 26.0 g of heptane and 35 g of octane?* **[NCERT]**

(a) 82.8 *kPa* (b) 73.5 *kPa*
(c) 39.2 *kPa* (d) 88.2 *kPa*

Interpret (*b*) Number of moles of octane

$$(n_A) = \frac{\text{Mass}}{\text{Molar mass}} = \frac{35\ \text{g}}{114\ \text{g mol}^{-1}}$$

$$= 0.307\ \text{mol}$$

[Molar mass of octane

$$C_8H_{18} = (12 \times 8) + (1 \times 18) = 114\ \text{g mol}^{-1}]$$

Number of moles of heptane

$$(n_B) = \frac{26\ \text{g}}{100\ \text{g mol}^{-1}} = 0.26\ \text{mol}$$

[Molar mass of heptane $C_7H_{16} = (12 \times 7) + 16 = 100\ \text{g mol}^{-1}$]

Mole fraction of octane

$$(\chi_A) = \frac{n_A}{n_A + n_B} = \frac{(0.307\ \text{mol})}{(0.307 + 0.26)\ \text{mol}} = 0.541$$

Mole fraction of heptane

$$(\chi_B) = \frac{n_B}{n_A + n_B} = \frac{(0.26\ \text{mol})}{(0.307 + 0.26)\ \text{mol}} = 0.458$$

Vapour pressure of pure heptane $(p_B^\circ) = 105.2$ kPa

Vapour pressure of pure octane $(p_A^\circ) = 46.8$ kPa

In the mixture of 26.0 *g heptane and* 35.0 *g octane*

(i) Vapour pressure of heptane $(p_B) = p_B^\circ\ \chi_B$

$$= (105.2\ \text{kPa} \times 0.458)$$
$$= 48.18\ \text{kPa}$$

(ii) Vapour pressure of octane

$$(p_A) = p_A^\circ\ \chi_A = (46.8\ \text{kPa} \times 0.541)$$
$$= 25.32\ \text{kPa}$$

(iii) Total vapour pressure of the mixture

$$(p) = p_A + p_B$$
$$= 25.32 + 48.18 = 73.5\ \text{kPa}$$

Sample **Problem 13** *The vapour pressure of chloroform* ($CHCl_3$) *and dichloromethane* (CH_2Cl_2) *at 298 K is 200 mm* Hg *and 415 mm* Hg*, respectively. If a solution is prepared by mixing 25.5 g of* $CHCl_3$ *and 40 g of* CH_2Cl_2 *at 298 K, calculate the mole fractions of chloroform in vapour phase.*

[NCERT Exemplar]

(a) 0.18 (b) 0.82 (c) 0.34 (d) 0.48

Interpret (*a*) Molar mass of $CH_2Cl_2 = 12 \times 1 + 1 \times 2 + 35.5 \times 2$

$$= 85\ \text{g mol}^{-1}$$

Molar mass of $CHCl_3 = 12 \times 1 + 1 \times 1 + 35.5 \times 3$

$$= 119.5\ \text{g mol}^{-1}$$

$$\text{Moles of } CH_2Cl_2 = \frac{40\ \text{g}}{85\ \text{g mol}^{-1}} = 0.47\ \text{mol}$$

$$\text{Moles of } CHCl_3 = \frac{25.5\ \text{g}}{119.5\ \text{g mol}^{-1}} = 0.213\ \text{mol}$$

Total number of moles $= 0.47 + 0.213 = 0.683$ mol

$$\chi_{CH_2Cl_2} = \frac{0.47\ \text{mol}}{0.683\ \text{mol}} = 0.688$$

$$\chi_{CHCl_3} = 1.00 - 0.688 = 0.312$$

$$p_{\text{total}} = p^\circ_{CHCl_3} + (p^\circ_{CH_2Cl_2} - p^\circ_{CHCl_3})\ \chi_{CH_2CH_2}$$
$$= 200 + (415 - 200) \times 0.688$$
$$= 347.9\ \text{mm Hg}$$

To calculate the mole fraction of component in vapour phase,

$$\chi_i^V = p_i / p_{\text{total}}$$

$$\therefore \quad p_{CH_2Cl_2} = 0.688 \times 415\ \text{mm Hg} = 285.5\ \text{mm Hg}$$

$$p_{CHCl_3} = 0.312 \times 200\ \text{mm Hg} = 62.4\ \text{mm Hg}$$

$$\chi^V_{CH_2Cl_2} = \frac{285.5}{347.9} = 0.82$$

$$\chi^V_{CHCl_3} = \frac{62.4}{347.9} = 0.18$$

Note Since CH_2Cl_2 is more volatile component than $CHCl_3$ [$p^\circ_{CH_2Cl_2} = 415$ mm Hg and $p^\circ_{CHCl_3} = 200$ mm Hg] and the vapour phase is also richer in CH_2Cl_2 [$\chi^V_{CH_2Cl_2} = 0.82$ and $\chi^V_{CHCl_3} = 0.18$], it may be concluded that at equilibrium, vapour phase will be always rich in the component which is more volatile.

Limitations of Raoult's Law

1. It is applicable only to very dilute solutions.
2. It is applicable only to solutions containing non-volatile and non-electrolytic solutes which exist as a single molecule.
3. It is not applicable to solutes which dissociate or associate in the particular solution.

2.5 Ideal Solutions

Ideal solutions are those, which obey Raoult's law with overall concentration ranges at a given temperature. The total vapour pressure of an ideal solution containing components *A* and *B* is given by

$$p = p_A + p_B = p_A{}^\circ\ \chi_A + p_B{}^\circ\ \chi_B$$

In an ideal solution of two components say *A* and *B*, all cohesive forces (*A*—*A*, *B*—*B* and *A*—*B*) must be identical. *Two liquids on mixing will form an ideal solution if following conditions be satisfied*

(i) both have similar structure,
(ii) both have similar molecular sizes,
(iii) both have identical intermolecular forces.

Characteristics of an Ideal Solution

The mixture of two liquids results in an ideal solution when

(i) they obey Raoult's law.

(ii) $\Delta H_{\text{mixing}} = 0$, *i.e.,* no energy evolved or absorbed on mixing.

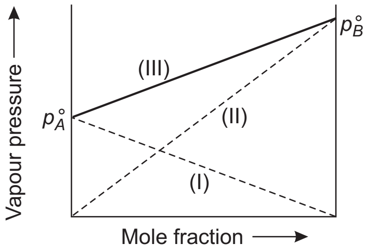
(iii) $\Delta V_{\text{mixing}} = 0$, *i.e.,* on mixing no expansion or contraction occurs.

Examples of the Ideal Solutions

Benzene-toluene, *n*-hexane-*n*-heptane; ethyliodide-ethyl bromide, chlorobenzene- bromobenzene.

Graphical Representation of Ideal Solutions

The curve I (straight line) gives variations of vapour pressure of liquid *A* and the curve II gives that of liquid *B* with their respective mole fractions.



The resultant graph III (representing $p = p_A^\circ \chi_A + p_B^\circ \chi_B$) is the plot for solution and is a straight line joining p_A° and p_B°. Hence, the vapour pressure at various compositions of ideal solutions is intermediate between the values of p_A° and p_B°.

2.6 Non-Ideal or Real Solutions

Solutions, which do not obey Raoult's law, are called **non-ideal solutions.** Hence, for such solutions $p_A \neq p_A^\circ \chi_A$ and $p_B \neq p_B^\circ \chi_B$.

For such mixtures,

$$\Delta H_{\text{mixing}} \neq 0$$

and $$\Delta V_{\text{mixing}} \neq 0;$$

Non-ideal solutions show the following two types of deviations from ideal behaviour

1. Solution Showing Positive Deviation

The vapour pressure of each component in such a mixture is more than what would be expected on the basis of Raoult's law of components *A* and *B* alone.

If the attraction between *A* and *B* molecules is less than the attractive forces between *A* to *A* and *B* to *B*, the escaping tendency in solution is higher than in either of the pure components.

For such a deviation

$$p_A > p_A^\circ \chi_A\ ,\ p_B > p_B^\circ \chi_B$$

and hence, $$p_{\text{total}} > p_A^\circ \chi_A + p_B^\circ \chi_B$$

also $$\Delta H_{\text{mixing}} > 0$$

as the new bonds formed are weaker and energy is absorbed.

$\Delta V_{\text{mixing}} > 0$ *i.e.*, there is increase in volume.

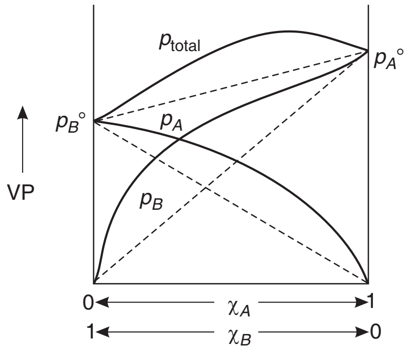


Fig. 2.1 Graph of solution showing positive deviation from Raoult's law

Examples Ethanol-water, ether-acetone, carbon disulphide-acetone, carbon tetrachloride-methanol, cyclohexane-ethanol, water-methanol, carbon tetrachloride-benzene, carbon tetrachloride-toluene, acetone-benzene.

2. Solutions Showing Negative Deviation

For such solutions, the partial vapour pressure of each component is less than what would be expected on the basis of Raoult's law.

In such a mixture, the attraction between molecules of *A* and *B* is greater than the force between *A*—*A* molecules or *B*—*B* hence the escaping tendencies of both the components are lowered.

For a mixture showing negative deviation

$$p_A < p_A^\circ \chi_A$$

or $$p_B < p_B^\circ \chi_B,$$

hence, $$p_{\text{total}} < p_A^\circ \chi_A + p_B^\circ \chi_B$$

$\Delta H_{\text{mixing}} < 0$, *i.e.*, heat is evolved due to the formation of stronger bonds.

$\Delta V_{\text{mixing}} < 0$, *i.e.,* there is decrease in volume.

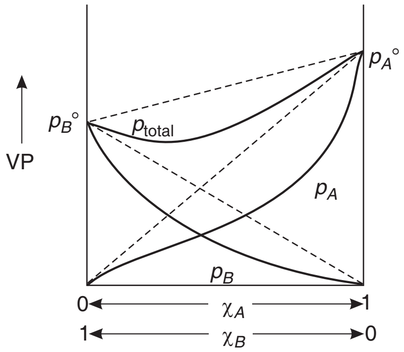


Fig. 2.2 Graph of solution showing negative deviation from Raoult's law

Examples Acetic acid-methanol, acetic acid-pyridine acetone-aniline, acetone-chloroform, benzene-chloroform, water-hydrochloric acid, water-nitric acid etc.

Azeotropic Mixtures

A mixture of two liquids which boils at a constant temperature and distils over without any change in composition is called azeotropic mixture.

Azeotropic mixtures are of two types

(a) Minimum Boiling Azeotropes

These are the mixture of two liquids boiling point of which is less than either of the two pure components. They are formed by non-ideal solutions showing positive deviations.

(b) Maximum Boiling Azeotropes

These are the mixtures of two liquids boiling point of which is more than either of the two pure components. They are formed by non-ideal solutions showing negative deviations.

2.7 Colligative Properties

The properties of a dilute solution which depends only upon the number of particles present in a solution and their concentration are called colligative properties. These depend on the dative fraction of solute and solvent particles but not on the chemical nature of solute *i.e.,* these are proportional to the number of solute particles in the solution.

These properties have their origin from the fact that the chemical potential of a species in an ideal solution is lower than the chemical potential of pure component.

Factors Affecting Colligative Properties

1. Fraction of solute and solvent particles in solution.
2. Nature of solvent.
3. Extent of association and dissociation of solute particles in solution.

There are four colligative properties, i.e.,

(i) Relative lowering of vapour pressure
(ii) Elevation in boiling point of the solvent
(iii) Depression in freezing point
(iv) Osmotic pressure

Caution Points

(*i*) *The freezing point and boiling point depend on the type of salt that's why these are not considered as colligative properties.*

(*ii*) *When a non-volatile solute is added to the solvent, vapour pressure and freezing point decrease whereas boiling point increases.*

Hot Spot 2

RELATIVE Lowering of Vapour Pressure

It is also an important topic of the chapter from JEE Main examination point of view. The nature of question is numerical type and their level vary from easy to moderate.

When a non-volatile solute is added to a solvent, the vapour pressure is lowered. So, vapour pressure of a solution (p) is always less than the vapour pressure of pure solvent (p°) at that temperature. Therefore, ($p^\circ - p$) is called the **lowering in vapour pressure** and the ratio $\left(\dfrac{p^\circ - p}{p^\circ}\right)$ is known as the **relative lowering in vapour pressure.**

According to **Raoult's law,** "the relative lowering in vapour pressure of a dilute solution is equal to the mole fraction of the solute present in the solution. *i.e.,*

$$\frac{p^\circ - p}{p^\circ} = \chi_B$$

where, χ_B = mole fraction of solute

Determination of Molecular Mass

If n moles of solute be dissolved in N moles of the solvent, the mole fraction of the solute $= \dfrac{n}{n + N}$

Then, according to Raoult's law,

$$\therefore \qquad \frac{p^\circ - p_s}{p^\circ} = \frac{n}{n + N}$$

$$\frac{p^\circ - p_s}{p^\circ} = \frac{\dfrac{w}{m}}{\dfrac{w}{m} + \dfrac{W}{M}} \qquad \left[\because \; n = \frac{w}{m} \text{ and } N = \frac{W}{M}\right]$$

For very dilute solutions

$$n <<< N$$

$$\therefore \qquad \frac{p^\circ - p_s}{p^\circ} = \frac{n}{N}$$

$$\text{or} \qquad \boxed{\frac{p^\circ - p_s}{p^\circ} = \frac{w \times M}{m \times W}}$$

This expression is used to find the molecular weight of an unknown solute dissolved in a given solvent.

Alternate Formula for the Relative Lowering of Vapour Pressure When the solution is not Dilute

$$\frac{p^\circ - p_s}{p^\circ} = \frac{n_B}{n_A + n_B} \qquad \text{...(i)}$$

On reversing Eq. (i), we get

$$\frac{p^\circ}{p^\circ - p_s} = \frac{n_A + n_B}{n_B} = 1 + \frac{n_A}{n_B}$$

$$\Rightarrow \qquad \frac{p^\circ}{p^\circ - p_s} - 1 = \frac{n_A}{n_B}$$

$$\Rightarrow \qquad \frac{p^\circ - p^\circ + p_s}{p^\circ - p_s} = \frac{n_A}{n_B}$$

$$\Rightarrow \qquad \frac{p_s}{p^\circ - p_s} = \frac{n_A}{n_B}$$

$$\text{or} \qquad \boxed{\frac{p^\circ - p_s}{p_s} = \frac{n_B}{n_A}}$$

Caution Point *This equation can be used to solve the problem quickly, whether the solution is dilute or not.*

Sample Problem 14 *Calculate the mass of a non-volatile solute (molar mass 40 g mol^{-1}) which should be dissolved in 114 g octane to reduce its vapour pressure to 80%.*

(*a*) 20 g (*b*) 10 g (*c*) 30 g (*d*) 45 g

Interpret (*b*) According to Raoult's law, relative lowering of vapour pressure,

$$\frac{p_A^\circ - p_S}{p_A^\circ} = \chi_B \qquad \text{...(i)}$$

$$\chi_B = \frac{n_B}{n_B + n_A} = \frac{W_B/M_B}{\dfrac{W_B}{M_B} + \dfrac{W_A}{M_A}} \qquad \text{...(ii)}$$

Given vapour pressure is reduced to 80% when non-volatile solute is dissolved in octane. It means

If $p_A^\circ = 1$ atm then $p_S = 0.8$ atm; $p_A^\circ - p_S = 0.2$ atm;
M_A (C_8H_{18}) = 114 g mol^{-1}; W_A = 114 g; M_B = 40 g mol^{-1}; W_B = ?

Applying Eq. (ii)

$$\frac{0.2}{1} = \frac{W_B/40}{\dfrac{W_B}{40} + \dfrac{114}{114}} = \frac{W_B/40}{\dfrac{W_B}{40} + 1}$$

$$0.2 = \frac{W_B}{W_B + 40}$$

$$0.2W_B + 8 = W_B$$

$$W_B = 10$$

Sample Problem 15 *The vapour pressure of 100 g water reduces from 17.53 mm to 17.22 mm when 17.10 g substance 'X' is dissolved in it. Substance X can be*

(*a*) *methanol* (*b*) *glucose*
(*c*) *carbon dioxide* (*d*) *cannot predict*

Interpret (*b*) $$\frac{p^\circ - p_s}{p^\circ} = \frac{n}{n+N} = \frac{\frac{w}{m}}{\frac{w}{m} + \frac{W}{M}}$$

$$\because \quad \frac{w}{m} <<< \frac{W}{M}$$

$$\therefore \quad \frac{p^\circ - p_s}{p^\circ} = \frac{w/m}{W/M} = \frac{w}{m} \times \frac{M}{W}$$

$$\Rightarrow \quad \frac{17.53 - 17.22}{17.53} = \frac{17.10}{m} \times \frac{18}{100}$$

$$\Rightarrow \quad m = \frac{17.10 \times 18 \times 17.53}{0.31 \times 100}$$

$$m = 174.05$$

174 is nearest to the molecular weight of glucose ($C_6H_{12}O_6$), thus the substance '*X*' can be glucose.

Experimental Method of Calculation of Relative Lowering in Vapour Pressure

Relative lowering in vapour pressure is experimentally calculated by Ostwald and Walker method. The experimental setup for determining relative lowering in vapour pressure is shown in the figure. It consists of two sets of bulbs. The first set of three bulbs is filled with solution, to half of their capacity and the second set of another three bulbs is filled with the pure solvent.

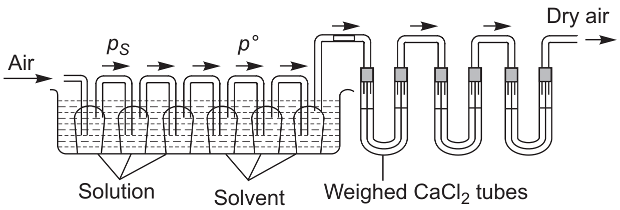


Fig. 2.3 Ostwald and Walker method

Each set is separately weighed accurately. Both sets are connected to each other and then with the accurately weighed set of guard tubes which contain anhydrous calcium chloride or some other dehydrating agents such as P_2O_5, concentrated H_2SO_4, etc. The bulbs of solution and pure solvent are kept in a thermostat maintained at a constant temperature.

A current of pure dry air is bubbled through the series of bulbs as shown in the figure. The air gets saturated with the vapour in each set of bulbs. The air takes up an amount of vapours proportional to the vapour pressure of the solution first and then it takes up more amount of vapour from the solvent which is proportional to the difference in the vapour pressure of solvent and the vapour pressure of solution, *i.e.*, $p^\circ - p_s$. The two sets of bulbs are weighed again. The guard tubes are also weighed.

Loss in mass in the solution bulbs $\propto p_s$

Loss in mass in the solvent bulbs $\propto (p^\circ - p_s)$

Total loss in the both sets of bulbs $\propto [p_s + (p^\circ + p_s)]$

$\propto p^\circ$

Total loss in the mass of both sets of bulbs is equal to gain in the mass of guard tubes.

$$\text{Thus,} \quad \frac{p^\circ - p_s}{p^\circ} = \frac{\text{loss in mass in solvent bulbs}}{\text{total loss in mass in both sets of bulbs}}$$

$$= \frac{\text{loss in mass in solvent bulbs}}{\text{gain in mass of guard tubes}}$$

Further we know from Raoult's law,

$$\frac{p^\circ - p_s}{p^\circ} = \frac{W_B/M_B}{W_A/M_A + W_B/M_B}$$

$$\text{Hence,} \quad \frac{\text{loss in mass in solvent bulbs}}{\text{gain in mass of guard tubes}} = \frac{W_B/M_B}{W_A/M_A + W_B/M_B}$$

The above relationship is used for the calculation of molecular masses of non-volatile solutes.

For very dilute solutions, the following relationship can be applied

$$\frac{p^\circ - p_s}{p^\circ} = \frac{\text{loss in mass in solvent bulbs}}{\text{gain in mass of guard tubes}} = \frac{W_B/M_B}{W_A/M_A}$$

Sample **Problem 16** *A current of dry air was bubbled through a bulb containing* 26.66 *g of an organic compound in* 200 *g of water, then through a bulb at the same temperature, containing water and finally through a tube containing anhydrous calcium chloride. The loss of mass in the bulb containing water was* 0.087 *g and the gain in the mass of calcium chloride tube was* 2.036 *g. Calculate the molecular mass of the organic substance.*

(*a*) 35.23 (*b*) 53.75

(*c*) 40.21 (*d*) 21.15

Interpret (*b*) $$\frac{p^\circ - p_s}{p^\circ} = \frac{\text{loss in the mass of solvent bulb}}{\text{gain in the mass of } CaCl_2 \text{ tube}}$$

$$= \frac{0.087}{2.036}$$

Let the molecular mass of the organic substance be M_2.

According to Raoult's law,

$$\frac{p^\circ - p_s}{p^\circ} = \frac{W_2/M_2}{\frac{W_2}{M_2} + \frac{W_1}{M_1}}$$

$$\frac{0.087}{2.036} = \frac{\frac{26.66}{M_2}}{\frac{26.66}{M_2} + \frac{200}{18}} = \frac{26.66}{26.66 + \frac{200}{18} M_2}$$

$$M_2 = 53.75 \text{ g mol}^{-1}$$

Elevation in Boiling Point of the Solvent

(Ebullioscopy)

The boiling point of a liquid may be defined as the temperature at which vapour pressure becomes equal to the atmospheric pressure (760 mm). As the vapour pressure of a solution is decreased due to the presence of a non-volatile solute, the solution boils at a higher temperature as compared to the pure solvent. The boiling point of the solution is therefore higher than the boiling point of the pure solvent. If $T_b°$ is the boiling point of pure liquid and T_b is the boiling point of solution then,

Elevation in boiling point, $\Delta T = T_b - T_b°$

The elevation in boiling point is proportional to the molality of the solution, i.e.,

$$\Delta T_b \propto m$$

or $$\Delta T_b = k_b m$$

Determination of Molecular Mass from Elevation in Boiling Point

We know that molality,

$$m = \frac{\text{weight of solute} \times 1000}{\text{mol. wt. of solute} \times \text{mass of solvent}}$$

$$= \frac{w \times 1000}{m' \times W}$$

On putting the value of m in expression of elevation in boiling point, we get

or $$\Delta T_b = \frac{k_b \times w \times 1000}{m' \times W}$$

or $$m' = \frac{k_b \times w \times 1000}{\Delta T_b \times W}$$

where, k_b = molal boiling point elevation constant or ebullioscopic constant of the solvent

w = weight of the solute

W = weight of solvent

m' = molecular weight of the solute

Sometimes the value of k_b is given per 0.1 kg (100 g), in such case the expression becomes

$$m = \frac{100 \times k_b \times w}{\Delta T_b \times W}$$

Definition of k_b

If $\frac{m}{w} = 1$ (*i.e.*, $m' = w$)

and, $w = 1$ kg = 1000 g

Then, $k_b = \Delta T_b$

Therefore, k_b is defined as the elevation in boiling point produced when 1 mole of the solute is dissolved in 1 kg of the solvent.

Unit of k_b $= \text{K (mol / kg)}^{-1}$

$= \text{K kg mol}^{-1}$

Molal boiling point elevation constant (k_b) can be calculated from molar enthalpy of vaporisation (ΔH_{vap}) of the solvent using the expression,

$$k_b = \frac{MR(T_b°)^2}{(\Delta H_{\text{vap}} \times 1000)}$$

where, M = molar mass of solvent,

$T_b°$ = boiling point of solvent

R = gas constant .

Molal boiling point elevation constant (k_b) can also be calculated from latent heat of evaporation (l_v) of pure solvent using the expression.

$$k_b = \frac{0.002\,(T°)^2}{l_v}$$

where, $T°$ = normal boiling point of the pure solvent

l_v = latent heat of evaporation in cal/g of pure solvent

Caution Point *k_b for water is 0.52 K-kg mol^{-1}.*

Sample Problem 17 *Calculate the boiling point of a solution containing 0.456 g of camphor (molar mass = 152) dissolved in 31.4 g of acetone (b.p. = 56.30°C), if the molecular elevation constant per 100 g of acetone is 17.2°C.*

(a) 56.46°C (b) 36.56°C

(c) 56.14°C (d) 72.52°C

Interpret (a) We know that

$$\Delta T_b = \frac{100 k_b \times w}{W \times m'} = \frac{100 \times 17.2 \times 0.456}{31.4 \times 152}$$

$$= 0.16°\text{ C}$$

∴ Boiling point of solution $(T_s) = T° + \Delta T_b$

$$= 56.30 + 0.16 = 56.46°\text{ C}$$

Hot Spot 3

DEPRESSION in Freezing Point of the Solvent (Cryoscopy)

It is a very important topic of the chapter for JEE Main examination. Most of the times, the questions are from this topic. The level of question is moderate and their nature is numerical type.

The temperature at which the liquid and solid states of a substance have the same vapour pressure is called **freezing point**. Since, the vapour pressure of a solvent is lowered by the addition of non-volatile solute, the freezing point of the solution (T_f) is always lower than the freezing point of the pure solvent (T_f°). Therefore,

depression in freezing point, $\Delta T_f = T_f^\circ - T_f$

The depression in freezing point is proportional to the molality of the solution, *i.e.*,

$$\Delta T_f \propto m$$

or $$\boxed{\Delta T_f = k_f m}$$

where, k_f = molal freezing point depression constant or cryoscopic constant of the solvent

Determination of Molecular Mass from Depression in Freezing Point

As we known, molality, $m = \dfrac{w \times 1000}{m' \times W}$

On putting this value in the expression of depression in freezing point, we get

$$\Delta T_f = \frac{k_f \times w \times 1000}{m' \times W} \quad \text{or} \quad m' = \frac{k_f \times w \times 1000}{\Delta T_f \times W}$$

where, w = weight of the solute

W = weight of the solvent

m' = molecular weight of the solute

Sometimes the value of k_f is given per 0.1 kg (100 g), in such case the expression becomes

$$m' = \frac{100 \times k_f \times w}{\Delta T_f \times W}$$

Definition of k_f

If $\dfrac{m}{w} = 1$ (*i.e.*, $m = w$), $W = 1\text{ kg} = 1000\text{ g}$

Then, $$k_f = \Delta T_f$$

Therefore, k_f is defined as the depression in freezing point produced when 1 mole of the solute is dissolved in 1 kg of the solvent.

Unit of k_f = K (mol/kg^{-1}) = K kg-mol^{-1}

Molal depression constant, k_f can be calculated from molar heat of fusion of the solvent using the expression

$$k_f = \frac{MR\,(T_f^\circ)^2}{(\Delta H_{\text{fusion}} \times 1000)}$$

where, M = molar mass of solvent, T_f° = boiling point of solvent

R = gas constant

Molal freezing point depression constant (k_f) can also be calculated from latent heat of fusion (l_f) of pure solvent using the expression

$$k_f = \frac{0.002\,(T^\circ)^2}{l_f}$$

where, T° = normal freezing point of the solvent

l_f = latent heat of fusion in cal/g of pure solvent

Caution Point *k_f for water is 1.86 K-kg mol^{-1}.*

Sample Problem 18 *Calculate the mass of ascorbic acid (Vitamin C, $C_6H_8O_6$) to be dissolved in 75 g of acetic acid to lower its melting point by 1.5° C. k_f = 3.9 K kg mol^{-1}.* **[NCERT]**

(a) 5 g (b) 4 g (c) 8 g (d) 9 g

Interpret (a) Mass of ascorbic acid $(W_A) = 75\text{ g} = 0.075\text{ kg}$

Depression in melting point $(\Delta T_f) = 1.5^\circ\text{ C} = 1.5\text{ K}$

Molar mass of ascorbic acid

$$(M_B) = (12 \times 6) + (8 \times 1) + (16 \times 6) = 176\text{ g mol}^{-1}$$

Molal depression constant $(k_f) = 3.9\text{ K kg mol}^{-1}$

Since, lowering of melting point is given, apply the formula for lowering of melting point, *i.e.*,

$$\Delta T_f = k_f \cdot m$$

$$\Delta T_f = \frac{k_f \cdot W_B}{M_B \times W_A} \quad \text{or} \quad W_B = \frac{\Delta T_f \cdot M_B \cdot W_A}{k_f}$$

$$W_B = \frac{(176\text{ g mol}^{-1}) \times (1.5\text{ K}) \times (0.075\text{ kg})}{(3.9\text{ K kg mol}^{-1})} = 5.08\text{ g}$$

Sample Problem 19 *An aqueous solution freezes at – 0.186°C (k_f = 1.86° and k_b = 0.512°). What is the elevation of boiling point?*

(a) 0.0512°C (b) 0.326°C

(c) 0.0592°C (d) 0.0256°C

Interpret (a) $\because \quad \Delta T_f = k_f \times \text{molality}$

$$\therefore \quad \text{Molality} = \frac{0.186}{1.86} = 0.1$$

Again, from, $\Delta T_b = k_b \times m = 0.512 \times 0.1 = 0.0512^\circ$

Osmosis and Osmotic Pressure

Osmosis is the spontaneous flow of the solvent molecules through semipermeable membrane from a pure solvent to a solution or from a dilute to a concentrated solution.

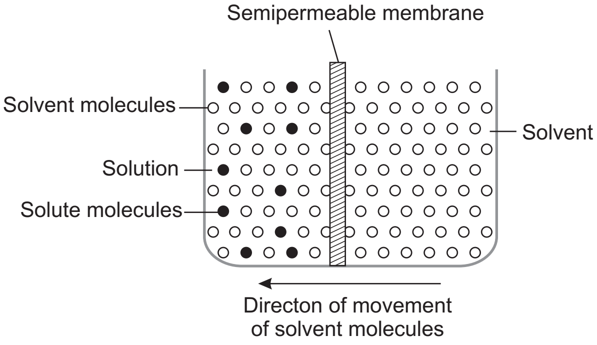


Fig. 2.4 Osmosis

Semipermeable membranes are thin sheets, which allow the passage of only solvent molecules through them. *e.g.,* egg membrane, goat's bladder, cell membrane are natural semipermeable membranes. Artifical membranes of gelatinous inorganic substances such as calcium phosphate, copper ferrocyanide, freshly prepared silicates of iron, cobalt nickel etc., are also semipermeable. Cellophane and perchment papers etc., are also used for the same purpose.

Difference Between Osmosis and Diffusion

1. Diffusion is intermingling of molecules or ion etc., resulting from the random thermal agitation thus there is no restriction to motion of any kind of particles while in osmosis only solvent molecules flow.
2. Osmosis takes place through a semipermeable membrane while for diffusion it is not required.
3. A homogeneous mixture is obtained as a result of diffusion. On the other hand no mixing is possible in osmosis.
4. Diffusion cannot be prevented while osmosis can be stopped by applying pressure to the solution.

Osmotic Pressure

The external pressure which must be applied on the solution in order to stop the flow of the solvent into the solution through semipermeable membrane is termed as osmotic pressure.

The hydrostatic pressure developed as a result of osmosis is a measure of osmotic pressure of the solution and is defined as the hydrostatic pressure built up on the solution which just stops the osmosis.

Osmotic pressure $(\pi) = hdg$ (approximate)

where, h = increase in level in the tube of unit cross-section

d = density of solution

Laws of Osmotic Pressure

van't Hoff realised that an analogy exists between the gases and solutions provided the osmotic pressure of solutions is used in place of ordinary gas pressure. He showed that for solutions of non-electrolytes the following laws hold good

(i) **Boyle-van't Hoff law** which states that the osmotic pressure (π) of a solution is directly proportional to its concentration (C), when the temperature is kept constant.

$$\pi \propto C \quad \text{(Temperature, } T \text{ is constant)}$$

If V litres of solution contain n moles of solute then

$$C = \frac{n}{V}, \text{ or } \pi \propto \frac{1}{V}$$

$$\pi V = \text{constant}$$

Caution Point *The osmotic pressure of a solution containing 1 mole of solute particles per litre (1M) at 0°C is 22.4 atm.*

(ii) **Charles'-van't Hoff law** (Gay-Lussac law) according to which the osmotic pressure of a dilute solution is directly proportional to its absolute temperature (T), when the concentration of solution is kept constant.

$$\pi \propto T \quad \text{(Concentration, } C \text{ is constant)}$$

or $$\frac{\pi}{T} = \text{constant}$$

(iii) **Avogadro-van't Hoff law** states that equal volumes of dilute solutions of different solutes, having the same temperature and osmotic pressure contain equal number of molecules, *i.e.,* isotonic solutions at a given temperature have same molar concentration.

$$\pi \propto n,$$

here, n = number of moles of solute per litres of solutions.

(iv) **General equation for dilute solutions** is obtained by combining the above three laws

$$\pi V = nRT \text{ or } \pi = CRT$$

On the basis of this analogy, van't Hoff proposed that a solute in dissolved state behave as a gas and the osmotic pressure of the solution is equal to the pressure which the solute would exert if it were a gas at the same temperature and occupying the same volume as that of solution.

These laws fail to deal with concentrated solution due to the fact that osmotic pressure is actually related to the activity and not to the concentration of the solution. Osmotic pressure is the most sensitive colligative property and its magnitude is proportional to the molality of the solution.

Sample Problem 20 *Calculate the osmotic pressure of 0.01 M solution of cane sugar at 300 K ($R = 0.0821$ L atm degree^{-1} mol^{-1}).*

(a) 0.3568 *atm* (b) 0.2463 *atm*
(c) 0.1562 *atm* (d) 0.5623 *atm*

Interpret (b) $C = 0.01\ M = 0.01$ mol / L,

$$R = 0.0821 \text{ L-atm/degree/mol}, T = 300 \text{ K}$$

$$\because \quad \pi = CRT$$

$$\therefore \quad \pi = 0.01 \times 0.0821 \times 300 = 0.2463 \text{ atm}$$

Sample Problem 21 *Osmotic pressure of a urea solution at 10°C is 500 mm. Osmotic pressure of the solution become 105.3 mm, when it is diluted and temperature is raised to 25°C. The extent of dilution is*

(a) 4 *times* (b) 3 *times*
(c) 5 *times* (d) 2 *times*

Interpret (c)

$$\pi V = nRT$$

$$\frac{500 V_1}{105.3 V_2} = \frac{nR \times 283}{nR \times 298}$$

$$\frac{V_1}{V_2} = \frac{1}{5}$$

or

$$V_2 = 5V_1$$

Determination of Molecular Mass from Osmotic Pressure

We know that number of moles $= \dfrac{\text{mass}}{\text{molar mass}}$

or

$$n = \frac{w}{m'}$$

where, w = gram of solute dissolved in V litre of the solution

m' = molecular mass of solute

$$\therefore \quad \pi V = \frac{w}{m'} RT$$

or

$$m' = \frac{wRT}{\pi V}$$

Sample Problem 22 *If 20 g of a solute was dissolved in 500 mL of water, osmotic pressure of the solution was found to be 600 mm of Hg at 15°C. The molecular weight of the solute is*

(a) 1200 (b) 1500 (c) 800 (d) 1000

Interpret (a) We know that $\pi = \dfrac{nRT}{V} = \dfrac{wRT}{V \times m}$

$$\frac{600}{760} = \frac{20 \times 0.0821 \times 288 \times 1000}{500 \times M}$$

or

$$M \simeq 1200 \text{ g mol}^{-1}$$

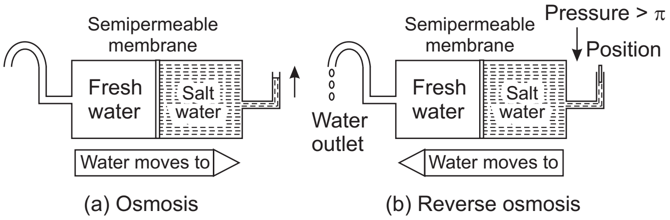
Total Osmotic Pressure

If a number of solutions are present in the solution and $\pi_1, \pi_2, \pi_3, \ldots$ are their individual osmotic pressure then

total osmotic pressure, $\pi = \pi_1 + \pi_2 + \pi_3 + \ldots$

Reverse Osmosis

When a pressure more than the osmotic pressure is applied to the solution, the solvent may pass from solution into the solvent through the semi-permeable membrane. This type of osmosis is known as **reverse osmosis.** Reverse osmosis is used for the **desalination of sea water.**



(a) Osmosis (b) Reverse osmosis

Fig. 2.5 A schematic set up for the reverse osmosis used for desalination of sea water

Caution Point *The osmotic pressure of sea water at 15°C is 25 atm.* ***Isotonic solutions*** *have the same osmotic pressure. If two solutions have different osmotic pressures, the one having lower pressure is called* ***hypotonic*** *and the other with higher pressure is* ***hypertonic solution.***

Sample Problem 23 *How many gram of glucose must be present in 0.5 L of solution for its osmotic pressure to be the same as that of 9.2 g of glucose per litre?*

(a) 4.6 g (b) 5.8 g (c) 3.6 g (d) 8.4 g

Interpret (a) For isotonic solution,

$$\frac{w_1}{m_1 V_1} = \frac{w_2}{m_2 V_2}$$

$$\frac{w_1}{180 \times 0.5} = \frac{9.2}{180 \times 1}$$

or

$$w = 4.60 \text{ g}$$

Applications of Osmotic Pressure

1. Osmotic pressure measurement provided very good method of determination of molecular mass of polymers like proteins etc., due to the following reasons
   (i) Osmotic pressure of a solution containing fewer particles is appreciable and can therefore be measured accurately as compared to ΔT_b or ΔT_f which are very small in these conditions.
   (ii) Osmotic pressure is measured at room temperature, hence the method is particularly useful for biomolecules which are generally unstable at higher temperatures.

2. Osmosis plays a vital role in biology also. *Some examples of it are*
   - (i) For normal functioning of the living systems, the fluid concentration has to be maintained in the plant and animal cells.
   - (ii) Movement of water from roots to the top of plants takes place *via* osmosis.
   - (iii) Flow of water to various parts of plants is due to osmosis.
   - (iv) Different movements of plants such as opening and closing of flowers, etc., are controlled by osmosis.
   - (v) A 0.91% solution of pure NaCl is isotonic with human red blood red cells (RBCs). Therefore, in this solution, RBCs neither swell nor undergo plasmolysis.
   - (vi) A pure NaCl solution with concentration less than 0.91% is called *hypotonic solution*. On placing RBCs in this solution, they will swell and even burst.
   - (vii) A pure NaCl solution with concentration more than 0.91% is called *hypertonic solution*. On placing RBCs in this solution, they shink due to plasmolysis.
   - (viii) People taking a lot of salt or salty food experience water osmosis. The resulting puffiness or swelling is called *edema*.
   - (ix) The use of salt and sugar as preservatives in pickels and jams has its basis in preventing growth of fungi and bacteria by osmosis.

Check Point 3

1. When two liquids *A* and *B* are mixed then their boiling points become greater than both of them. What is the nature of this solution?
2. When ethanol mixes in cyclohexane, cyclohexane reduces the intermolecular forces between ethanol molecule. Should this pair show any deviation from Raoult's law?
3. Distinguish between the boiling point of a liquid and the normal boiling point of the liquid.
4. Explain the flow of water through a semipermeable membrane during osmosis.

2.8 Abnormal Colligative Properties : van't Hoff Factor

Various relations of colligative properties hold good in dilute solutions only when there is no change in molecular state of solute. In case the total number of particles of solute changes in solution, the colligative properties also change accordingly.

This change occur in the following two ways

By Dissociation

When substance is an electrolyte, the number of particles increases in solution and the colligative property increases accordingly.

In case of dissociation suppose 1 molecule of solute *A* dissociates to give *n* ions and α is the degree of dissociation.

$$\begin{array}{ccc} A & \rightleftharpoons \; nB & \\ 1\text{ mol} & 0 & \text{initially} \\ (1-\alpha)\text{ mol} & n\alpha & \text{after dissociation} \end{array}$$

Total number of moles present in solution

$$= (1-\alpha) + n\alpha = 1 + (n-1)\,\alpha$$

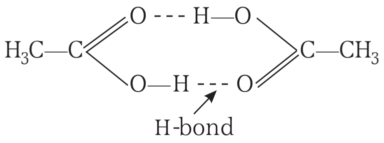
van't Hoff factor, $i = 1 + (n-1)\,\alpha > 1$ if $n \geq 2$

and $$\alpha = \frac{(i-1)}{(n-1)}$$

By Association

When substance undergoes association, the number of particles decreases in solution and consequently the value of colligative property decreases. Association of molecules is depicted as follows

$$2CH_3COOH \rightleftharpoons (CH_3COOH)_2$$



Molecules of acetic acid dimerise in benzene due to hydrogen bonding. It generally happens in solvents having low dielectric constant.

In case of association suppose *n* molecules associate to form one giant molecule and α is the degree of association.

$$\begin{array}{ccc} nA & \rightleftharpoons \; (A)_n & \\ 1\text{ mol} & 0 & \text{initially} \\ (1-\alpha)\text{ mol} & \dfrac{\alpha}{n} & \text{at equilibrium} \end{array}$$

Total number of moles in solution

$$= (1-\alpha) + \frac{\alpha}{n} = 1 + \left(\frac{1}{n} - 1\right)\alpha$$

van't Hoff factor $= 1 + \left(\dfrac{1}{n} - 1\right)\alpha < 1$ if $n \geq 2$

and $$\alpha = \frac{(i-1)}{\dfrac{1}{n} - 1}$$

van't Hoff Factor

Normal value of colligative property $\propto$ number of particles of solute taken and abnormal value of colligative property $\propto$ number of particles of solute after dissociation or association.

The ratio of two values *i.e.*,

$\dfrac{\text{abnormal colligative property}}{\text{normal colligative property}}$ is termed as van't Hoff factor (i).

Thus,

$$i = \frac{\pi_{\text{obs}}}{\pi_{\text{theo}}} = \frac{(\Delta p)_{\text{obs}}}{(\Delta p)_{\text{theo}}}$$

$$= \frac{(\Delta T_b)_{\text{obs}}}{(\Delta T_b)_{\text{theo}}} = \frac{(\Delta T_f)_{\text{obs}}}{(\Delta T_f)_{\text{theo}}}$$

$$= \frac{\text{actual number of particles in solution}}{\text{number of particles taken}}$$

Abnormal Molecular Weight

As, colligative properties $\propto \dfrac{1}{(\text{molecular weight})}$

$$\therefore \quad \frac{\text{abnormal colligative property}}{\text{normal colligative property}}$$

$$= \frac{\text{normal molecular weight}}{\text{abnormal molecular weight}}$$

$$= 1 + (n-1)\,\alpha > 1 \text{ in case of dissociation}$$

$$= 1 + \left(\frac{1}{n} - 1\right)\alpha < 1 \text{ in case of association}$$

In case van't Hoff factor is known, the various colligative properties would be given by

$$\Delta T_f = i\,k_f\,m$$

$$\Delta T_b = i\,k_b\,m$$

$$\pi V = inRT$$

$$\frac{p^\circ - p}{p^\circ} = ix_B$$

where, m is the molality of solution, $i \times m$ is sometimes referred to as **effective molality** or **colligative molality** (m_i).

$$\therefore \quad m_i = i \times m$$

$$\text{and} \quad \Delta T_f = k_f\,m_i$$

$$\Delta T_b = k_b m_i$$

Sample Problem 24 *The van't Hoff factor for sodium phosphate would be*

(*a*) 1 (*b*) 2 (*c*) 3 (*d*) 4

Interpret (*d*) van't Hoff factor is the number of ions produced

$$\text{Na}_3\text{PO}_4 \longrightarrow 3\text{Na}^+ + \text{PO}_4^{3-}$$

So, van't Hoff factor = 3 + 1 = 4

Sample Problem 25 *The freezing point depression of* 0.1 *molal solution of acetic acid in benzene is* 0.256 *K.* k_f *for benzene is* 5.12 *K kg mol*$^{-1}$*. What conclusion can you draw about the molecular state of acetic acid in benzene?*

(*a*) *Acetic acid is doubly associated*
(*b*) *Benzene is doubly associated*
(*c*) *Both are equally associated*
(*d*) *None of the above*

Interpret (*a*) $i = \dfrac{\text{observed colligative property}}{\text{calculated colligative property}} = \dfrac{0.256}{0.512} = \dfrac{1}{2}$

Also, $i = \dfrac{\text{calculated molecular mass}}{\text{observed molecular mass}}$

Calculated molecular mass of $\text{CH}_3\text{COOH} = 60$

$\therefore$ Observed molecular mass $= \dfrac{60}{1/2} = 120$

Hence, acetic acid exists as doubly associated.

Sample Problem 26 *Lowering of vapour pressure is highest for*

(*a*) 0.1 *M urea*
(*b*) 0.1 *M glucose*
(*c*) 0.1 *M* MgSO_4
(*d*) 0.1 *M* BaCl_2

Interpret (*d*) $\dfrac{p^\circ - p_s}{p^\circ} = i \times \chi_{\text{solute}}$

or $\dfrac{p^\circ - p_s}{p^\circ} \propto i$

$\therefore$ $p^\circ - p_s$ is maximum for BaCl_2.

Sample Problem 27 *Which one of the following aqueous solutions will exhibit highest boiling point?*

(*a*) 0.01 M Na_2SO_4
(*b*) 0.01 *M* KNO_3
(*c*) 0.015 *M urea*
(*d*) 0.015 *M glucose*

Interpret (a) $\Delta T \propto im$ (as k_f is a constant)

(a) $\Delta T \propto 3 \times 0.01 = 0.03$ (because it gives 3 ions)
(b) $\Delta T \propto 2 \times 0.01 = 0.02$ (because it gives 2 ions)
(c) $\Delta T \propto 0.015 \times 1 = 0.015$ (No ions are obtained)
(d) $\Delta T \propto 0.015 \times 1 = 0.015$

Since, ΔT is highest for 0.01 M Na_2SO_4 so it will exhibit highest boiling point.

WORKED OUT Examples

Example 1 *Calculate the molarity of solution of* $CaCl_2$ *if on chemical analysis it is found that 200 mL of* $CaCl_2$ *contains* 3.01×10^{22} Cl^- *ions.*

(*a*) 40 *M* (*b*) 3.01 *M* (*c*) 0.125 *M* (*d*) 0.250 *M*

Solution (*c*) $\underset{1\ \text{mol}}{CaCl_2} \longrightarrow Ca^{2+} + \underset{2 \times 6.023 \times 10^{23}\ \text{ions}}{2Cl^-}$

$2 \times 6.023 \times 10^{23}$ Cl^- ions are present in = 1 mole of $CaCl_2$

$$3.01 \times 10^{22}\ Cl^-\ \text{ions are present in } \frac{1 \times 3.01 \times 10^{22}}{2 \times 6.02 \times 10^{23}}$$

$$= 0.025 \text{ mol of } CaCl_2$$

$$M = \frac{\text{number of moles}}{\text{volume of solution (in L)}} = \frac{0.025}{200} \times 1000 = 0.125 \text{ M}$$

Example 2 *What volume of 12 N and 3 N* HCl *must be mixed to give* 1.00 *L of* 6.00 *N* HCl?

(*a*) 0.33 *L*, 0.66 *L* (*b*) 0.33 *L*, 0.33 *L*
(*c*) 0.66 *L*, 0.66 *L* (*d*) 0.8 *L*, 0.2 *L*

Solution (*a*) L-equivalents of solution

$$= 1 \text{ L} \times \left(\frac{6.00 \text{ eq.}}{\text{L}}\right) = 6.00 \text{ eq.}$$

Let x = volume of concentrated solution. Then

$1.00 - x$ = volume of dilute solution

$$(x)\left(\frac{12.0 \text{ eq}}{\text{L}}\right) + (1.00 - x)\left(\frac{3.00 \text{ eq}}{\text{L}}\right) = 6.00 \text{ eq.}$$

On solving

$x = 0.333$

∴ Volume of concentrated solution = 0.33 L

and, Volume of dilute solution = 1 − 0.33 = 0.67 L

Example 3 *How many mL of* 0.1*M* HCl *are required to react completely with* 1g *mixture of* Na_2CO_3 *and* $NaHCO_3$ *containing equimolar amounts of both?* **[NCERT]**

(a) 157.8 *mL* (*b*) 110.2 *mL* (*c*) 98.4 *mL* (*d*) 175 *mL*

Solution (*a*) ***Step I*** *Calculating mass of* Na_2CO_3 *and* $NaHCO_3$

Mass of the mixture = 1.0 g

Let the mass of Na_2CO_3 = x g

Then the mass of $NaHCO_3$ = $(1 - x)$ g

$$\text{Moles of } Na_2CO_3 = \frac{\text{mass}}{\text{molar mass}}$$

$$= \frac{x \text{ g}}{[(23 \times 2) + (12) + (16 \times 3)] \text{ g mol}^{-1}}$$

$$= \frac{x}{106} \text{ mol}$$

$$\text{Moles of } NaHCO_3 = \frac{\text{mass}}{\text{molar mass}}$$

$$= \frac{(1 - x) \text{ g}}{[(23) + (1) + (12) + (16 \times 3)] \text{ g mol}^{-1}}$$

$$= \frac{(1 - x)}{84} \text{ mol}$$

According to the question, the mixture contains equimolar amounts of Na_2CO_3 and $NaHCO_3$.

$$\text{Moles of } Na_2CO_3 = \text{Moles of } NaHCO_3$$

$$\frac{x}{106} \text{ mol} = \frac{(1 - x)}{84} \text{ mol}$$

$$84x = 106 - 106\,x;\ 106x + 84x = 106$$

$$190x = 106;\ x = \frac{106}{190} = 0.558 \text{ g}$$

∴ Mass of Na_2CO_3 = 0.558 g

Mass of $NaHCO_3$ = (1 − 0.558) = 0.442 g

Step II *Calculating total mass of* HCl *required*

$$\underset{106\ \text{g}}{Na_2CO_3(s)} + \underset{73\ \text{g}}{2HCl\,(aq)} \longrightarrow 2NaCl\,(aq) + H_2O\,(l) + CO_2\,(g)$$

According to the above equation

∵ 106 g Na_2CO_3 require HCl to react completely = 73 g

∴ 0.558 g Na_2CO_3 require HCl to react completely

$$= \frac{73 \times 0.558}{106} \text{ g}$$

$$= 0.384 \text{ g}$$

$$\underset{84\ \text{g}}{NaHCO_3(s)} + \underset{36.5\ \text{g}}{HCl\,(aq)} \longrightarrow NaCl\,(aq) + H_2O\,(l) + CO_2(g)$$

∵ 84 g $NaHCO_3$ require HCl = 36.5 g

$$\therefore\ 0.442 \text{ g } NaHCO_3 \text{ require HCl} = \frac{36.5 \times 0.442}{84} \text{ g} = 0.192 \text{ g}$$

Total mass of HCl required = (0.384 + 0.192) g = 0.576 g

Step III *Calculating volume of* HCl *required*

Mass of HCl required = 0.576 g

Molarity of HCl solution = 0.1M

$$\text{Molarity}\,(M) = \frac{\text{mass / molar mass}}{\text{volume of HCl in litres}}$$

$$(0.1\ \text{mol L}^{-1}) = \frac{(0.576\ \text{g})\,/\,(36.5\ \text{g mol}^{-1})}{\text{volume in litres}}$$

$$\text{Volume}\,(V) = \frac{0.576}{36.5 \times 0.1} = 0.1578\ \text{L} = 157.8\ \text{mL}$$

Example 4 *The volume of water to be added to* 100 cm^3 *of* 0.5 *N* H_2SO_4 *to get decinormal concentration is*

(*a*) 400 *cm*^{3} (*b*) 500 *cm*^{3} (*c*) 450 *cm*^{3} (*d*) 100 *cm*^{3}

Solution (*a*) Let the total volume of solution = *x*

$$\therefore \qquad V_2 = \frac{N_1V_1}{N_2} = \frac{0.5 \times 100}{0.1} = 500\ \text{cm}^3$$

$\therefore$ The volume of water added = 500 − 100 cm^3 = 400 cm^3

Example 5 *A dry air is passed through the solution, containing the* 10 *g of solute and* 90 *g of water and then it is passed through pure water. There is the depression in weight of solution by* 2.5 *g and in weight of pure solution by* 0.05 *g. Calculate the molecular weight of solute.*

(*a*) 25 (*b*) 50 (*c*) 100 (*d*) 180

Solution (*c*) $\because$ Lowering in weight of solution $\propto$ solution pressure (p_s)

and lowering in weight of solvent $\propto p^\circ - p_s$

($\because$ p° = vapour pressure of pure solvent)

$$\text{Thus,} \qquad \frac{p^\circ - p_s}{p_s} = \frac{\text{lowering in weight of solvent}}{\text{lowering in weight of solution}} = \frac{0.05}{2.5}$$

But according to Raoult's law,

$$\frac{p^\circ - p_s}{p_s} = \frac{w}{m} \times \frac{M}{W}$$

$$\therefore \qquad \frac{0.05}{2.5} = \frac{10 \times 18}{90 \times m} \quad \Rightarrow \quad m = \frac{10 \times 18 \times 2.5}{90 \times 0.05} = 100\ \text{g mol}^{-1}$$

Example 6 *Mark the correct relationship between the boiling points of very dilute solutions of* $BaCl_2(t_1)$ *and* KCl (t_2), *having the same molarity.*

(*a*) $t_1 = t_2$ (*b*) $t_1 < t_2$

(*c*) $t_2 < t_1$ (*d*) *cannot be calculated*

Solution (c) $BaCl_2$ furnishes more ions than KCl and thus, shows higher boiling point, *i.e.*, $t_1 > t_2$

Example 7 *A solution of urea in water has a boiling point of* 100.128°C. *Find the freezing point of the same solution. Molal constants of water* k_f *and* k_b *are* 1.86°C *and* 0.512°C *respectively.*

(*a*) −0.346°C (*b*) −0.465°C (*c*) +0.465°C (*d*) −0.256°C

Solution (*b*) $\because \quad \Delta T_b = k_b \times m$

$$m = \frac{\Delta T_b}{k_b} = \frac{0.128}{0.512} = 0.25$$

$$\text{Now,} \qquad k_f = 1.86^\circ\ \text{C}, m = 0.25$$

$$\therefore \qquad \Delta T_f = k_f \times m$$

$$\therefore \qquad \Delta T_f = 1.86 \times 0.25 = 0.465^\circ\ \text{C}$$

$\therefore$ Freezing point of the solution $(T_b) = T^\circ - \Delta T_f$

$$= 0 - 0.465 = -0.465^\circ\ \text{C}$$

Example 8 *What is the freezing point of a* 10% *(by weight) solution of* CH_3OH *in water?*

(*a*) 90°*C* (*b*) 10°*C* (*c*) 6.45°*C* (*d*) −6.45°*C*

Solution (*d*) 1.00 kg contains 0.100 kg CH_3OH (and 0.900 kg H_2O)

$$(100\ \text{g CH}_3\text{OH})\left(\frac{1\ \text{mol}}{32.0\ \text{g}}\right) = 3.12\ \text{mol}$$

$$= \frac{3.12\ \text{mol}}{0.900\ \text{kg}} = 3.47\ \text{m}$$

$$\Delta T_f = k_f \times m = (1.86^\circ\ \text{C / m})(3.47\ \text{m}) = 6.45^\circ\ \text{C}$$

Freezing point of the solution $(T_b) = T^\circ - \Delta T_f = 0 - 6.45$

$$= -6.45^\circ\ \text{C}$$

Example 9 *The osmotic pressure of blood is* 7.65 *atm at* 37°C. *How much glucose should be used per litre for an intravenous injection that is to have the same osmotic pressure as blood?*

(*a*) 54.2 *g* (*b*) 180 *g* (*c*) 12 *g* (*d*) 0.30 *g*

Solution (*a*) $\pi V = nRT$

$$n = \frac{\pi V}{RT} = \frac{(7.65\ \text{atm})(1.00\ \text{L})}{(0.0821\ \text{L atm / mol K})(310\ \text{K})}$$

$$= 0.301\ \text{mol}$$

$$= (0.301\ \text{mol})\left(\frac{180\ \text{g C}_6\text{H}_{12}\text{O}_6}{\text{mol}}\right)$$

$$= 54.2\ \text{g}$$

Example 10 *A* 1% *(w/V)* KCl *solution is ionised to the extent of* 82%. *What would be its osmotic pressure at* 291 *K?* (*R* = 0.083 *L bar K*$^{-1}$ *mol*$^{-1}$)

(*a*) 1.82 *bar* (*b*) 5.9 *bar* (*c*) 82 *bar* (*d*) 100 *bar*

Solution (*b*) $KCl \longrightarrow K^+ + Cl^-$

$$\alpha = \frac{i-1}{n-1} \quad \text{or} \quad 0.82 = \frac{i-1}{2-1} \quad \text{or} \quad i = 1.82$$

$$\pi V = i\,\frac{W_B}{M_B} \times RT$$

$$\text{Volume of solution} = 100\ \text{mL} = \frac{100}{1000}\ \text{L}$$

$$\pi \times \frac{100}{1000} = 1.82 \times \frac{1}{74.5} \times 0.083 \times 291$$

$$\pi = \frac{439.58}{74.5} = 5.9\ \text{bar}$$

Start Practice for JEE Main

Round I (Topically Divided Problems)

Different Solutions and their Concentrations

1. A beaker contains a solution of substance '*A*'. Precipitation of substance '*A*' takes place when small amount of '*A*' is added to the solution. The solution is **[NCERT Exemplar]**

(a) saturated (b) supersaturated
(c) unsaturated (d) concentrated

2. Value of Henry's constant K_H **[NCERT Exemplar]**

(a) increases with increase in temperature
(b) decreases with increase in temperature
(c) remains constant
(d) first increases then decreases

3. Low concentration of oxygen in the blood and tissues of people living at high altitude is due to **[NCERT Exemplar]**

(a) low temperature
(b) low atmospheric pressure
(c) high atmospheric pressure
(d) both low temperature and high atmospheric pressure

4. K_H value for $Ar(g), CO_2(g)$, $HCHO(g)$ and $CH_4(g)$ are 40.39, 1.67, 1.83×10^{-5} and 0.413 respectively. Arrange these gases in the order of their increasing solubility. **[NCERT Exemplar]**

(a) $HCHO < CH_4 < CO_2 < Ar$
(b) $HCHO < CO_2 < CH_4 < Ar$
(c) $Ar < CO_2 < CH_4 < HCHO$
(d) $Ar < CH_4 < CO_2 < HCHO$

5. Calculate the mass percentage of aspirin ($C_9H_8O_4$) in acetonitrile (CH_3CN) when 6.5 g of $C_9H_8O_4$ is dissolved in 450 g of CH_3CN. **[NCERT]**

(a) 1.40 (b) 1.90
(c) 2.60 (d) 2.29

6. A sample of drinking water was found to be severely contaminated with chloroform ($CHCl_3$) supposed to a carcinogen. The level of contamination was 15 ppm (by mass). Express this in per cent by mass. **[NCERT]**

(a) $15 \times 10^{-3}\%$ (b) $1.5 \times 10^{-4}\%$
(c) $1.5 \times 10^{-3}\%$ (d) $15 \times 10^{-6}\%$

7. Henry's law constant for the molality of methane in benzene at 298 K is 4.27×10^5 mm Hg. Calculate the solubility of methane in benzene at 298 K under 760 mm Hg. **[NCERT]**

(a) 1.78×10^{-4} (b) 1.78×10^{-5}
(c) 17.8×10^{-4} (d) 1.78×10^{-6}

8. 4L of 0.02 M aqueous solution of NaCl was diluted by adding 1 L of water. The molality of the resultant solution is **[NCERT Exemplar]**

(a) 0.004 (b) 0.008
(c) 0.012 (d) 0.016

9. If 5.85 g of NaCl (molecular weight 58.5) is dissolved in water and the solution is made up to 0.5 L, the molarity of the solution will be

(a) 0.1 (b) 0.2 (c) 0.3 (d) 0.4

10. Calculate the amount of benzoic acid (C_6H_5COOH) required for preparing 250 mL of 0.15 M solution in methanol. **[NCERT]**

(a) 1.89 g (b) 4.57 g
(c) 2.99 g (d) 3.54 g

11. An antifreeze solution is prepared from 222.6 g of ethylene glycol ($C_2H_6O_2$) and 200 g of water. If the density of the solution is 1.072 g mL^{-1} then what shall be the molarity of the solution? **[NCERT]**

(a) 91 M (b) 9.1 M
(c) 0.91 M (d) 0.0091 M

12. Increasing the temperature of an aqueous solution will cause

(a) decrease in molarity
(b) decrease in molality
(c) decrease in mole fraction
(d) decrease in % *w*/*w*

13. The normality of 10% (weight/volume) acetic acid is

(a) 1 N (b) 1.3 N
(c) 1.7 N (d) 1.9 N

14. 19.85 mL of 0.1 N NaOH reacts with 20 mL of HCl solution for complete neutralisation. The molarity of HCl solution is

(a) 9.9 (b) 0.99
(c) 0.099 (d) 0.0099

15. The normality of 0.3 M phosphorous acid (H_3PO_3) is

(a) 0.2 (b) 0.4
(c) 0.6 (d) 0.8

16. What is the molarity of H_2SO_4 solution that has a density 1.84 g/cc at 35°C and contains 98% solute by weight?

(a) 4.18 M (b) 1.84 M
(c) 8.41 M (d) 18.4 M

17. Molecular weight of glucose is 180. A solution of glucose which contains 18 g/L, is

(a) 0.1 molal (b) 0.2 molal
(c) 0.3 molal (d) 0.4 molal

18. If 20 mL of 0.4 N NaOH solution completely neutralizes 40 mL of a dibasic acid, the molarity of the acid solution is

(a) 0.1 M (b) 0.3 M
(c) 0.5 M (d) 0.7 M

19. Calculate the molality of 1 L solution of 93% H_2SO_4 (weight/volume). The density of the solution is 1.84 g/mL.

(a) 11.05 (b) 12.05
(c) 13.05 (d) 10.05

20. Which of the following solutions has the highest normality?

(a) 6 g of NaOH/100 mL
(b) 0.5 M H_2SO_4
(c) N phosphoric acid
(d) 8 g of KOH/L

21. 100 mL of 0.3 N HCl is mixed with 200 mL of 0.6 N H_2SO_4. The final normality of the resulting solution will be

(a) 0.3 N (b) 0.2 N
(c) 0.5 N (d) 0.1 N

22. Based on solute-solvent interactions, arrange the following in the order of increasing solubility in *n*-octane. Cyclohexane, KCl, CH_3OH, CH_3CN. **[NCERT]**

(a) KCl < CH_3OH < CH_3CN < Cyclohexane
(b) CH_3OH < KCl < CH_3CN < Cyclohexane
(c) CH_3OH < CH_3CN < KCl < Cyclohexane
(d) None of the above

Raoult's Law
(Ideal and Non-Ideal Solutions)

23. If two liquids *A* and *B* form minimum boiling azeotrope at some specific composition then **[NCERT Exemplar]**

(a) *A*–*B* interactions are stronger than those between *A*–*A* or *B*–*B*
(b) vapour pressure of solution increases because more number of molecules of liquids *A* and *B* can escape from the solution
(c) vapour pressure of solution decreases because less number of molecules of only one of the liquids escape from the solution
(d) *A*–*B* interactions are weaker than those between *A*–*A* or *B*–*B*

24. Considering the formation, breaking and strength of hydrogen bond, predict which of the following mixtures will show a positive deviation from Raoult's law? **[NCERT Exemplar]**

(a) Methanol and acetone
(b) Chloroform and acetone
(c) Nitric acid and water
(d) Phenol and aniline

25. Formation of a solution from two components can be considered as

(1) Pure solvent → separated solvent molecules; ΔH_1
(2) Pure solute → separated solute molecules; ΔH_2
(3) Separated solvent and solute molecules → solution, ΔH_3

Solution so formed will be ideal if

(a) $\Delta H_{\text{sol}} = \Delta H_1 - \Delta H_2 - \Delta H_3$
(b) $\Delta H_{\text{sol}} = \Delta H_3 - \Delta H_1 - \Delta H_2$
(c) $\Delta H_{\text{sol}} = \Delta H_1 + \Delta H_2 + \Delta H_3$
(d) $\Delta H_{\text{sol}} = \Delta H_1 + \Delta H_2 - \Delta H_3$

26. Which of the following is true when components forming an ideal solution are mixed?

(a) $\Delta H_m = \Delta V_m = 0$ (b) $\Delta H_m < \Delta V_m$
(c) $\Delta H_m = \Delta V_m = 1$ (d) $\Delta H_m > \Delta V_m$

27. When two liquids A and B are mixed then their boiling points becomes greater than both of them. What is the nature of this solution?

(a) Ideal solution
(b) Normal solution
(c) Negative deviation with non-ideal solution
(d) Positive deviation with non-ideal solution

28. For the determination of molecular weights, Raoult's law is applicable only to

(a) dilute solutions of electrolytes
(b) concentrated solutions of electrolytes
(c) dilute solutions of non-electrolytes
(d) concentrated solutions of non-electrolytes

29. Vapour pressure of CCl_4 at 25°C is 143 mm of Hg and 0.5 g of a non-volatile solute (mol. wt. = 65) is dissolved in 100 mL CCl_4. Find the vapour pressure of the solution. (Density of $CCl_4 = 1.58 \text{ g / cm}^3$).

(a) 94.39 mm
(b) 141.93 mm
(c) 134.44 mm
(d) 199.34 mm

30. The vapour pressure of pure liquids A and B are 450 and 700 mm Hg respectively, at 350 K. If total vapour pressure is 600 mm Hg, find the composition of B in vapour phase. **[NCERT]**

(a) 0.30 (b) 0.40 (c) 0.60 (d) 0.70

31. 100 g of liquid A (molar mass 140 g mol^{-1}) was dissolved in 1000 g of liquid B (molar mass 180 g mol^{-1}). The vapour pressure of pure liquid B was found to be 500 torr. Calculate the vapour pressure of pure liquid A and its vapour pressure in the solution if the total vapour pressure of the solution is 475 torr. **[NCERT]**

(a) 500, 450
(b) 280, 500
(c) 280, 32
(d) 500, 280

32. The vapour pressure of two liquids P and Q are 80 and 60 Torr, respectively. The total vapour pressure of solution obtained by mixing 3 moles of P and 2 moles of Q would be

(a) 140 Torr
(b) 20 Torr
(c) 68 Torr
(d) 72 Torr

Colligative Properties

33. Which of the following is a colligative property?

(a) Boiling point
(b) Freezing point
(c) Osmotic pressure
(d) Vapour pressure

34. Lowering of vapour pressure is highest for

(a) 0.1 M $BaCl_2$
(b) 0.1 M glucose
(c) 0.1 M $MgSO_4$
(d) Urea

35. Which one of the statements given below concerning properties of solutions, describes a colligative effect?

(a) Vapour pressure of pure water decreases by the addition of nitric acid
(b) Boiling point of pure water decreases by the addition of ethanol
(c) Boiling point of pure benzene increases by the addition of toluene
(d) Vapour pressure of pure benzene decreases by the addition of naphthalene

36. The vapour pressure of water at 20°C is 17.54 mm. When 20 g of a non-ionic substance is dissolved in 100 g of water, the vapour pressure is lowered by 0.30 mm. What is the molecular mass of the substance?

(a) 200.8
(b) 206.88
(c) 210.5
(d) 215.2

37. Vapour pressure of pure water at 298 K is 23.8 mm Hg. 50 g urea (NH_2CONH_2) is dissolved in 850 g of water. Calculate the relative lowering of vapour pressure. **[NCERT]**

(a) 0.017 (b) 0.023 (c) 0.089 (d) 0.012

38. Vapour pressure of water at 293 K is 17.535 mm Hg. Calculate the vapour pressure of water at 293 K when 25 g of glucose is dissolved in 450 g of water. **[NCERT]**

(a) 17.43 mm Hg
(b) 18.93 mm Hg
(c) 20.12 mm Hg
(d) 25.31 mm Hg

39. The unit of ebullioscopic constant is **[NCERT Exemplar]**

(a) K kg mol^{-1} or K (molality)^{-1}
(b) mol kg K^{-1} or K^{-1} (molality)
(c) $\text{kg mol}^{-1} \text{K}^{-1}$ or $\text{K}^{-1} \text{(molality)}^{-1}$
(d) K mol kg^{-1} or K (molality)

40. If the elevation in boiling point of a solution of 10 g of solute (mol. wt. = 100) in 100 g of water is ΔT_b, the ebullioscopic constant of water is

(a) 10
(b) $100T_b$
(c) ΔT_b
(d) $\frac{\Delta T_b}{10}$

41. Boiling point of water at 750 mm Hg is 99.63°C. How much sucrose is to be added to 500 g of water such that it boils at 100° C. [k_b for water is $0.52 \text{ K kg mol}^{-1}$] **[NCERT]**

(a) 121 g (b) 150 g (c) 180 g (d) 300 g

42. When 10 g of a non-volatile solute is dissolved in 100 g of benzene, it raises boiling point by 1°C then molecular mass of the solute is (k_b for $C_6H_6 = 2.53 \text{ K kg-mol}^{-1}$)

(a) 223 g (b) 233 g (c) 243 g (d) 253 g

43. If 0.15 g of a solute dissolved in 15 g of solvent is boiled at a temperature higher by 0.216°C than that of the pure solvent, the molecular weight of the substance is (molal elevation constant for the solvent is 2.16°C)

(a) 100 (b) 102 (c) 104 (d) 1.02

44. The molar freezing point constant for water is $1.86^\circ \text{C mol}^{-1}$. If 342 g of cane sugar ($C_{12}H_{22}O_{11}$) is dissolved in 1000 g of water, the solution will freeze at

(a) -1.86°C (b) -2.86°C
(c) $+1.86^\circ$C (d) $+2.86^\circ$C

45. The amount of ice that will separate out on cooling a solute containing 50 g of ethylene glycol in 200 g water to –9.3°C will be ($k_g = 1.86 \text{ K kg mol}^{-1}$)

(a) 8.37 g (b) 161.3 g
(c) 3.87 g (d) 38.7 g

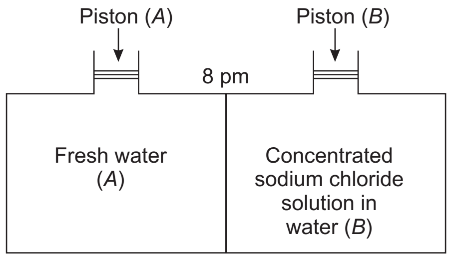
46. The molecular weight of NaCl determined by studying freezing point depression of its 0.5% aqueous solution is 30. The apparent degree of dissociation of NaCl is

(a) 0.60 (b) 0.50
(c) 0.30 (d) 0.95

47. Which of the following statements is false?
[NCERT Exemplar**]**

(a) Units of atmospheric pressure and osmotic pressure are the same
(b) In reverse osmosis, solvent molecules move through a semipermeable membrane from a region of lower concentration of solute to a region of higher concentration
(c) The value of molal depression constant depends on nature of solvent
(d) Relative lowering of vapour pressure is a dimensionless quantity

48. Consider the figure and mark the correct option.



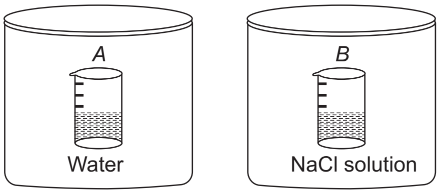
[NCERT Exemplar**]**

(a) Water will move from side (*A*) to side (*B*) if a pressure lower than osmotic pressure is applied on piston (*B*)
(b) water will move from side (*B*) to side (*A*) if a pressure greater than osmotic pressure is applied on piston (*B*)
(c) Water will move from side (*B*) to side (*A*) if a pressure equal to osmotic pressure is applied on piston (*B*)
(d) Water will move from side (*A*) to side (*B*) if pressure equal to osmotic pressure is applied on piston (*A*)

49. An unripe mango placed in a concentrated salt solution to prepare pickle, shrivels because
[NCERT Exemplar**]**

(a) it gains water due to osmosis
(b) it loses water due to reverse osmosis
(c) it gains water due to reverse osmosis
(d) it loses water due to osmosis

50. Two beakers of capacity 500 mL were taken. One of these beakers, labelled as "*A*", was filled with 400 mL water whereas the beaker labelled "*B*" was filled with 400 mL of 2 M solution of NaCl. At the same temperature both the beakers were placed in closed containers of same material and same capacity as shown in the figure. **[NCERT** Exemplar**]**



At a given temperature, which of the following statement is correct about the vapour pressure of pure water and that of NaCl solution.

(a) Vapour pressure in container (*A*) is more than that in container (*B*)
(b) Vapour pressure in container (*A*) is less than that in container (*B*)
(c) Vapour pressure is equal in both the containers
(d) Vapour pressure in container (*B*) is twice the vapour pressure in container (*A*)

51. Which of the following associated with isotonic solutions is not correct?

(a) They will have the same osmotic pressure
(b) They will have the same vapour pressure
(c) They have same weight concentrations
(d) Osmosis does not take place when the two solutions are separated by a semipermeable membrane

52. Calculate the osmotic pressure in pascals exerted by a solution prepared by dissolving 1.0 g of polymer of molar mass 185000 in 450 mL of water at 37°C.
[NCERT]

(a) 10.9 (b) 35.8
(c) 20.5 (d) 30.9

53. The relationship between osmotic pressure at 273 K when 10 g glucose (p_1), 10 g urea (p_2) and 10 g sucrose (p_3) are dissolved in 250 mL of water is
(a) $p_1 > p_2 > p_3$ (b) $p_3 > p_2 > p_1$
(c) $p_2 > p_1 > p_3$ (d) $p_2 > p_3 > p_1$

54. A 6% solution of urea is isotonic with
(a) 1 M solution of glucose
(b) 0.05 M solution of glucose
(c) 6% solution of glucose
(d) 25% solution of glucose

55. The osmotic pressure of a 5% (wt./vol) solution of cane sugar at 150°C is
(a) 3.078 atm (b) 4.078 atm
(c) 5.078 atm (d) 2.45 atm

56. A 5% solution of sugar cane (mol. wt. = 342) is isotonic with 1% solution of X under similar conditions. The molecular weight of X is
(a) 136.2 (b) 68.4
(c) 34.2 (d) 171.2

57. At 300 K, 36 g of glucose present in a litre of its solution has an osmotic pressure of 4.98 bar. If the osmotic pressure of the solution is 1.52 bar at the same temperature, what would be its concentration? **[NCERT]**
(a) 0.02 (b) 0.04 (c) 0.08 (d) 0.06

58. Which of the following units is useful in relating concentration of solution with its vapour pressure? **[NCERT Exemplar]**
(a) Mole fraction (b) Parts per million
(c) Mass percentage (d) Molality

Abnormal Colligative Properties : van't Hoff Factor

59. We have three aqueous solutions of NaCl labelled as '*A*', '*B*' and '*C*' with concentrations 0.1 M, 0.01 M and 0.001 M, respectively. The value of van't Hoff factor for these solutions will be in the order **[NCERT Exemplar]**
(a) $i_A < i_B < i_C$ (b) $i_A > i_B > i_C$
(c) $i_A = i_B = i_C$ (d) $i_A < i_B > i_C$

60. Which of the following solution in water possesses the lowest vapour pressure?
(a) 0.1 (N) $BaCl_2$ (b) 0.1 (M) NaCl
(c) 0.1 (M) KCl (d) None of these

61. Which of the following aqueous solutions should have the highest boiling point? **[NCERT Exemplar]**
(a) 1.0 M NaOH (b) 1.0 M Na_2SO_4
(c) 1.0 M NH_4NO_3 (d) 1.0 M KNO_3

62. Which has minimum osmotic pressure?
(a) 200 mL of 2 M NaCl solution
(b) 200 mL of 1 M glucose solution
(c) 200 mL of 2 M urea solution
(d) All have same osmotic pressure

63. Two solutions of KNO_3 and CH_3COOH are prepared separately. Molarity of both is 0.1 M and osmotic pressures are p_1 and p_2 respectively. The correct relationship between the osmotic pressures is
(a) $p_1 = p_2$ (b) $p_1 > p_2$
(c) $p_2 > p_1$ (d) $\frac{p_1}{p_1 + p_2} + \frac{p_2}{p_1 + p_2}$

64. When 20 g of naphthoic acid ($C_{11}H_8O_2$) is dissolved in 50 g of benzene (k_f = 1.72 K kg mol^{-1}), a freezing point depression of 2 K is observed. The van't Hoff factor (i) is
(a) 0.5 (b) 1 (c) 2 (d) 13

65. The freezing point depression of 0.001 m, $K_x[Fe(CN)_6]$ is 7.10×10^{-3} K. If for water, k_f is 1.86 K kg mol^{-1}, value of x will be
(a) 4 (b) 3 (c) 2 (d) 1

66. The elevation in boiling point of a solution of 13.44 g of $CuCl_2$ in 1 kg of water using the following information will be (molecular weight of $CuCl_2$ = 134.4 and k_b = 0.52 K $molal^{-1}$)
(a) 0.16 (b) 0.05 (c) 0.1 (d) 0.2

67. What is the freezing point of a solution containing 8.1 g HBr in 100 g water assuming the acid to be 90% ionised (k_f for water = 1.86 kg mol^{-1})?
(a) −0.35°C (b) −1.35°C
(c) −2.35°C (d) −3.53°C

68. Determine the amount of $CaCl_2$ (i = 2.47) dissolved in 2.5 L of water such that its osmotic pressure is 0.75 atm at 27°C. **[NCERT]**
(a) 1.82 g (b) 3.42 g (c) 2.98 g (d) 1.45 g

69. Determine the osmotic pressure of a solution prepared by dissolving 25 mg of K_2SO_4 in 2 L of water at 25°C, assuming that it is completely dissociated. **[NCERT]**
(a) 2.39×10^{-2} atm (b) 4.29×10^{-3} atm
(c) 5.27×10^{-3} atm (d) 1.39×10^{-4} atm

70. 19.5 g of CH_2FCOOH is dissolved in 500 g of water. The depression in the freezing point of water observed is 1.0°C. Calculate the degree of dissociation and dissociation constant of fluoroacetic acid. K_f = 1.86 K kg mol^{-1} **[NCERT]**
(a) 0.07 and 3.07×10^{-3} (b) 0.04 and 3.07×10^{-3}
(c) 0.082 and 4.23×10^{-4} (d) 0.07 and 4.23×10^{-4}

Round II (Mixed Bag)

Only One Correct Option

1. The air is a mixture of a number of gases. The major components are oxygen and nitrogen with approximate proportion of 20% and 79% by volume at 298 K. The water is in equilibrium with air at a pressure of 10 atm. At 298 K if the Henry's law constants for oxygen and nitrogen at 298 K are 3.30×10^7 mm and 6.51×10^7 mm respectively, the composition of O_2 and N_2 gases in water respectively are **[NCERT]**

(a) $4.6 \times 10^{-5}, 9.22 \times 10^{-5}$

(b) $9.22 \times 10^{-5}, 4.6 \times 10^{-5}$

(c) $4.6 \times 10^{-5}, 4.12 \times 10^{-5}$

(d) $4.12 \times 10^{-5}, 4.6 \times 10^{-5}$

2. Henry's law constant for CO_2 in water is 1.67×10^8 Pa at 298 K. Calculate the quantity of CO_2 in 500 mL of soda water when packed under 2.5 atm CO_2 pressure at 298 K. **[NCERT]**

(a) 2.82 g (b) 1.85 g

(c) 9.62 g (d) 11.2 g

3. Nalorphene ($C_{19}H_{21}NO_3$), similar to morphine, is used to combat withdrawal symptoms in narcotic users. Dose of nalorphene generally given is 1.5 mg. Calculate the mass of 1.5×10^{-3} m aqueous solution required for the above dose. **[NCERT]**

(a) 3.2×10^{-2} kg (b) 3.2×10^{-4} kg

(c) 3.2×10^{-3} kg (d) 3.2×10^{-5} kg

4. A solution is obtained by mixing 300 g of 25% solution and 400 g of 40% solution by mass. Calculate the mass percentage of solute in the resulting solution. **[NCERT]**

(a) 33.57 (b) 66.43

(c) 87.23 (d) 19.24

5. The molarity of pure water is

(a) 55.6 (b) 5.56

(c) 6.55 (d) 65.5

6. On the basis of information given below mark the correct option.

Information

(A) In bromoethane and chloroethane mixture intermolecular interactions of *A*—*A* and *B*—*B* type are nearly same as *A*—*B* type interactions.

(B) In ethanol and acetone mixture *A*—*A* or *B*—*B* type intermolecular interactions are stronger than *A*—
B type interactions.

(C) In chloroform and acetone mixture *A*—*A* or *B*—*B* type intermolecular interactions are weaker than *A*—*B* type interactions. **[NCERT Exemplar]**

(a) Solution (B) and (C) will follow Raoult's law

(b) Solution (A) will follow Raoult's law

(c) Solution (B) will show negative deviation from Raoult's law

(d) Solution (C) will show positive deviation from Raoult's law

7. When mercuric iodide is added to the aqueous solution of potassium iodide, the

(a) freezing point is raised

(b) freezing point is lowered

(c) freezing point does not change

(d) boiling point does not change

8. Which of the following aqueous solutions produce the same osmotic pressure?

(i) 0.1 M NaCl solution

(ii) 0.1 M glucose solution

(iii) 0.6 g urea in 100 mL solution

(iv) 1.0 g of a non-electrolyte solute (*X*) in 50 mL solution (molar mass of $X = 200$)

(a) (i), (ii), (iii) (b) (ii), (iii), (iv)

(c) (i), (ii), (iv) (d) (i), (iii), (iv)

9. A 0.025 M solution of monobasic acid had a freezing point of –0.060°C. The pK_a for the acid is ($k_b = 1.86 \text{ K kg mol}^{-1}$)

(a) 1.2 (b) 2 (c) 2.5 (d) 5.7

10. How many gram of sucrose (mol. wt. = 342) should be dissolved in 100 g water in order to produce a solution with a 105.0°C difference between the freezing point and boiling temperature? ($k_f = 1.860°\text{C / m}, k_b = 0.151°\text{C/m}$)

(a) 34.2 g (b) 72 g

(c) 342 g (d) 460 g

11. The vapour pressure of water is 12.3 kPa at 300 K. Calculate the vapour pressure of 1 molal solution of a non-volatile solute in it. **[NCERT]**

(a) 12 kPa (b) 10 kPa

(c) 15 kPa (d) 13 kPa

12. A 5% solution (by mass) of cane sugar in water has freezing point 271 K. Calculate the freezing point of 5% glucose in water if freezing point of pure water is 273.15 K. **[NCERT]**

(a) 250 K
(b) 269 K
(c) 310 K
(d) 275 K

13. Benzene and naphthalene form ideal solution over the entire range of composition. The vapour pressure of pure benzene and naphthalene at 300 K are 50.71 mm Hg and 32.06 mm Hg respectively. Calculate the mole fraction of benzene in vapour phase if 80 g of benzene is mixed with 100 g of naphthalene. **[NCERT]**

(a) 0.67
(b) 0.32
(c) 0.85
(d) 0.42

14. A certain substance '*A*' tetramerises in water to the extent of 80%. A solution of 2.5 g of *A* in 100 g of water lowers the freezing point by 0.3°C. The molar mass of *A* is

(a) 31
(b) 62
(c) 122
(d) 244

15. Two solutions of glucose have osmotic pressure 1.0 and 3.5 atm. If 1 L of first solution is mixed with *V* L of second solution, the osmotic pressure of the resultant solution becomes 2.5 atm. Volume of second solution is

(a) 1.0 L
(b) 1.5 L
(c) 2.5 L
(d) 3.5 L

16. A solution containing 30 g of non-volatile solute exactly in 90 g of water has a vapour pressure of 2.8 kPa at 298 K. Further, 18 g of water is then added to the solution and the new vapour pressure becomes 2.9 kPa at 298 K. Calculate the vapour pressure of water at 298 K. **[NCERT]**

(a) 3.5 kPa
(b) 8.2 kPa
(c) 4.2 kPa
(d) 1.9 kPa

17. Two elements *A* and *B* form compounds having formula AB_2 and AB_4. When dissolved in 20 g of benzene (C_6H_6), 1 g AB_2 lowers the freezing point by 2.3 K whereas 1.0 g of AB_4 lowers it by 1.3 K. The molal depression constant for benzene is 5.1 K kg mol^{-1}. The atomic masses of *A* and *B* are respectively. **[NCERT]**

(a) 25.6, 42.9
(b) 30.9, 50.2
(c) 42.64, 25.6
(d) 42.5, 25.6

18. Calculate the depression in the freezing point of water when 10 g of $CH_3CH_2CHClCOOH$ is added to 250 g of water. $K_a = 1.4 \times 10^{-3}$; $K_f = 1.86$ K kg mol^{-1}. **[NCERT]**

(a) 0.42 K
(b) 0.82 K
(c) 0.19 K
(d) 0.65 K

More than One Correct Option

19. Which of the following factor(s) affect the solubility of a gaseous solute in the fixed volume of liquid solvent? **[NCERT Exemplar]**

(i) nature of solute (ii) temperature (iii) pressure
(a) (i) and (iiii) at constant *T*
(b) (i) and (ii) at constant *p*
(c) (ii) and (iii) only
(d) (iii) only

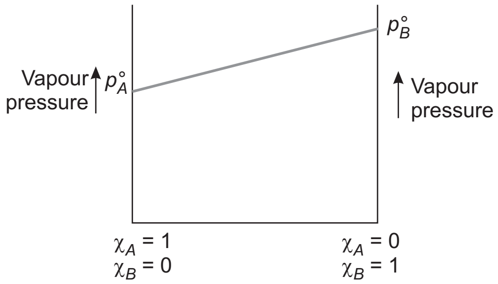
20. Which of the following is/are not affected by temperature?

(a) Molarity
(b) Molality
(c) Normality
(d) Mole fraction

21. Isotonic solutions must have the same **[NCERT Exemplar]**

(a) solute
(b) density
(c) elevation in boiling point
(d) depression in freezing point

22. The following is a graph plotted between the vapour pressure of two volatile liquids against their respective mode fractions.



Which of the following statement is/are correct?

(a) When $\chi_A = 1$ and $\chi_B = 0$, then $p = p_A^\circ$.
(b) When $\chi_B = 1$ and $\chi_A = 0$, then $p = p_B^\circ$.
(c) When $\chi_A = 1$ and $\chi_B = 0$, then $p < p_B^\circ$.
(d) When $\chi_B = 1$ and $\chi_A = 0$, then $p > p_A^\circ$.

23. Molecular weight of urea is 60. A solution of urea containing 6 g of urea in 1 L is a

(a) 1 N
(b) 0.1 M
(c) 0.1 N
(d) 1 M

Assertion and Reason

Directions (Q. Nos. 24 to 28) *Each of these questions contains two statements : Statement* I (*Assertion*) *and Statement* II (*Reason*). *Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes* (*a*), (*b*), (*c*), (*d*) *given below*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

24. **Statement I** Molarity of a solution in liquid state changes with temperature.

Statement II The volume of a solution changes with change in temperature. **[NCERT Exemplar]**

25. **Statement I** ΔH_{mix} and ΔV_{mix} in an ideal solution are zero.

Statement II $A - B$ interactions in ideal solutions are same as between $A - B$ and $B - B$.

26. **Statement I** When NaCl is added to water a depression in freezing point is observed.

Statement II The lowering of vapour pressure of a a solution causes depression in the freezing point. **[NCERT Exemplar]**

27. **Statement I** One molar aqueous solution has always higher concentration than one molal.

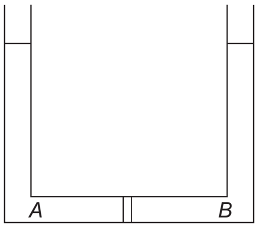
Statement II The molality of a solution depends upon the density of the solution whereas molarity does not.

28. **Statement I** The difference in the boiling points of equimolar solution of HCl and HF decreases as their molarity is decreased.

Statement II The extent of dissociation decreases steadily with increasing dilution.

Comprehension Based Questions

Directions (Q.Nos. 29 to 31)



Compartments A and B have the following combinations solution :

	A	B
1.	0.1 M KCl	0.2 M KCl
2.	0.1% (m/V) NaCl	10% (m/V) NaCl
3.	18 gL^{-1} glucose	34.2 gL^{-1} sucrose
4.	20% (m/V) glucose	10% (m/V) glucose

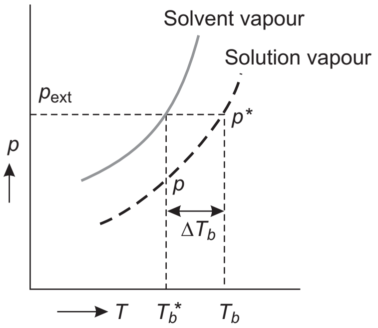
Answer the following questions

29. Indicate the number of solutions which is/are isotonic
(a) 1 only (b) 3 only
(c) 4 only (d) 2 only

30. The solutions in which compartment B is hypertonic.
(a) 1, 2 (b) 2, 3 (c) 3, 4 (d) 1, 4

31. Indicate the solution(s) in which compartment B will show an increase in volume.
(a) 1, 2, 4 (b) 1, 2 (c) 2, 3 (d) 3, 4

Directions (Q. Nos. 32 to 34) The variation of vapour pressure of the solvent and that of the solution with temperature are given by the respective solvent-vapour and solution-vapour curves of the phase diagram.

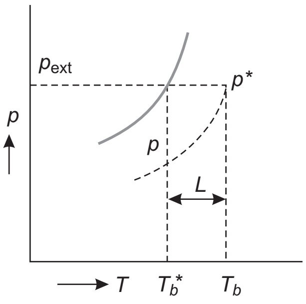


For a given value of the external pressure, the pure solvent will boil at temperature T_b^* and at temperature T_b let p_{ext} be equal to p^*, the vapour pressure of pure solvent.

Applying the Clausius-Clapeyron equation to the solution vapour equilibrium for the two values of p, T_b^* and p^*, T_b we have

$$\ln \frac{p^*}{p} = \frac{\Delta_{vap} H_{1m}}{R}\left(\frac{1}{T_b^*} - \frac{1}{T_b}\right) = \frac{\Delta_{vap} H_{1m}}{R}\,\frac{\Delta T_b}{T_b^* T_b}$$

32. The phase diagram for the pure solvent and solution are recorded below. The quantity indicated by L in the figure is



(a) Δp
(b) $k_b \cdot m$
(c) $k_f m$
(d) m

33. The vapour pressure of pure benzene and toluene are 160 and 60 torr respectively. The mole fraction of toluene in vapour phase in contact with equimolar solution of benzene and toluene is

(a) 0.50 (b) 0.93
(c) 0.6 (d) 0.27

34. At certain hill-station, pure water boils at 99.725°C. If K_b for water is 0.513°C kg mol^{-1}, the boiling point of 0.69 m solution of urea will be

(a) 100.359°C (b) 103°C
(c) 100.073°C (d) unpredictable

Previous Years' Questions

35. The density of a solution prepared by dissolving 120 g of urea (mol. mass = 60 u) in 1000 g of water is 1.15 g/mL. The molarity of this solution is **[AIEEE 2012]**

(a) 0.50 M (b) 1.78 M
(c) 1.02 M (d) 2.05 M

36. K_f water is 1.86 K kg mol^{-1}. If your automobiles radiator holds 1.0 kg of water, how many grams of ethylene glycol ($C_2H_6O_2$) must you add to get the freezing point of the solution lowered to –2.8°C? **[AIEEE 2012]**

(a) 72 g (b) 93 g
(c) 39 g (d) 27 g

37. A 5.2 molal aqueous solution of methyl alcohol, CH_3OH, is supplied. What is the mole fraction of methyl alcohol in the solution ? **[AIEEE 2011]**

(a) 0.100 (b) 0.190
(c) 0.086 (d) 0.050

38. Ethylene glycol is used as an antifreeze in a cold climate. Mass of ethylene glycol which should be added to 4 kg of water to prevent it from freezing at – 6° C will be (k_f for water = 1.86 K kg mol^{-1} and molar mass of ethylene glycol = 62 g mol^{-1}) **[AIEEE 2011]**

(a) 804.32 g (b) 204.30 g
(c) 400.00 g (d) 304.60 g

39. The degree of dissociation (α) of a weak electrolyte, A_xB_y is related to van't Hoff factor (i) by the expression **[AIEEE 2011]**

(a) $\alpha = \dfrac{i-1}{(x+y-1)}$ (b) $\alpha = \dfrac{i-1}{x+y+1}$
(c) $\alpha = \dfrac{x+y-1}{i-1}$ (d) $\alpha = \dfrac{x+y+1}{i-1}$

40. A 5% solution of cane sugar (molar mass 342) is isotonic with 1% of a solution of an unknown solute. The molar mass of unknown solute in g/mol is **[AIEEE 2011]**

(a) 136.2 (b) 171.2
(c) 68.4 (d) 34.2

41. If sodium sulphate is considered to be completely dissociated into cations and anions in aqueous solution, the change in freezing point of water (ΔT_f), when 0.01 mole of sodium sulphate is dissolved in 1 kg of water, is (k_f = 1.86 K kg mol^{-1}) **[AIEEE 2010]**

(a) 0.0372 K (b) 0.0558 K
(c) 0.0744 K (d) 0.0186 K

42. On mixing, heptane and octane form an ideal solution. At 373 K, the vapour pressures of the two liquid components (heptane and octane) are 105 kPa and 45 kPa respectively. Vapour pressure of the solution obtained by mixing 25 g of heptane and 35 g of octane will be (molar mass of heptane = 100 g mol^{-1} and of octane = 114 g mol^{-1}). **[AIEEE 2010]**

(a) 72.0 kPa (b) 36.1 kPa
(c) 96.2 kPa (d) 144.5 kPa

43. Two liquids X and Y form an ideal solution at 300 K, vapour pressure of the solution containing 1 mole of X and 3 moles of Y is 550 mm Hg. At the same temperature, if 1 mole of Y is further added to this solution, vapour pressure of the solution increases by 10 mm Hg. Vapour pressure (in mm Hg) of X and Y in their pure states will be, respectively **[AIEEE 2009]**

(a) 200 and 300 (b) 300 and 400
(c) 400 and 600 (d) 500 and 600

44. A binary liquid solution is prepared by mixing n-heptane and ethanol. Which one of the following statements is correct regarding the behaviour of the solution?

(a) The solution formed is an ideal solution
(b) The solution is non-ideal showing positive deviation from Raoult's law
(c) The solution is non-ideal showing negative deviation from Raoult's law
(d) n-heptane shows positive deviation while ethanol show negative deviation from Raoult's law

45. At 80°C, the vapour pressure of pure liquid 'A' is 520 mm Hg and that of pure liquid 'B' is 1000 mm Hg. If a mixture solution of 'A' and 'B' boils at 80°C and 1 atm pressure, the amount of 'A' in the mixture is (1 atm = 760 mmHg) **[AIEEE 2008]**

(a) 52 mol per cent (b) 34 mol per cent
(c) 48 mol per cent (d) 50 mol per cent

46. The vapour pressure of water at 20°C is 17.5 mm Hg. If 18 g of glucose ($C_6H_{12}O_6$) is added to 178.2 g of water at 20°C, the vapour pressure of the resulting solution will be [AIEEE 2008]

(a) 17.675 mm Hg (b) 15.750 mm Hg
(c) 16.500 mm Hg (d) 17.325 mm Hg

47. A mixture of ethyl alcohol and propyl alcohol has a vapour pressure of 290 mm at 300 K. The vapour pressure of propyl alcohol is 200 mm. If the mole fraction of ethyl alcohol is 0.6, its vapour pressure (in mm) at the same temperature will be [AIEEE 2007]

(a) 350 (b) 300
(c) 700 (d) 360

48. A 5.25% solution of a substance is isotonic with a 1.5% solution of urea (molar mass = 60 g mol^{-1}) in the same solvent. If the densities of both the solutions are assumed to be equal to 1.0 g cm^{-3}, molar mass of the substance will be [AIEEE 2007]

(a) 90.0 g mol^{-1} (b) 115.0 g mol^{-1}
(c) 105.0 g mol^{-1} (d) 210.0 g mol^{-1}

49. Density of a 2.05 M solution of acetic acid in water is 1.02 g/mL. The molality of the solution is [AIEEE 2006]

(a) 1.14 mol kg^{-1} (b) 3.28 mol kg^{-1}
(c) 2.28 mol kg^{-1} (d) 0.44 mol kg^{-1}

50. Two solutions of a substance (non-electrolyte) are mixed in the following manner.
480 mL of 1.5 M first solution + 520 mL of 1.2 M second solution.
What is the molarity of the final mixture ? [AIEEE 2005]

(a) 2.70 M (b) 1.34 M
(c) 1.50 M (d) 1.20 M

51. Benzene and toluene form nearly ideal solutions. At 20°C, the vapour pressure of benzene is 75 Torr and that of toluene is 22 Torr. The partial vapour pressure of benzene at 20°C for a solution containing 78 g of benzene and 46 g of toluene in Torr is [AIEEE 2005]

(a) 53.5 (b) 37.5
(c) 25 (d) 50

52. To neutralise completely 20 mL of 0.1 M aqueous solution of phosphorous acid (H_3PO_3), the volume of 0.1 M aqueous KOH solution required is [AIEEE 2004]

(a) 10 mL (b) 20 mL
(c) 40 mL (d) 60 mL

53. Which of the following liquid pairs shows a positive deviation from Raoult's law ? [AIEEE 2004]

(a) Water — hydrochloric acid
(b) Benzene — methanol
(c) Water — nitric acid
(d) Acetone — chloroform

54. Which one of the following statements is false ? [AIEEE 2004]

(a) Raoult's law states that the vapour pressure of a component over a solution is proportional to its mole fraction
(b) The osmotic pressure (π) of a solution is given by the equation $\pi = MRT$, where M is the molarity of the solution
(c) The correct order of osmotic pressure for 0.01 M aqueous solution of each compound is $BaCl_2 > KCl > CH_3COOH >$ sucrose
(d) Two sucrose solutions of same molality prepared in different solvents will have the same freezing point depression

55. 25 mL of a solution of barium hydroxide on titration with 0.1 molar solution of hydrochloric acid gave a titre value of 35 mL. The molarity of barium hydroxide solution was [AIEEE 2003]

(a) 0.07 (b) 0.14 (c) 0.28 (d) 0.35

56. A pressure cooker reduces cooking time for food because [AIEEE 2003]

(a) heat is more evenly distributed in the cooking space
(b) boiling point of water involved in cooking is increased
(c) the higher pressure inside the cooker crushes the food material
(d) cooking involves chemical changes helped by a rise in temperature

57. In a 0.2 molal aqueous solution of a weak acid HX, the degree of ionisation is 0.3. Taking k_f for water as 1.85, the freezing point of the solution will be nearest to [AIEEE 2003]

(a) $-0.480°$ C (b) $-0.360°$ C
(c) $-0.260°$ C (d) $+0.480°$ C

58. In a mixture of A and B, components show negative deviation when [AIEEE 2002]

(a) $A—B$ interaction is stronger than $A—A$ and $B—B$ interaction
(b) $A—B$ interaction is weaker than $A—A$ and $B—B$ interaction
(c) $\Delta V_{mix} > 0, \Delta S_{mix} > 0$
(d) $\Delta V_{mix} = 0, \Delta S_{mix} > 0$

Answers

Round I

1. (b)	**2.** (a)	**3.** (b)	**4.** (c)	**5.** (a)	**6.** (c)	**7.** (b)	**8.** (d)	**9.** (b)	**10.** (b)
11. (b)	**12.** (a)	**13.** (c)	**14.** (c)	**15.** (c)	**16.** (d)	**17.** (a)	**18.** (a)	**19.** (d)	**20.** (a)
21. (c)	**22.** (a)	**23.** (d)	**24.** (a)	**25.** (c)	**26.** (a)	**27.** (c)	**28.** (c)	**29.** (b)	**30.** (d)
31. (c)	**32.** (d)	**33.** (c)	**34.** (a)	**35.** (a)	**36.** (c)	**37.** (a)	**38.** (a)	**39.** (a)	**40.** (c)
41. (a)	**42.** (d)	**43.** (a)	**44.** (a)	**45.** (d)	**46.** (d)	**47.** (b)	**48.** (b)	**49.** (d)	**50.** (a)
51. (c)	**52.** (d)	**53.** (c)	**54.** (a)	**55.** (c)	**56.** (b)	**57.** (d)	**58.** (a)	**59.** (c)	**60.** (a)
61. (b)	**62.** (b)	**63.** (b)	**64.** (a)	**65.** (b)	**66.** (a)	**67.** (d)	**68.** (b)	**69.** (c)	**70.** (a)

Round II

1. (a)	**2.** (b)	**3.** (c)	**4.** (a)	**5.** (a)	**6.** (b)	**7.** (a)	**8.** (b)	**9.** (c)	**10.** (b)
11. (a)	**12.** (b)	**13.** (a)	**14.** (b)	**15.** (b)	**16.** (a)	**17.** (b)	**18.** (d)	**19.** (b)	**20.** (b,d)
21. (b,c)	**22.** (a,b)	**23.** (b,c)	**24.** (a)	**25.** (a)	**26.** (a)	**27.** (b)	**28.** (c)	**29.** (b)	**30.** (a)
31. (b)	**32.** (b)	**33.** (d)	**34.** (c)	**35.** (d)	**36.** (b)	**37.** (c)	**38.** (a)	**39.** (a)	**40.** (c)
41. (b)	**42.** (a)	**43.** (c)	**44.** (b)	**45.** (d)	**46.** (d)	**47.** (a)	**48.** (d)	**49.** (c)	**50.** (b)
51. (d)	**52.** (c)	**53.** (b)	**54.** (d)	**55.** (a)	**56.** (b)	**57.** (a)	**58.** (a)		

the Guidance

Round I

1. Precipitation occurs when the solution is supersaturated.

2. Value of Henry's constant K_H increases with increase in temperature.

3. At high altitudes, atmospheric pressure is low and solubility of gases varies directly with pressure thus, decreases at high altitudes.

This is the reason for low concentration of oxygen in blood and tissues of people living at high altitude.

4. The order of increasing solubility are

$$\text{Ar} < \text{CO}_2 < \text{CH}_4 < \text{HCHO}$$

(As solubility increases as the values of K_H decreases)

5. Mass of aspirin $= 6.5$ g

Mass of acetonitrile $= 450$ g

$$\text{Mass of solution} = (6.5 + 450)\text{ g} = 456.5\text{ g}$$

$$\text{Mass \%} = \frac{(6.5\text{ g})}{(456.5\text{ g})} \times 100 = 1.424\%$$

6. Percentage (%) by mass of $CHCl_3$

$$= \frac{\text{mass of CHCl}_3}{\text{mass of solution}} \times 100$$

$$= \frac{(15.0\text{ g})}{(10^6\text{ g})} \times 100 = 1.5 \times 10^{-3}\%$$

7. $K_H = 4.27 \times 10^5$ mm Hg (at 298 K)

$$p = 760\text{ mm}$$

Applying Henry's law

$$p = K_H\,\chi \; [\chi = \text{Mole fraction or solubility of methane}]$$

$$x = \frac{p}{K_H} = \frac{(760\text{ mm})}{(4.27 \times 10^5\text{ mm})} = 178 \times 10^{-5} = 1.78 \times 10^{-3}$$

8.
$$M_1V_1 = M_2V_2$$
$$0.02 \times 4 = 5 \times M$$
$$M = 0.06$$

9. $$M = \frac{W}{\text{mol. wt.} \times \text{V}\,(L)} = \frac{5.85}{58.5 \times 0.5} = 0.2\text{ M}$$

10. Molarity $= 0.15$ M or 0.15 mol L^{-1}

Volume of solution $= 250$ mL $= 0.25$ L

$$\text{Molar mass of solute} = (12 \times 6) + (1 \times 5) + (12) + (16 \times 2) + (1)$$
$$= 122\text{ g mol}^{-1}$$

$$\text{Molarity} = \frac{\text{mass}}{\text{molar mass}} \times \frac{1}{\text{volume (L)}};$$

$$(0.15\text{ mol L}^{-1}) = \frac{W}{(122\text{ g mol}^{-1})} \times \frac{1}{(0.25\text{ L})}$$

$$\underset{\text{(Benzoic acid)}}{\text{Mass of solute}} = (0.15 \times 122 \times 0.25)\text{ g} = 4.575\text{ g}$$

11. Density of the solution $= 1.072 \text{ g mL}^{-1}$

$$\text{Mass of solution} = \text{Mass of solute} + \text{Mass of solution}$$
$$= 222.6 \text{ g} + 200 \text{ g} = 422.6 \text{ g}$$
$$\text{Volume} = \frac{\text{mass}}{\text{density}} = \frac{422.6 \text{ g}}{1.072 \text{ g mL}^{-1}} = 394.2 \text{ mL}$$
$$= 0.3942 \text{ L}$$
$$\text{Molarity } (M) = \frac{\text{mass of ethylene glycol/molar mass}}{\text{volume in litres}}$$
$$= \frac{(222.6 \text{ g})/(62 \text{ g mol}^{-1})}{0.3942 \text{ L}}$$
$$= 9.10 \text{ mol L}^{-1} = 9.10 \text{ M}$$

12. An increases in temperature increase the volume of the solution and thus, decreases its molarity.

13. $N = \dfrac{w \times 1000}{\text{eq. wt.} \times V \text{ (mL)}} = \dfrac{10 \times 1000}{60 \times 100} = 1.66 \text{ N}$

14. Molarity of base $= \dfrac{\text{normality}}{\text{acidity}}$

$$= \frac{0.1}{1} = 0.1$$
$$M_1V_1 = M_2V_2$$
$$0.1 \times 19.85 = M_2 \times 20$$
$$M_2 = 0.09925 \approx 0.099$$

16. Molarity $= \dfrac{\text{weight \% of solute} \times \text{density of the solution} \times 10}{\text{molecular weight of the solution}}$

$$= \frac{98 \times 1.84 \times 10}{98} = 18.4$$

17. Molality $= \dfrac{18}{180} = 0.1$ molal

18. $20 \times 0.4 = 40 \times N$ $\quad (\because N_1V_1 = N_2V_2)$

or $\quad N = 0.2$

$\therefore \quad M = \dfrac{0.2}{2} = 0.1 \text{ M}$

20. (a) 6 g of NaOH/100 mL

$$N = \frac{6 \times 1000}{40 \times 100} = 1.5 \text{ N}$$

(b) 0.5 M H_2SO_4

$$N = M \times \text{basicity} = 0.5 \times 2 = 1.0$$

(c) N phosphoric acid, normality $= 1$

(d) 8 g of KOH/L

$$\text{Normality} = \frac{\text{strength in g / L}}{\text{equivalent weight}} = \frac{8}{56} = 0.14 \text{ N}$$

21.
$$N_1V_1 + N_2V_2 = N_3V_3$$
$$0.3 \times 100 + 0.6 \times 200 = N_3 \times 300$$
$$0.3 + 1.2 = 3N_3$$
$$N_3 = 0.5$$

22. (i) Cyclohexane and *n*-octane both are non-polar. So, they mix completely in all proportions.

(ii) KCl is an ionic compound, but *n*-octane is non-polar. So, KCl does not dissolve in *n*-octane.

(iii) CH_3OH and CH_3CN both are polar but CH_3CN is less polar than CH_3OH. As the solvent is non-polar, CH_3CN will dissolve more than CH_3OH in *n*-octane.

Order of solubility is KCl < CH_3OH < CH_3CN < cyclohexane.

23. If two liquids *A* and *B* form minimum boiling azeotrope at some specific composition then *A* – *B* interactions are weaker than those between *A* – *A* or *B* – *B*.

25. For an ideal solution

$$\Delta H_{\text{solution}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

27. The one whose boiling point is more than that of either of the two pure components is known as azeotropic mixture with maximum boiling point. This is formed by non-ideal solutions showing negative deviation.

29. Relative lowering in vapour pressure,

$$\frac{p^\circ - p_s}{p^\circ} = \frac{w \times M}{m \times W}$$
$$\frac{143 - p_s}{143} = \frac{0.5}{65} \times \frac{154}{1.58 \times 100}$$

[$\because$ molecular weight of $CCl_4 = 154$ and weight = density × volume]

$$143 - p_s = 1.07 \Rightarrow p_s = 141.93 \text{ mm}$$

30. Vapour pressure of pure liquid *A* $(p_A^\circ) = 450$ mm

Vapour pressure of pure liquid *B* $(p_B^\circ) = 700$ mm

Total vapour pressure of the solution $(p) = 600$ mm

According to Raoult'a law,

$$p = p_A^\circ \chi_A + p_A^\circ \chi_B = p_A^\circ \chi_A + p_B^\circ (1 - \chi_A)$$
$$(600 \text{ mm}) = 450 \text{ mm} \times \chi_A + 700 \text{ mm} (1 - \chi_A)$$
$$= 700 \text{ mm} + \chi_A (450 - 700) \text{ mm}$$
$$= 700 - \chi_A (250 \text{ mm})$$
$$\chi_A = \frac{(600 - 700)}{-(250 \text{ mm})} = 0.40$$

Mole fraction of *A* $(\chi_A) = 0.40$

Mole fraction of *B* $(\chi_B) = 1 - 0.40 = 0.60$

$$p_A = p_A^\circ \chi_A = (450 \text{ mm}) \times 0.40 = 180 \text{ mm}$$
$$p_B = p_B^\circ \chi_B = (700 \text{ mm}) \times 0.60 = 420 \text{ mm}$$

Mole fraction of *A* in vapour phase

$$= \frac{p_A}{p_A + p_B}$$
$$= \frac{(180) \text{ mm}}{(180 + 420) \text{ mm}} = 0.30$$

Mole fraction of *B* in vapour phase

$$= \frac{p_B}{p_A + p_B} = \frac{(420) \text{ mm}}{(180 + 420) \text{ mm}} = 0.70$$

31. ***Step I* Calculation of vapour pressure of pure liquid** $A\,(p_A^\circ)$

Number of moles of liquid A

$$(n_A) = \frac{W_A}{M_A} = \frac{(100\text{ g})}{(140\text{ g mol}^{-1})} = 0.7143\text{ mol}$$

Number of moles of liquid B

$$(n_B) = \frac{W_B}{M_B} = \frac{(1000\text{ g})}{(180\text{ g mol}^{-1})} = 5.5556\text{ mol}$$

Mole fraction of A

$$(\chi_A) = \frac{n_A}{n_A + n_B} = \frac{(0.7143\text{ mol})}{(0.7143 + 5.5556)\text{ mol}}$$

$$= \frac{0.7143}{6.2699} = 0.1139$$

Mole fraction of $B\,(\chi_B) = 1 - 0.1139 = 0.8861$

Vapour pressure of pure liquid $B\,(p_B^\circ) = 500$ torr

Total vapour pressure of solution (p) = 475 torr

According to the Raoult's law

$$p = p_A^\circ \chi_A + p_B^\circ \chi_B$$

$$475\text{ torr} = p_A^\circ \times (0.1139) + 500\text{ torr} \times (0.8861)$$

$$475\text{ torr} = p_A^\circ \times (0.1139) + 443.05\text{ torr}$$

$$p_A^\circ = \frac{(475 - 443.05)\text{ torr}}{(0.1139)} = \frac{31.95}{0.1139}\text{ torr}$$

$$= 280.5\text{ torr}$$

***Step II* Calculation of vapour pressure of *A* in the solution** (p_A)

According to Raoult's law,

$$p_A = p_A^\circ \chi_A = (280.5\text{ torr}) \times (0.1139)$$

$$p_A = 32.0\text{ torr}$$

32. Mole fraction of $P = \frac{3}{3+2} = \frac{3}{5}$

Mole fraction of $Q = \frac{2}{3+2} = \frac{2}{5}$

Hence, total vapour pressure

= mole fraction of $P \times$ V.P. of P + mole fraction of $Q \times$ V.P. of Q

$$= \frac{3}{5} \times 80 + \frac{2}{5} \times 60 = 72\text{ Torr}$$

34. $\frac{p^\circ - p_s}{p^\circ}$ = molality $\times (1 - \alpha + x\alpha + y\alpha)$

The value of $p^\circ - p_s$ is maximum for $BaCl_2$.

35. Due to addition of nitric acid in water, the vapour pressure of pure water decreases.

36. Relative lowering in vapour pressure,

$$\frac{p^\circ - p_s}{p^\circ} = \frac{w}{m} \times \frac{M}{W}$$

$$\frac{0.30\text{ mm}}{17.54\text{ mm}} = \frac{20}{m} \times \frac{18}{100}$$

$$\Rightarrow \qquad m = \frac{20 \times 18 \times 17.54}{0.30 \times 100} = 210.48$$

37. According to Raoult's law,

Relative lowering in vapour pressure,

$$\frac{p_A^\circ - p_S}{p_A^\circ} = \frac{n_B}{n_A + n_B}$$

$$n_A = \frac{850}{18} = 47.22 \quad \text{and} \quad n_B = \frac{50}{60} = 0.833$$

$$\frac{p_A^\circ - p_s}{p_A^\circ} = \frac{0.833}{48.053} = 0.017$$

38. W_B (solute) = 25 g ; $M_B = 180$ g mol^{-1}; $p_A^\circ = 17.535$ mm

W_A (water) = 450 g; $M_A = 18$ g mol ; p_s = ?

$$\frac{p_A^\circ - p_s}{p_A^\circ} = \chi_B = \frac{n_B}{n_B + n_A}$$

$$n_B = \frac{W_B}{M_B} = \frac{25}{180} = 0.1389$$

$$n_A = \frac{W_A}{M_A} = \frac{450}{18} = 25$$

$$\frac{17.535 - p_s}{17.535} = \frac{0.1389}{0.1389 + 25}$$

$$\frac{17.535 - p_s}{17.535} = 0.00552$$

$$p_s = 17.535 - 0.097$$

$$p_s = 17.438\text{ mm Hg}$$

39. The unit of ebullioscopic constant is K kg mol^{-1} or K (molality)$^{-1}$.

40. We know that, $\Delta T_b = \frac{1000 \times k_b \times w}{W \times M}$

$$M = \frac{1000 \times k_b \times w}{W \times \Delta T_b}$$

$$\Delta T_b = \frac{1000 \times k_b \times 10}{100 \times 100}$$

$$\Delta T_b = k_b$$

41. Mass of water (W_A) = 500 g = 0.5 kg

Elevation in boiling point

$$(\Delta T_b) = 100°\text{ C} - 99.63°\text{ C} = 0.37°\text{ C} = 0.37\text{ K}$$

Molal elevation constant (k_b) = 0.52 K kg mol^{-1}

Molar mass sucrose $C_{12}H_{22}O_{11}$

$$(M_B) = (12 \times 12) + (22 \times 1) + (16 \times 11)$$

$$= 342\text{ g mol}^{-1}$$

$$W_B = \frac{M_B \times \Delta T_b \times W_A}{k_b} = \frac{(342\text{ g mol}^{-1}) \times (0.37\text{ K}) \times (0.5\text{ kg})}{(0.52\text{ K kg mol}^{-1})}$$

$$= 121.7\text{ g}$$

42. $\Delta T_b = \frac{k_b \times w \times 1000}{m \times W}$

$$\therefore\ m = \frac{k_b \times w \times 1000}{\Delta T_b \times W} = \frac{2.53 \times 10 \times 1000}{1 \times 100} = 253\text{ g}$$

43. $m = \frac{k_b \times w \times 1000}{\Delta T_b \times W} = \frac{2.16 \times 0.15 \times 1000}{0.216 \times 15} = 100$

44. $\Delta T_f = 1.86 \times \frac{342}{342} = 1.86°\text{ C}$

$$\therefore\ T_f = T - \Delta T_f = 0 - 1.86 = -1.86°\text{ C}$$

45. From depression in freezing point expression,

$$M = \frac{1000 \times k_f \times w}{\Delta T \times W}$$

$$62 = \frac{1000 \times 1.86 \times 50}{9.3 \times W}$$

$$W = 161.3 \text{ g}$$

Total water = 200 g

Hence, ice separated = (200 − 161.3) g = 38.7 g

46.

$$i = 1 + \alpha$$

$$= \frac{\text{cal. mol. weight}}{\text{exp. mol. wt}} = \frac{58.5}{30} = 1.95$$

$$\therefore \quad 1 + \alpha = 1.95$$

$$\alpha = 0.95$$

48. In the figure water will move from side (*B*) to side (*A*) if a pressure greater than osmotic pressure is applied on piston (*B*). Thus, (b) is the correct option.

49. An unripe mango placed in a concentrated salt solution to prepare pickle, shivels because it loses water due to osmosis.

51. The solutions having the same osmotic pressure are called isotonic solution. They may have different weight concentrations.

52. Mass of polymer (W_B) = 1.0 g

Molar mass of polymer (M_B) = 185000 g mol^{-1}

Volume of solution (V) = 450 mL = 0.450 L

Temperature (T) = 37 + 273 = 310 K

Solution constant (R) = 8.314×10^3 Pa L K^{-1} mol^{-1}

Osmotic pressure (π) = CRT

$$= \frac{W_B \times R \times T}{M_B \times V}$$

$$\therefore \quad \pi = \frac{(1.0 \text{ g}) \times (8.314 \times 10^3 \text{ Pa L K}^{-1} \text{ mol}^{-1}) \times (310 \text{ K})}{(185000 \text{ g mol}^{-1}) \times (0.450 \text{ L})}$$

= 30.96 Pa

53. $p = \frac{w}{mV} RT$, since, wRT/V are constant thus, $p \propto \frac{1}{m}$

$$\therefore \quad p_2 > p_1 > p_3$$

54. Molarity of urea = $\dfrac{\frac{6}{60}}{\frac{100}{1000}} = 1\text{M}$

Hence, 1 M solution of glucose is isotonic with 6% urea solution.

55. $C = \frac{5}{342} \times \frac{1}{100} \times 1000 = \frac{50}{342}$ mol / L

$$\pi = \frac{50}{342} \times 0.082 \times 423 = 5.07 \text{ atm}$$

56. For isotonic solution

$$\frac{w_1}{m_1} = \frac{w_2}{m_2} \Rightarrow \frac{5}{342} = \frac{1}{m_2} \Rightarrow m_2 = \frac{342}{5} = 68.4$$

57. $\pi = CRT = \frac{W_B \times R \times T}{M_B \times V}$

For both the solutions, R, T and V are constants.

For I solution

$$(4.98 \text{ bar}) = \frac{(36 \text{ g}) \times R \times T}{(180 \text{ g mol}^{-1}) \times V} \quad \text{...(i)}$$

For II solution

$$(1.52 \text{ bar}) = \frac{W_B \times R \times T}{M_B \times V} \quad \text{... (ii)}$$

On dividing Eq. (ii) by Eq. (i), we get

$$\frac{(1.52 \text{ bar})}{(4.98 \text{ bar})} = \frac{W_B \times R \times T}{M_B \times V} \times \frac{180 \times V}{36 \times R \times T}$$

$$\frac{W_B}{M_B} = \frac{1.52}{4.98 \times 5} = 0.0610 \text{ mol L}^{-1}$$

58. Mole fraction units is useful in relating concentration of solution with its vapour pressure.

60. $BaCl_2$ gives maximum ion hence, it shows lowest vapour pressure.

61. Elevation in bp = $ik_b \cdot m$

If k_b and m are same,

Elevation in boiling point $\propto i$

$$NaOH \longrightarrow \underbrace{Na^+ + OH^-}_{\text{2 ions}}$$

$$Na_2SO_4 \longrightarrow \underbrace{2Na^+ + SO_4^{2-}}_{\text{3 ions}}$$

$$NH_4NO_3 \longrightarrow \underbrace{NH_4^+ + NO_3^-}_{\text{2 ions}}$$

$$KNO_3 \longrightarrow \underbrace{K^+ + NO_3^-}_{\text{2 ions}}$$

62. Osmotic pressure is a colligative property.

Osmotic pressure $\propto$ no. of particles

$$NaCl \longrightarrow Na^+ + Cl^-$$

Concentration of particles = 2 × 2M = 4M

Glucose does not dissociate

∴ Concentration of particles = 1 × 1M = 1 M

Urea does not dissociate,

∴ Concentration of urea = 1 × 2 M = 2 M

∴ Glucose solution will have minimum osmotic pressure.

63. KNO_3 dissociates completely while CH_3COOH dissociates to a small extent hence, $p_1 > p_2$.

64. Actual molecular weight of naphthoic acid ($C_{11}H_8O_2$) = 172

Molecular mass (calculated) = $\dfrac{1000 \times k_f \times w}{W \times \Delta T_f}$

$$= \frac{1000 \times 1.72 \times 20}{50 \times 2} = 344$$

$$\text{van't Hoff factor } (i) = \frac{\text{actual mol. wt.}}{\text{calculated mol. wt.}} = \frac{172}{344} = 0.5$$

65.
$$\Delta T_f = i \times k_f \times m$$
$$7.10 \times 10^{-3} = i \times 1.86 \times 0.001$$
$$i = 3.817$$
$$\alpha = \frac{i-1}{n-1}$$
$$1 = \frac{3.817-1}{(x+1)-1}$$
$$x = 2.817 \approx 3$$

∴ Molecular formula of the compound is $K_3[Fe(CN)_6]$.

66.
$$\begin{array}{llll} CuCl_2 & \rightleftharpoons Cu^{2+} & + 2Cl^- & \\ 1\text{ mol} & 0 & 0 & \text{before ionisation} \\ (1-\alpha) & \alpha & 2\alpha & \text{after ionisation} \end{array}$$

Thus, number of particles after ionisation
$$= 1 - \alpha + \alpha + 2\alpha = 1 + 2\alpha$$
$$\therefore \text{ vant' Hoff factor } (i) = \frac{1+2\alpha}{1} \text{ (On 100\% ionisation, } \alpha = 1)$$
$$i = \frac{1 + 2 \times 1}{1} = 3$$

The elevation of boiling point,
$$\Delta T_b = 3 \times k_b \times m$$

Molality of $CuCl_2$ solution
$$(m) = \frac{\text{wt. of } CuCl_2 \text{ in g / mol wt. of } CuCl_2}{\text{wt. of water in kg}}$$
$$= \frac{\frac{13.44}{134.4}}{1} = 0.1 \text{ m}$$

Thus, $\Delta T_b = 3 \times 0.52 \times 0.1 = 0.156° \text{ C} \approx 0.16° \text{ C}$

67.
$$\begin{array}{ccc} HBr & \rightleftharpoons H^+ & + Br^- \\ (1-\alpha) & \alpha & \alpha \end{array}$$
$$i_{\text{total}} = (1-\alpha) + \alpha + \alpha = (1+\alpha)$$
$$i = 1 + 0.9 = 1.9$$
$$\Delta T_f = ik_f m = 1.9 \times 1.86 \times \frac{8.1}{81} \times \frac{1000}{100} = 3.53° \text{ C}$$
$$T_f = T - \Delta T_f = 0 - 3.53° \text{ C} = -3.53° \text{ C}$$

68. According to van't Hoff equation

$$\text{Osmotic pressure } (\pi) = i\,CRT = \frac{in_B RT}{V}$$
$$i = 2.47; \quad V = 2.5 \text{ L}; \quad R = 0.0821 \text{ L atm K}^{-1}\text{mol}^{-1}$$
$$T = 27 + 273 = 300 \text{ K}; \quad \pi = 0.75 \text{ atm}$$
$$n_B = \frac{\pi V}{iRT} = \frac{(0.75 \text{ atm}) \times (2.5 \text{ L})}{(2.47) \times (0.0821 \text{ L atm K}^{-1}\text{mol}^{-1}) \times (300 \text{ K})}$$
$$= 0.0308 \text{ mol}$$

Amount of $CaCl_2$ dissolved $= n_B \times M_B$
$$= (0.0308 \text{ mol}) \times (111 \text{ g mol}^{-1})$$
$$= 3.42 \text{ g}$$

69. Amount of K_2SO_4 dissolved = 25 mg = 0.025 g

Volume of solution = 2 L
$$T = 25° \text{ C} = 25 + 273 \text{ K} = 298 \text{ K}$$

Molar mass of
$$K_2SO_4 = (2 \times 39) + (32) + (4 \times 16) = 174 \text{ g mol}^{-1}$$

Since, K_2SO_4 dissociates completely as
$$K_2SO_4 \xrightarrow{aq} 2\,K^+ + SO_4^{2-}$$

Total ions produced after dissociation (per mol) = 3

$$\text{So, } i = 3, \quad \pi = iCRT = i \times \frac{n}{V} RT = \frac{i \times W \times R \times T}{M \times V}$$
$$= \frac{3 \times (0.025 \text{ g}) \times (0.0821 \text{ L atm K}^{-1}\text{mol}^{-1}) \times (298 \text{ K})}{(174 \text{ g mol}^{-1}) \times (2 \text{ L})}$$
$$= 5.27 \times 10^{-3} \text{ atm}$$

70. ***Step I*** **Calculation of van't Hoff factor of acid**
$$\Delta T_f = 1^\circ\text{C} = 1\text{K}; \; k_f = 1.86 \text{ K kg mol}^{-1}$$
$$\Delta T_f = i\,k_f\,m$$
$$\text{or} \qquad i = \frac{\Delta T_f}{k_f\,m} \qquad \text{...(i)}$$
$$m = \frac{W_B}{M_B \times W_A}$$
$$= \frac{(19.5 \text{ g})}{(78 \text{ g mol}^{-1}) \times (0.5 \text{ kg})}$$
$$= 0.5 \text{ mol kg}^{-1} \qquad \text{... (ii)}$$

Placing the values in Eq. (i), we find the value of van't Hoff factor (i)
$$i = \frac{1}{(1.86 \text{ K kg mol}^{-1}) \times (0.5 \text{ mol kg}^{-1})}$$
$$= 1.0753$$

Step II **Calculation of degree of dissociation of the acid**

Suppose degree of dissociation at the given concentration is α.

$$\begin{array}{llll} & CH_2FCOOH & \overset{aq}{\rightleftharpoons} CH_2FCOO^- & + H^+ \\ \text{Initial conc. } C \text{ mol kg}^{-1} & & 0 & 0 \\ \text{At equilibrium} & C\,(1-\alpha) & C\alpha & C\alpha \end{array}$$
$$\text{Total} = C(1+\alpha)$$
$$\therefore \qquad i = \frac{C\,(1+\alpha)}{C} = 1 + \alpha$$
$$\alpha = i - 1 = 1.0753 - 1 = 0.0753$$

Step III **Calculation of dissociation constant for the acid**
$$\text{(Molal) } C = 0.5 \text{ m} \qquad \text{(From Eq. (ii))}$$
$$K_a = \frac{[CH_2FCOO^-]\,[H^+]}{[CH_2FCOOH]} = \frac{C\alpha \cdot C\alpha}{C\,(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$
$$K_a = \frac{(0.5)\,(0.0753)^2}{(1-0.0753)} = \frac{(0.5) \times (0.0753)^2}{(0.9247)} = 3.07 \times 10^{-3}$$

Round II

1. ***Step I* Calculation of partial pressure of oxygen and nitrogen**

Partial pressure of O_2

$$(p_{O_2}) = (10\text{ atm}) \times \frac{20}{100} = 2\text{ atm} = 2 \times 760\text{ mm}$$

$$\text{Partial pressure of } N_2\ (p_{N_2}) = (10\text{ atm}) \times \frac{79}{100} = 7.9\text{ atm}$$

$$= 7.9 \times 760\text{ mm}$$

***Step II* Composition of O_2 and N_2 dissolved in water**

The amount of gases dissolved in water is calculated in terms of their mole fractions.

$$\chi_{O_2} = \frac{p_{O_2}}{K_H} = \frac{(2 \times 760\text{ mm})}{(3.30 \times 10^7\text{ mm})}$$

$$= 4.6 \times 10^{-5}$$

$$\chi_{N_2} = \frac{p_{N_2}}{K_H} = \frac{(7.9 \times 760\text{ mm})}{(6.51 \times 10^7\text{ mm})}$$

$$= 9.22 \times 10^{-5}$$

2. ***Step I* Calculation of number of moles of CO_2**

According to Henry's law,

$$\text{Mole fraction of } CO_2\ (\chi_{CO_2}) = \frac{\text{partial pressure of } CO_2}{K_H \text{ for } CO_2}$$

$$K_H = 1.67 \times 10^8\text{ Pa} = \frac{(1\text{ atm})}{(101325\text{ Pa})} \times (1.67 \times 10^8\text{ Pa})$$

$$= 1.648 \times 10^3\text{ atm}$$

$$\chi_{CO_2} = \frac{2.5\text{ atm}}{(1.648 \times 10^3\text{ Pa})} = 1.52 \times 10^{-3}$$

$$n_{H_2O} = \frac{(500\text{ g})}{(18\text{ g mol}^{-1})} = 27.78\text{ mol}$$

$$\chi_{CO_2} = \frac{n_{CO_2}}{n_{CO_2} + n_{H_2O}} = \frac{n_{CO_2}}{n_{H_2O}} = \frac{n_{CO_2}}{(27.78\text{ mol})}$$

$$n_{CO_2} = \chi_{CO_2} \times (27.78\text{ mol})$$

$$= (1.52 \times 10^{-3}) \times (27.78\text{ mol})$$

$$= 0.0422\text{ mol}$$

Note n_{CO_2} is considered negligible due to its little solubility in water.

***Step II* Calculation of mass of dissolved CO_2 in water**

$$\text{Mass of } CO_2 = \text{no}\cdot\text{ of moles of } CO_2 \times \text{molar mass of } CO_2$$

$$= (0.0422\text{ mol}) \times (44\text{ g mol}^{-1})$$

$$= 1.857\text{ g}$$

3. $m = 1.5 \times 10^{-3}$ m or 1.5×10^{-3} mol kg^{-1}

Mass of solute $= 1.5 \times 10^{-3}$ g or 1.5 mg

Mass of solvent = ?

Molar mass of solute

$$(C_{19}H_{21}NO_3) = (12 \times 19) + (1 \times 21) + (14) + (16 \times 3)$$

$$= 311\text{ g mol}^{-1}$$

$$\text{Number of moles of solute} = \frac{\text{mass}}{\text{molar mass}}$$

$$= \frac{(1.5 \times 10^{-3}\text{ g})}{(311\text{ g mol}^{-1})}$$

$$\text{Molality } (m) = \frac{\text{number of moles}}{\text{mass of solvent in kg}}$$

$$\text{Mass of solvent} = \frac{\text{number of moles}}{\text{molality}}$$

$$= \frac{(1.5 \times 10^{-3}\text{ g})}{(311\text{ g mol}^{-1})} \times \frac{1}{(1.5 \times 10^{-3}\text{ mol kg})}$$

$$= \frac{1}{311} = 0.0032\text{ kg or } 3.2\text{ g}$$

4. $\text{Mass of solute in I solution} = \frac{25}{100} \times 300\text{ g} = 75\text{ g}$

$\text{Mass of solute in II solution} = \frac{40}{100} \times 400\text{ g} = 160\text{ g}$

After mixing both solutions,

$$\text{Total mass of solute} = (75 + 160)\text{ g} = 235\text{ g}$$

$$\text{Total mass of solution} = (300 + 400)\text{ g} = 700\text{ g}$$

$$\text{Mass \% of solute in final solution} = \frac{(235\text{ g})}{(700\text{ g})} \times 100 = 33.57\%$$

5. $\text{Molarity of pure water} = \frac{100}{18} = 55.6\text{ M}$

6. When A — A and B—B interactions are nearly same as A—B type interaction, ideal solution is obtained which follows Raoult's law in all conditions of temperature and pressure. Thus, A follows Raoult's law.

When A — A or B — B interactions are stronger than A — B interaction, a solution showing positive deviation from Raoult's law in obtained. Thus, B exhibits positive deviation from Raoult's law.

When A — A or B — B interaction are weaker than A — B interaction a solution showing negative deviation from Raoult's law is obtained. Thus, C exhibits negative deviation from Raoult's law.

7. HgI_2 although insoluble in water but shows complex formation with KI and therefore, freezing point decreases.

8. (ii) 0.1 M glucose,

$$\pi = CRT = 0.1RT$$

(iii) 0.6 g urea in 100 mL solution

$$\pi = \frac{n}{V}RT = \frac{w/m}{V}RT = \frac{0.6/60 \times 1000}{100} \times RT = 0.1RT$$

(iv) 1.0 g of non electrolyte solute (X) is 50 mL solution

$$\pi = \frac{1.0/200}{50} \times 1000RT = 0.1\,RT$$

Hence, option (ii), (iii), (iv) have some osmotic pressure, osmotic pressure of 0.1 M NaCl is higher than (ii), (iii), (iv) because it dissociates to give maximum number or particles.

9. $m = \frac{\Delta T_b}{k_b} = \frac{-0.060}{-1.86} = 3.2\times 10^{-2} = 0.032$

i.e., 0.032 = total particles

∴ The number of $H^+ = (0.032 - 0.025)\,m = 0.007\,MH^+$

$$HA \rightleftharpoons H^+ + A^-$$

$$[H^+] = [A^-] = 0.007\,M$$

$$\therefore \quad HA = 0.018$$

$$K_a = \frac{(0.007)^2}{0.018} = 3\times 10^{-3}$$

$$pK_a = -\log K_a = -\log(3\times 10^{-3}) = 2.5$$

10. Boiling point $(T_b) = 100 + \Delta T_b = 100 + k_b m$

Freezing point $(T_f) = 0 - \Delta T_f = -k_f m$

$$T_b - T_f = (100 + k_b m) - (-k_f m)$$

$$105 = 100 + 0.51m + 1.86\,m$$

$$2.37m = 5 \quad \text{or} \quad m = \frac{5}{2.37} = 2.11$$

∴ Weight of sucrose to be dissolved in 100 g water

$$= \frac{2.11\times 342}{1000}\times 100 = 72\text{ g}$$

11. Molality of solution is 1m. It means that one mole of solute is dissolved in 1000 g of water.

Number of moles of solute $(n_B) = 1$ mol

Number of moles of water

$$(n_A) = \frac{\text{mass of water}}{\text{molar mass}} = \frac{(1000\text{ g})}{(18\text{ g mol}^{-1})}$$

$$= 55.55\text{ mol}$$

Mole fraction of solute

$$(\chi_B) = \frac{n_B}{n_A + n_B} = \frac{(1\text{ mol})}{(55.55 + 1.0)\text{ mol}} = \frac{1}{56.55}$$

$$= 0.0177$$

Mole fraction water $(\chi_A) = 1 - 0.0177 = 0.9823$

Vapour pressure of solution

$$(p_A) = p_A^\circ\,\chi_A = (12.3\text{ kPa})\times 0.9823 = 12.08\text{ kPa}$$

12. For cane sugar solution

W_b (sugar) = 5 g; W_A (water) = 100 − 5 = 95 g

M_B (sugar) = 342 g mol^{-1}; $\Delta T_f = (273.15 - 271.00)$ K

$$= 2.15\text{ K}$$

$$\Delta T_f = \frac{k_f\times W_B}{M_B\times W_A}$$

$$(2.15\text{ K}) = \frac{k_f\times(5\text{ g})}{(342\text{ g mol}^{-1})\times(95\text{ g})} \qquad \text{....(i)}$$

For glucose solution

W_B (glucose) = 5 g; W_A (water) = 100 − 5 = 95 g

M_B (glucose) = 180 g mol^{-1}; ΔT_f = ?

$$\Delta T_f = \frac{k_f\times(5\text{ g})}{(180\text{ g mol}^{-1})\times(95\text{ g})} \qquad \text{...(ii)}$$

On dividing Eq. (ii) by Eq. (i)

$$\frac{\Delta T_f}{(2.15\text{ K})} = \frac{k_f\times(5\text{ g})}{(180\text{ g mol}^{-1})\times(95\text{ g})}\times\frac{(342\text{ g mol}^{-1})\times(95\text{ g})}{(k_f)\times(5\text{ g})}$$

$$\Delta T_f = \frac{342\times 2.15}{180}\text{ K} = 4.085\text{ K}$$

Freezing point for 5% glucose solution

$$= (273.15 - 4.085)\text{ K} = 269.07\text{ K}$$

13. For ideal solution, Raoult's law is $p_T = p_A^\circ\,\chi_A + p_B^\circ\,\chi_B$ and vapour pressure in vapour phase $= \frac{p_A^\circ\,\chi_A}{p_T}$

Thus, the required quantities are χ_A, χ_B and p_T as we know p_A° and p_B°.

Molar mass of benzene (C_6H_6) = 78 g mol^{-1}

Molar mass of naphthalene $(C_{10}H_8)$ = 128 g mol^{-1}

$n_{C_6H_6}$ (Number of moles of benzene)

$$= \frac{80\text{ g}}{(78\text{ g mol}^{-1})} = 1.026\text{ mol}$$

$n_{C_{10}H_8}$ (Number of moles of naphthalene)

$$= \frac{(100\text{ g})}{(128\text{ g mol}^{-1})} = 0.781\text{ mol}$$

Mole fraction of benzene

$$(\chi_{C_6H_6}) = \frac{(1.026\text{ mol})}{(1.026 + 0.781)\text{ mol}} = 0.568$$

Mole fraction of naphthalene $(\chi_{C_{10}H_8}) = 1 - 0.568 = 0.432$

Applying Raoult's law

Partial vapour pressure of benzene in solution $(p_{C_6H_6})$

$$= p^\circ_{C_6H_6}\times\chi_{C_6H_6}$$

$$= (50.71\text{ mm})\times(0.568)$$

$$= 28.80\text{ mm}$$

Partial vapour pressure of naphthalene in solution

$$(p_{C_{10}H_8}) = p^\circ_{(C_{10}H_8)}\times\chi_{C_{10}H_8}$$

$$= (32.06\text{ mm})\times(0.432)$$

$$= 13.85\text{ mm}$$

Total vapour pressure of solution (p) = (28.80 + 13.85) mm

$$= 42.65\text{ mm}$$

Mole fraction of benzene in vapour phase

$$= \frac{\chi_{C_6H_6}\times p^\circ{}_{C_6H_6}}{p_{\text{total}}}$$

$$= \frac{0.568\times(50.71\text{ mm})}{(42.65\text{ mm})} = 0.675$$

14. Degree of association,

$$\alpha = \frac{1-i}{1-\frac{1}{n}}$$

$$0.8 = \frac{1-i}{1-\frac{1}{4}}$$

$$i = 0.4$$

$$\because \quad \Delta T = i \times k_f \times m$$

$$0.3 = 0.4 \times 1.86 \times \frac{w_B \times 1000}{m_B \times w_A}$$

$$0.3 = 0.4 \times 1.86 \times \frac{2.5 \times 1000}{m_B \times 100}$$

$$m_B = \frac{0.4 \times 1.86 \times 2.5 \times 1000}{0.3 \times 100} = 62 \text{ g mol}^{-1}$$

15.

$$\pi_1 V_1 + \pi_2 V_2 = \pi_R (V_1 + V_2)$$

$$1 \times 1 + 3.5V = 2.5(1 + V)$$

$$1 + 3.5V = 2.5 + 2.5V$$

or $$V = 1.5 \text{ L}$$

16. Steps involved to solve the problem are

- (i) In the equation of Raoult's law $(p_A = p^\circ_A \chi_A)$, mole fraction is required, so first find the moles of solute and solvent and then mole fraction in case first.
- (ii) Now put the value of mole fraction in the equation of Raoult's law.
- (iii) Make an another equation in the similar way as mentioned above, when 18 g water is added (so the mass of water will become $= 18 + 19 = 108$ g).
- (iv) Solve two equation to find molar mass.
- (v) Put the value of molar mass in any of the two equations to find vapour pressure.

Step I **Calculation of molar mass of the solute**

Case I Number of mole of solute

$$(n_B) = \frac{\text{mass}}{\text{molar mass}} = \frac{(30 \text{ g})}{(M \text{ g mol}^{-1})} = \frac{30}{M} \text{ mol}$$

Number of moles of water

$$(n_A) = \frac{\text{mass}}{\text{molar mass}} = \frac{(90 \text{ g})}{(18 \text{ g mol}^{-1})} = 5 \text{ mol}$$

Mole fraction of water

$$(\chi_A) = \frac{n_A}{n_A + n_B} = \frac{(5 \text{ mol})}{\left(5 \text{ mol} + \frac{30}{M} \text{ mol}\right)} = \frac{M}{(6 + M)}$$

Vapour pressure of first solution (p_A) = 2.8 kPa

According to Raoult's law, $p_A = p^\circ_A \chi_A$

$$(2.8 \text{ kPa}) = p^\circ_A \text{ x } \frac{M}{(6 + M)} \qquad \text{...(i)}$$

Case II Number of moles of solute $(n_B) = \frac{30}{M}$ mol

Number of moles of water

$$(n_A) = \frac{\text{mass}}{\text{molar mass}} = \frac{(108 \text{ g})}{(18 \text{ g mol}^{-1})} = 6 \text{ mol}$$

Mole fraction of water $(\chi_A) = \frac{n_A}{n_A + n_B}$

$$= \frac{(6 \text{ mol})}{\left(6 \text{ mol} + \frac{30}{M} \text{ mol}\right)}$$

$$= \frac{M}{(5 + M)}$$

Vapour pressure of solution (p_A) = 2.9 kPa

According to Raoult's law, $p_A = p^\circ_A \chi_A$

$$(2.9 \text{ kPa}) = p^\circ_A \times \frac{M}{(5 + M)} \qquad \text{... (ii)}$$

Dividing Eq. (i) by Eq. (ii)

$$\frac{(2.8 \text{ kPa})}{(2.9 \text{ kPa})} = \frac{(5 + M)}{(6 + M)}$$

$$0.9655 = \frac{(5 + M)}{(6 + M)}$$

$$(0.9655 \times 6) + 0.9655 \text{ M} = 5 + M$$

$$0.0345 \text{ M} = 0.793$$

$$M = \frac{0.793}{0.0345} = 23 \text{ g mol}^{-1}$$

Step II **Calculation of vapour pressure of water**

According to Raoult's law, $p_A = p^\circ_A \chi_A$

or $$(2.8 \text{ kPa}) = p^\circ_A = \frac{M}{(6 + M)} \qquad \text{...(iii)}$$

Placing the value of M in Eq. (i)

$$2.8 \text{ kPa} = p^\circ_A \frac{(23 \text{ g mol}^{-1})}{(6 + 23) \text{ g mol}^{-1}}$$

$$p^\circ_A = \frac{2.8 \times 29}{23}$$

$$= \frac{81.2}{23} = 3.53 \text{ kPa}$$

17. ***Step I*** **Calculation of molecular masses of compounds *AB_2* and *AB_4***

For compound *AB_2*

$$W_B(AB_2) = 1 \text{ g};\ W_A(C_6H_6) = 20 \text{ g};\ \Delta T_f = 2.3 \text{ K}$$

$$k_f = 5.1 \text{ K kg mol}^{-1} = 5.1 \times 1000 \text{ K g mol}^{-1}$$

$$M_B = \frac{k_f \times W_B}{\Delta T_f \times W_A} = \frac{(5.1 \times 1000 \text{ K g mol}^{-1}) \times (1 \text{ g})}{(2.3 \text{ K}) \times (20 \text{ g})}$$

$$= 110.87 \text{ g mol}^{-1}$$

For compound *AB_4*

$$W_B(AB_4) = 1 \text{ g};\ W_A(C_6H_6) = 20 \text{ g};\ \Delta T_f = 1.3 \text{ K}$$

$$k_f = 5.1 \text{ K kg mol}^{-1}$$

$$M_B = \frac{(5.1 \text{ K kg mol}^{-1}) \times 1000 \times (1 \text{ g})}{(1.3 \text{ K}) \times (20 \text{ g})}$$

$$= 196.15 \text{ g mol}^{-1}$$

Step II **Calculation of the atomic masses of elements *A* and *B***

Let the atomic mass of element $A = a$

Let the atomic mass of element $B = b$

$$\text{Molecular mass of } AB_2 = a + 2b$$
$$\text{Molecular mass of } AB_4 = a + 4b$$

According to the available data

$$a + 2b = 110.87 \quad \ldots \text{(i)}$$
$$a + 4b = 196.15 \quad \ldots \text{(ii)}$$

Substract Eq. (i) from Eq. (ii)

$$a + 4b - a - 2b = 196.15 - 110.87$$
$$2b = 85.28;\ b = \frac{85.28}{2} = 42.64$$

Substituting the value of b in Eq. (i)

$$a + 2 \times 42.64 = 110.87$$
$$a + 85.28 = 110.87;\ a = 110.87 - 85.28 = 25.59$$

This, atomic mass of element $A = 25.59$

Atomic mass of element $B = 42.64$

18. ***Step I*** **Calculation of degree of dissociation**

Mass of solute $= 10$ g

Molar mass of solute

$$(CH_3CH_2CHClCOOH) = (12 \times 4) + (1 \times 7) + (35.5) + (16 \times 2)$$
$$= 48 + 7 + 35.5 + 32$$
$$= 122.5 \text{ g mol}^{-1}$$

Molal concentration of solution

$$= \frac{\text{mass / molar mass}}{\text{mass of solvent (kg)}}$$
$$= \frac{(10 \text{ g})}{(122.5 \text{ g mol}^{-1}) \times (0.25 \text{ kg})}$$
$$= 0.326 \text{ m}$$

If α is the degree of dissociation of $CH_3CH_2CHCl\ COOH$, then

$$CH_3CH_2CHClCOOH \rightleftharpoons CH_3CHClCOO^- + H^+$$

Initial conc. C mol^{-1} kg		0	0
At equilibrium	$C\ (1-\alpha)$	$C\alpha$	$C\alpha$

$$\therefore \quad K_a = \frac{C\alpha \times C\alpha}{C\ (1-\alpha)} = C\alpha^2$$

[Considering $(1-\alpha) = 1$ for dilute solutions]

$$\alpha^2 = \frac{K_a}{C} \quad \text{or} \quad \alpha = \sqrt{\frac{K_a}{C}}$$

$$\text{So,} \quad \alpha = \sqrt{\frac{1.4 \times 10^{-3}}{0.326}} = \sqrt{42.9 \times 10^{-4}}$$
$$= 6.55 \times 10^{-2} = 0.065$$

Step II **Calculation of van't Hoff factor** (i)

$$CH_3CH_2CHClCOOH \rightleftharpoons CH_3CH_2CHCl\ COO^- + H^+$$

Initial no. of moles	1	0	0
Moles at equilibrium	$1-\alpha$	α	α

Total number of moles after dissociation

$$= (1-\alpha) + (\alpha) + (\alpha) = (1+\alpha)$$

van't Hoff factor

$$(i) = \frac{\text{Total number of moles after dissocation}}{\text{Number of moles before dissocation}}$$
$$i = \frac{(1+\alpha)}{1} = (1+\alpha)$$
$$= 1 + 0.065 = 1.065$$

Step III **Calculation of depression in freezing point** (ΔT_f)

$$\Delta T_f = i\, k_f\, m = (1.065) \times (1.86 \text{ K kg mol}^{-1}) \times (0.326 \text{ mol kg}^{-1})$$
$$\Delta T_f = 0.65 \text{ K}$$

19. Solubility is affected by nature of solute and pressure at constant T and nature of solute and temperature at constant p.

20. Molality and mole fraction are not affected by temperature because they involve masses of the solute and the solvent which do not change with temperature.

21. Isotonic solutions must have the same density and elevation in boiling point.

22. In the graph, when $\chi_A = 1$ and $\chi_B = 0$, then $p = p_A^\circ$ and when $\chi_B = 1$ and $\chi_A = 0$ thus $p = p_B^\circ$

23. Molarity $= \frac{6}{60} = 0.1$. In case of urea, molarity and normality are the same.

24. Molarity depends upon volume which changes with change in temperature. That's why molarity changes with change in temperature.

25. An ideal solution of the components *A* and *B* is defined as the solution in which the intermolecular interactions between *A* and *B* are of the same magnitude as between the pure components or it is a solution there is no volume change or enthalpy change on mixing.

26. When sodium chloride (NaCl) is added to water, depression in freezing point is observed because the vapour pressure reduces.

27. One molar aqueous solution has 1 mole in less than 1000 g of water. Hence, 1000 g of water will be associated with more than 1 mole while 1 molal has 1 mole in 1000 g of water.

28. Extent of dissociation increases steadily with increasing dilution.

29. Isotonic solution have same molarity.

$$\text{Molarity of 18 g glucose} = \frac{18}{180} \Big/ \frac{1000}{1000} = 0.1$$
$$\text{Molarity of 34.2 g sucrose} = \frac{34.2}{342} \Big/ \frac{1000}{1000} = 0.1$$

The concentration of 18 g L^{-1} glucose is same to 34.2 gL^{-1} sucrose.

30. For solutions 1 and 2 the concentration in compartment *B* is higher than in *A*.

31. In hypertonic solution osmotic pressure is higher, therefore, volume rise is higher in *B*.

32. L represents $\Delta T_b = k_b \cdot m$

33. For equimolar solutions $\chi_B = \chi_T = 0.5$

$$p_B = \chi_B \times p_B^\circ = 0.5 \times 160 = 80 \text{ mm}$$

$$p_T = \chi_T \times p_T^\circ = 0.5 \times 60 = 30 \text{ mm}$$

$$p_{\text{Total}} = 80 + 30 = 110 \text{ mm}$$

Mole fraction of toluene in vapour phase $= \dfrac{30}{110} = 0.27$

34. $\Delta T_b = k_b \times m = 0.513 \times 0.69 = 0.354$

$$T_b = T + \Delta T_b = 99.725 + 0.354 = 100.079^\circ \text{ C}$$

35. Total mass of solution $= 1000$ g water $+ 120$ g urea

$$= 1120 \text{ g}$$

Density of solution $= 1.15$ g/mL

Thus, volume of solution $= \dfrac{\text{mass}}{\text{density}} = \dfrac{1120 \text{ g}}{1.15 \text{ g/mL}}$

$$= 973.91 \text{mL}$$

$$= 0.974 \text{ L}$$

$$\text{Moles of solute} = \frac{120}{60} = 2$$

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume (L) of solution}}$$

$$= \frac{2}{0.974} = 2.05 \text{ mol L}^{-1}$$

36. Coolant is glycol ($C_2H_6O_2$) and is non-electrolyte

$$\Delta T_f = 2.8^\circ$$

$$\Delta T_f = \frac{1000 k_f w_1}{m_1 w_2}$$

$$2.8 = \frac{1000 \times 1.86 \times w_1}{62 \times 1000}$$

$$\therefore \quad w_1 = 93.33 \text{ g}$$

37. $\text{Molality} = \dfrac{\text{moles of solute}}{\text{kg of solvent}}$

$$= \frac{5.2 \text{ mol CH}_3\text{OH}}{1 \text{ kg } (= 1000 \text{ g}) \text{ H}_2\text{O}}$$

$$n_1(\text{CH}_3\text{OH}) = 5.2$$

$$n_2(\text{H}_2\text{O}) = \frac{1000}{18} = 55.56$$

$$\therefore \quad n_1 + n_2 = 5.20 + 55.56 = 60.76 \text{ mol}$$

$$\therefore \quad X_{\text{CH}_3\text{OH}} = \text{Mole fraction of CH}_3\text{OH}$$

$$= \frac{n_1}{n_1 + n_2}$$

$$= \frac{5.2}{60.76} = 0.086$$

38. ΔT_f = Freezing point of H_2O − freezing point of ethylene glycol solution $= 0 - (-6^\circ) = 6^\circ$

$k_f = 1.86^\circ \text{ kg mol}^{-1}$

w_1 = Mass of ethylene glycol in gram

w_2 = Mass of solvent (H_2O) in grams = 4000 g

m_1 = Molar mass of ethylene glycol
$= 62 \text{ g mol}^{-1}$

i = van't Hoff factor = 1

(ethylene glycol being non-electrolyte)

$$\Delta T_f = \frac{1000 \, k_f \, w_1(i)}{m_1 \, w_2}$$

$$\therefore \quad 6 = \frac{1000 \times 1.86 \times w_1 \times 1}{62 \times 4000}$$

$$w_1 = 800 \text{ g}$$

39.

$$\begin{array}{lccc} & A_xB_y & \rightleftharpoons & xA^{y+} + yB^{x-} \\ \text{After dissociation} & (1-\alpha) & & x\alpha \qquad y\alpha \end{array}$$

$$i = n(A_xB_y) + n(A^{y+}) + n(B^{x-})$$

$$= 1 - \alpha + x\alpha + y\alpha$$

$$= 1 + \alpha(x + y - 1)$$

$$\therefore \quad \alpha = \frac{i - 1}{(x + y - 1)}$$

40. Two solutions are isotonic if their osmotic pressures are equal.

$$\pi_1 = \pi_2$$

$$M_1ST_1 = M_2ST_2$$

(M_1 and M_2 are molarities)

At a given temperature,

$$M_1 = M_2$$

$$\frac{1000w_1}{m_1V_1} = \frac{1000w_2}{m_2V_2} \qquad (V_1 = V_2 = 100 \text{ mL})$$

Cane sugar   Unknown

$$\therefore \quad \frac{w_1}{m_1} = \frac{w_2}{m_2}$$

$$\frac{5}{342} = \frac{1}{m_2}$$

$$m_2 = \frac{342}{5} = 68.4 \text{ g mol}^{-1}$$

41. $\text{Na}_2\text{SO}_4 \longrightarrow 2\text{Na}^+ + \text{SO}_4^{2-}$

van't Hoff factor for $\text{Na}_2\text{SO}_4 = 3$

$$\Delta T_f = i \times k_f \times m$$

$$= 3 \times 1.86 \times 0.01 \qquad \left[\because m = \frac{0.01}{1} = 0.01\right]$$

$$= 0.0558 \text{ K}$$

42. $p_T = X_H \cdot p_H^\circ + X_O \cdot p_O^\circ$

$$X_H = \frac{\dfrac{25}{100}}{\dfrac{25}{100} + \dfrac{35}{114}} = 0.45 \text{ and}$$

$$\therefore \quad X_O = 0.55$$

$$p_T = 0.45 \times 105 + 0.55 \times 45$$

$$= 72 \text{ kPa}$$

43. $$p_T = p_A^\circ X_A + p_B^\circ X_B$$

$$550 = p_A^\circ \times \frac{1}{4} + p_B^\circ \times \frac{3}{4}$$

Thus, $p_A^\circ + 3p_B^\circ = 2200$ ...(i)

When, 1 mol of Y is further added to the solution

$$560 = p_A^\circ + \frac{1}{5} + p_B^\circ \times \frac{4}{5}$$

Thus, $p_A^\circ + 4p_B^\circ = 2800$ ...(ii)

On subtraction, II – I

$$p_B^\circ = 2800 - 2200$$

$$p_B^\circ = 600$$

Putting the value of p_B° in Eq. (i)

$$p_A^\circ + 3 \times 600 = 2200$$

$$p_A^\circ = 2200 - 1800 = 400.$$

44. *n*-heptane and ethanol forms non-ideal solution, as resultant *n*-heptane-either molecular interaction is very poor in comparison to ethanol-ethanol or *n*-heptane so gives positive deviation.

45. $p_T = p_A^\circ \chi_A + p_B^\circ \chi_B$

Mixture solution boils at 1 atm = 760 mm = total pressure.

$$760 = 520\chi_A + 1000\,(1 - \chi_A)$$

$$\chi_A = 0.5, \text{mol \% of } A = 50\%$$

46. Moles of glucose $= \frac{18}{180} = 0.1$

Moles of $H_2O = \frac{178.2}{18} = 9.9$

According to Raoult's law

$$\frac{p^\circ - p_s}{p^\circ} = X_{\text{solute}}$$

$$\frac{17.5 - p_s}{17.5} = \frac{0.1}{10}$$

So, $p_s = 17.325$ mm Hg

47. According to Raoult's law :

$$p = p^\circ{}_A\,\chi_A + p^\circ{}_B\,\chi_B$$

$$290 = 200 \times 0.4 + p^\circ{}_B \times 0.6$$

$$p^\circ{}_B = 350$$

48. Solution is isotonic.

$$C_1RT = C_2RT$$

$$C_1 = C_2$$

Density of both the solutions are assumed to be equal to $1.0 \text{ g cm}^{-3} \Rightarrow$ molality = molarity 5.25%

In 100 g 5.25 g of substance, so in 1000 g 52.5 g of substance

Hence, $\frac{52.5}{M} = \frac{15}{60}$,

M = molecular mass of the substance

$$M = \frac{52.5 \times 60}{15} = 210$$

49. Molality $(m) = \frac{M}{1000\,d - MM_1} \times 100$

M = molarity

M_1 = molecular mass

d = density

$$= \frac{2.05}{(1000 \times 1.02) - (2.05 \times 60)} \times 1000$$

$$= 2.28 \text{ mol kg}^{-1}$$

50. Total molarity $= \frac{M_1V_1 + M_2V_2}{V_1 + V_2}$

$$= \frac{1.5 \times 480 + 1.2 \times 520}{480 + 520}$$

$$= 1.34 \text{ M}$$

51. Mixture contains 78 g benzene = 1 mol benzene and 46 g toluene = 0.5 mole toluene

Total moles of benzene and toluene = 1.5 mol

Mole fraction of benzene in mixture $= \frac{1}{1.5} = \frac{2}{3}$

Vapour pressure of benzene $p_b^\circ = 75$ Torr

$\therefore$ Partial vapour pressure of benzene $= p^\circ{}_b\,\chi_b$

$$= 75 \times \frac{2}{3} = 50 \text{ Torr}$$

52. H_3PO_3 is a dibasic acid (*i.e.*, contains two ionisable protons attached directly to O).

$$H_3PO_3 \rightleftharpoons 2H^+ + HPO_4^{2-}$$

$\therefore$ $0.1 \text{ M } H_3PO_3 = 0.2 \text{ N } H_3PO_3$

and $0.1 \text{ M KOH} = 0.1 \text{ N KOH}$

$$\underset{(KOH)}{N_1V_1} = \underset{(H_3PO_3)}{N_2V_2}$$

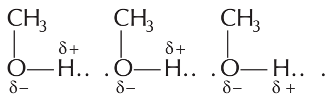
$$0.1V_1 = 0.2 \times 20$$

$$V_1 = 40 \text{ mL}$$

53. Water and hydrochloric acid; and water and nitric acid form miscible solutions. They show negative deviation.

In case of CH_3COCH_3 and $CHCl_3$, there is interaction between them, thus force of attraction between $CH_3COCH_3 \ldots. CHCl_3$ is larger than between $CHCl_3 \ldots. CHCl_3$ or $CH_3COCH_3 \ldots. CH_3COCH_3$ and thus, vapour pressure is less than expected—a negative deviation.

In case of CH_3OH, there is association by intermolecular H-bonding. When benzene is added to CH_3OH, H-bonding breaks and thus, force of attraction between CH_3OH and benzene molecule is smaller than between CH_3OH or benzene molecules (in pure state). Vapour pressure of mixture is greater than expected—a positive deviation.



$$\underset{\delta-}{\overset{\overset{CH_3}{|}}{O}}-\overset{\delta+}{H}\ldots\underset{\delta-}{\overset{\overset{CH_3}{|}}{O}}-\overset{\delta+}{H}\ldots\underset{\delta-}{\overset{\overset{CH_3}{|}}{O}}-\underset{\delta+}{H}\ldots$$

54. (a) $p_A = \chi_A p_A^\circ$ true

(b) $\pi = iMRT = MRT$ true (if van't Hoff factor, $i = 1$)

(c) $i = [1 + (y - 1)\alpha]$

where, y = number of ions

α = degree of ionisation

$i = 3$ for $BaCl_2$, $\alpha = 1$ (strong electrolyte)

$i = 2$ for KCl, $\alpha = 1$ (strong electrolyte)

$i = (1 + \alpha)$ for CH_3COOH $\alpha << 1$ (weak)

$i = 1$ for sucrose (non-electrolyte)

i (for $BaCl_2$) > KCl > CH_3COOH > sucrose

Thus, (c) is also true.

(d) $\Delta T_f = k_f m$.

k_f is dependent on solvent.

Thus, freezing points = [T (solvent) $- \Delta T_f$] are different.

Thus, (d) is false.

55. Let molarity of $Ba(OH)_2 = M_1$

$\therefore$ Normality $= 2\,M_1$

Molarity of HCl = 0.1 M = 0.1 N

$$N_1V_1 = N_2V_2$$

$$2M_1 \times 25 = 0.1 \times 35$$

$$M_1 = 0.07\ \text{M}$$

56. Higher pressure inside the cooker increases boiling point, thus, heat consistently given is used up by food material instead in boiling and constant boiling evaporation.

57. $HX \rightleftharpoons H^+ + X^{-1}$

$$\alpha = 0.3$$

$$i = 1 + \alpha = 1.3$$

$$\Delta T_f = \text{molality} \times k_f \times i$$

$$= 0.2 \times 1.85 \times 1.3 = 0.481^\circ$$

$\therefore$ Freezing point $= -\ 0.481^\circ$ C

58. Negative deviation means lower vapour pressure, it suggests high boiling point, thus resultant intermolecular force should be stronger than individual one.

3 Electrochemistry

JEE Main MILESTONE

- Electrolytic and Metallic Conduction
- Conductance in Electrolytic Solutions
- Electrochemical Cells
- Daniell Cell
- Electrodes and Their Types
- Electrode Potential
- Electrochemical Series
- Battery
- Fuel Cells

3.1 Electrolytic and Metallic Conduction

The substances which allow the passage of electric current through them are called **conductors,** *e.g.,* metals such as Cu, Ag, Sn etc. On the other hand, the substances which do not allow such passage through them are called **insulators**, *e.g.,* rubber, wood, sand etc.

The conductors are of two types on the basis of their physical state

Electrochemistry is the branch of chemistry which deals with inter-conversion of chemical energies and electrical energies. The chemical changes involving flow of electric current are referred as electrochemical changes.

(a) Metallic Conductors

These are the metallic substances which allow electricity to pass through them without undergoing any chemical change. Most of them are solids. Free electrons and holes (positive charges) are responsible for the conduction of such conductors. The conduction due to metallic conductors is called **electronic conductivity.** *It depends upon*

(i) nature and structure of metal
(ii) number of valence electrons per atom
(iii) density of metal
(iv) temperature (inverse relation)

Cs, Hg and Ga are metallic conductors but are liquids at room temperature.

(b) Electrolytes or Electrolytic Conductors

These are the substances which allow the electricity to pass through them in their molten states or in the form of their aqueous solutions. These undergo chemical decomposition when electricity pass through them. In real sense an electrolyte can be defined as '*a substance which dissociate into its ions when dissolved in a polar solvent like water*'**.**

The conduction of electricity because of ions is called **electrolytic conduction.** The conductivity of electrolytic solutions depends upon,

(i) nature of electrolyte
(ii) size of ions produced and their solvation (hydration)
(iii) nature of solvent and its viscosity
(iv) concentration of the electrolytes
(v) temperature (direct relation)

Acids, bases and their salts all are the examples of electrolytes. An electrolyte can be **strong** or **weak.** The strength of electrolyte depends upon its ability to dissociate. **Strong electrolytes** (*e.g.,* NaCl, HCl, KCl, NaOH, HNO_3, H_2SO_4 etc.) have the ability to dissociate completely or almost completely while **weak electrolytes** (*e.g.,* H_2CO_3, CH_3COOH, $ZnCl_2$, $HgCl_2$ etc.) on the other hand are very less dissociated as compared to former one.

Table 3.1 **Distinction between Metallic and Electrolytic Conduction**

S.N.	Metallic conduction	Electrolytic conduction
1.	Electric current flows by the movement of electrons.	Electric current flows by the movement of ions.
2.	No chemical change takes place.	Oxidation or reduction of ion occurs at the electrodes.
3.	If does not involve the transfer of any matter.	It involves transfer of matter in the form of ions.
4.	Resistance increases with increase of temperature.	Resistance decreases with increase of temperature.
5.	Faraday law is not followed.	Faraday law is followed.

3.2 Conductance in Electrolytic Solutions

The power of an electrolyte to conduct electric current is called **conductance** or **conductivity.** Just like metallic conductors, electrolytic solutions also obey Ohm's law, which states, "The current flowing through a conductor is directly proportional to the potential difference across it." *i.e.,*

$$I \propto V$$

where, I = current in ampere
V = potential difference in volt

or $$I = \frac{V}{R} \text{ or } V = IR$$

where, R = proportionality constant, called **resistance** of the conductor. Actually, resistance is the obstruction in the flow of current through a conductor and is expressed in ohm (Ω).

The **conductance** and **resistance** have reciprocal relationship *i.e.,*

$$C \propto \frac{1}{R}$$

Thus, the unit of conductance is **ohm^{-1}** or **mho** and is denoted by Ω^{-1}. In SI system, its unit is **siemen** (S).

The resistance of a conductor, is directly proportional to the length (l) and inversely proportional to the area of cross-section (a) of that conductor *i.e.,*

$$R \propto l \text{ and } R \propto \frac{1}{a}$$

i.e., $$R \propto \frac{l}{a}$$

or $$R = \rho \cdot \frac{l}{a}$$

where, ρ is again a proportionality constant, called **specific resistance** or **resistivity.**

If $l = 1$ cm and $a = 1\text{ cm}^2$, then $R = \rho$.

Hence, specific resistance is defined as *the resistance of a conductor of* 1 *cm length and having a cross-sectional area of* 1 *cm*^{2}. The unit of specific resistance is *ohm-cm*.

The factor, $\frac{l}{a}$ is known as **cell constant** and is expressed in cm^{-1}.

The reciprocal of specific resistance is called *specific conductance*, *i.e., the conductance of a solution of* 1 *cm length and having* 1 *cm*^{2} *area of cross-section. It is denoted by* κ *(Kappa).*

$$\kappa = \frac{1}{R} \times \frac{l}{a}$$

or $$\kappa = C \times \frac{l}{a}$$

where, C and R are conductance and resistance respectively.

Units of specific conductance are **ohm^{-1} cm^{-1}** or **mho cm^{-1}** or **siemens m^{-1}** (in SI system). (IUPAC has recommended the use of term conductivity over specific conductance.)

The measurement of resistance of an electrolytic solution may be done with the help of a **conductivity cell** in a Wheatstone bridge.

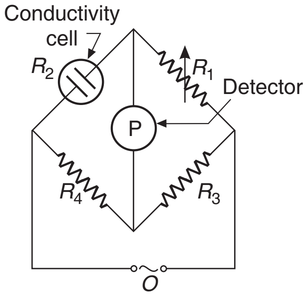


Fig. 3.1 Arrangement for measurement of resistance of a solution of an electrolyte

When null point is obtained, $\frac{R_1}{R_2} = \frac{R_3}{R_4}$

$$\text{Unknown resistance, } R_2 = \frac{R_1 R_4}{R_3}$$

Knowing the values of R_1, R_3 and R_4, R_2 can be calculated. Nowadays, inexpensive conductivity meters are available which can directly read the conductance or resistance of the solution in the conductivity cell.

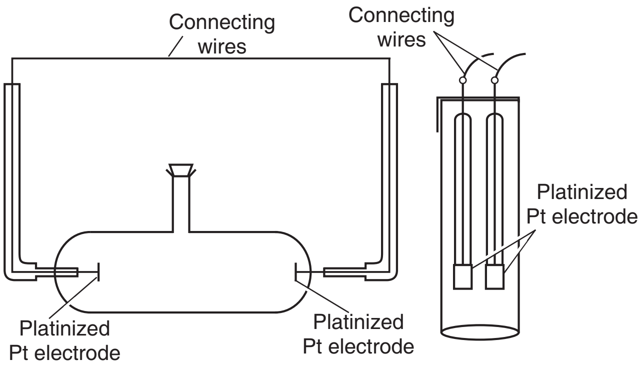


Fig. 3.2 Two different types of conductivity cells

Conductivity cell contains platinum electrodes of area of cross-section a and separated from each other by a distance l. The formula, $\kappa = C \times l/a$ for a conductivity cell is

$$\kappa = C \times C^*$$

where, C^* = cell constant = $\frac{l}{a}$

For a cell it is determined by measuring the resistance of the cell containing a solution whose conductivity is already known. *The Wheatstone bridge here is fed by an AC source and, not by the DC source which may changes the composition of solution taken.*

Caution Point *For accurate results, the solutions should be prepared in a specially purified water, conductance of which is very small. This water is called conductivity water.*

Sample Problem 1 *The resistance of a conductivity cell containing* 0.001 *M* KCl *solution at* 298 *K is* $1500\ \Omega$. *What is the cell constant if conductivity of* 0.001 M KCl *solution at* 298 *K is* 0.146×10^{-3} *S* cm^{-1}? **[NCERT]**

(*a*) $0.219\ cm^{-1}$
(*b*) $0.187\ cm^{-1}$
(*c*) $0.325\ cm^{-1}$
(*d*) $0.018\ cm^{-1}$

Interpret (*a*) $R = 1500\ \Omega;\ \kappa = 0.146 \times 10^{-3}\ \text{S cm}^{-1}$

$$\begin{aligned}\text{Cell constant} &= R \times \kappa \\ &= (1500\ \Omega) \times (0.146 \times 10^{-3}\ \text{S cm}^{-1}) = 0.219\ \text{cm}^{-1}\end{aligned}$$

Sample Problem 2 *When a certain conductivity cell was filled with* 0.020 *M* KCl *which has a specific conductivity* $0.2768\ \Omega^{-1}\ m^{-1}$, *it had a resistance of* $82.40\ \Omega$ *at* 25°C. *With* 0.0025 *M* K_2SO_4, *it has a resistance of* $326.0\ \Omega$. *The conductivity of* K_2SO_4 *solution is*

(*a*) 2.28
(*b*) 0.07
(*c*) 0.54
(*d*) 0.005

Interpret (*b*) $\kappa = \frac{\text{cell constant}}{R}$

$$\begin{aligned}\therefore \quad \text{Cell constant} &= \kappa \times R \\ &= 0.2768 \times 82.4 \\ &= 22.81\ \text{m}^{-1}\end{aligned}$$

$$\therefore \ \text{Specific conductance of } K_2SO_4, \kappa_{K_2SO_4} = \frac{22.81}{326} = 0.07\ \Omega^{-1}\ \text{m}^{-1}$$

Molar Conductivity

The conducting power of all the ions produced by dissolving 1 g-mole of an electrolyte in solution is called **molar conductivity** of that solution. It is denoted by λ_m or μ and is related to specific conductance (κ) as :

$$\lambda_m \text{ or } \mu = \frac{\kappa \times 1000}{M}$$

where, M = concentration in mol/L, *i.e.,* molarity of the solution

Its units are $\mathbf{ohm^{-1}\ cm^2\ mol^{-1}}$ or $\mathbf{mho\ cm^2\ mol^{-1}}$ or $\mathbf{S\ cm^2\ mol^{-1}}$.

Sample Problem 3 *The conductivity of* 0.20 *M solution of* KCl *at* 298 *K is* 0.0248 *S* cm^{-1}. *Its molar conductivity is* **[NCERT]**

(*a*) $1.24\ \Omega^{-1}\ mol^{-1}\ cm^2$
(*b*) $124\ S\ mol^{-1}\ cm^2$
(*c*) $12.4\ \Omega^{-1}\ mol^{-1}\ cm^2$
(*d*) $0.124\ S\ mol^{-1}\ cm^2$

Interpret (*b*) $\mu = \frac{\kappa \times 1000}{m} = \frac{0.0248 \times 1000}{0.20}$

$$= 124\ \text{S mol}^{-1}\ \text{cm}^2$$

Sample Problem 4 *The electrical resistance of a column of* 0.05 M NaOH *solution of diameter* 1 cm *and length* 50 cm *is* 5.55×10^3 *ohm. Calculate its molar conductivity.* **[NCERT]**

(a) 114.8 $S\ cm^2\ mol^{-1}$ (b) 229.6 $S\ cm^2\ mol^{-1}$
(c) 346.9 $S\ cm^2\ mol^{-1}$ (d) 175.3 $S\ cm^2\ mol^{-1}$

Interpret (b) Area (a) $= \pi r^2 = 3.14 \times \left(\frac{1\text{ cm}}{2}\right)^2$

$$= 0.785\text{ cm}^2$$

$$l = 50\text{ cm}$$

$$R = \frac{\rho l}{a} \quad \text{or} \quad \rho = \frac{Ra}{l} = \frac{5.55 \times 10^3\text{ ohm} \times 0.785\text{ cm}^2}{50\text{ cm}}$$

$$= 87.135\text{ ohm cm}$$

$$\text{Conductivity } (\kappa) = \frac{1}{\rho} = \left(\frac{1}{87.135}\right)\text{ S cm}^{-1}$$

$$= 0.01148\text{ S cm}^{-1}$$

$$\text{Molar conductivity } (\lambda_m) = \frac{\kappa \times 100}{M}\text{ cm}^2\text{ L}^{-1}$$

$$= \frac{0.01148\text{ S cm}^{-1} \times 1000\text{ cm}^3\text{ L}^{-1}}{0.05\text{ mol L}^{-1}}$$

$$= 229.6\text{ S cm}^2\text{ mol}^{-1}$$

Equivalent Conductivity

The conducting power of all the ions produced by dissolving 1 g-equivalent of an electrolyte in solution is called its **equivalent conductivity.** It is denoted by λ_{eq} or Λ.

It is related to specific conductance as,

$$\lambda_{eq} \text{ or } \Lambda = \frac{\kappa \times 1000}{C_{eq}\,(N)}$$

where, C_{eq} = concentration of solution in equivalent per litre (*i.e.,* normality)

Its units are **ohm $^{-1}$ cm ^{2}** (equiv^{-1}) or **mho cm ^{2}** (equiv^{-1}). or **S cm ^{2}** (g- equiv^{-1}).

Sample Problem 5 *The resistance of a decinormal solution of a salt occupying a volume between two platinum electrodes* 1.80 cm *apart and* 5.4 cm^2 *in area was found to be* 50 *ohm. The equivalent conductance of the solution is*

(a) 6.66 (b) 66.7
(c) 0.667 (d) 57.8

Interpret (b) Given, $C = \frac{1}{\text{resistance}} = \frac{1}{50}\text{ ohm}^{-1} = 0.02\text{ S}$

$$\text{Cell constant} = \frac{l}{a} = \frac{\text{distance}}{\text{area}} = \frac{1.80}{5.40} = \frac{1}{3}\text{ cm}^{-1}$$

Normality = 0.1 N

$$\therefore \quad \Lambda_{eq} = \frac{1000 \times \text{conductance} \times \text{cell constant}}{\text{concentration (normality)}}$$

$$= \frac{1000 \times 0.02}{0.1} \times \frac{1}{3}$$

$$= 66.66\text{ S cm}^2\text{ equivalent}^{-1}$$

Effect of Nature of Electrolyte over Conductivity

The conductivity of an electrolyte depends upon the **nature of electrolyte** as the conductivity of strong electrolytes is higher in comparison to weak electrolytes. The reason for such a difference is difference in availability of ions present in their solutions. Strong electrolytes dissociate completely, hence more ions are present in their solutions resulting to higher conductivity. Weak electrolytes, on the other hand, dissociate less, hence less ions are present in their solutions resulting to lesser conductivity.

Variation of Conductivity with Dilution (or Concentration)

For both weak and strong electrolytes, the electrolytic conductance as well as the equivalent conductivity (Λ_{eq}) and molar conductivity (Λ_m) increase with dilution. This is because the total volume V of a solution containing 1 g equivalent or 1 mole of electrolyte also increases. It may be noted that decrease in κ on dilution of a solution is more than that compensated by increase in its volume.

Conductivity (or specific conductivity, κ) always decreases with dilution, both for weak and strong electrolytes.

This is due to the fact that the total number of ions in the solution increases on dilution but the number of ions per unit volume that carry the current in the solution decreases on dilution.

(a) For Strong Electrolytes

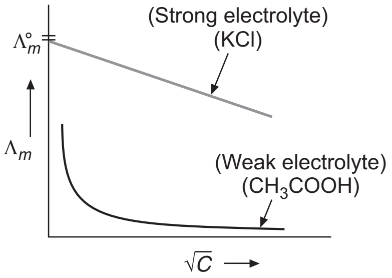
The Λ_{eq} or Λ_m of strong electrolyte increases slowly with dilution and can be represented by **Debye Huckel-Onsager equation**

$$\Lambda^c_{eq} = \Lambda^\circ_{eq} - b\sqrt{c} \quad \text{or} \quad \Lambda^c_{eq} = \Lambda^\infty_{eq} - b\sqrt{c}$$

$$\Lambda^c_m = \Lambda^\circ_m - b\sqrt{c} \quad \text{or} \quad \Lambda^c_m = \Lambda^\infty_m - b\sqrt{c}$$

If a plot of Λ_{eq} or Λ_M against $\sqrt{c}$ is plotted (as shown in figure), a straight line with intercept equal to Λ°_{eq} or Λ°_m and a slope equal to $-b$ is obtained at lower concentration, but it is not linear for higher concentration. The value of the constant b for a given solvent and temperature depends on the type of electrolytes, *i.e.,* the charges on the cation and anion produced during the dissociation of the electrolyte in the solution.

Therefore, electrolytes of a particular type have the same value of *b*. *e.g.,* $CaSO_4$ and $MgSO_4$ (2–2 type) have the same value of *b*.



Moreover, the curve obtained for a strong electrolyte shows that there is a small increase in Λ_{eq}, or Λ_m with dilution. This is because a strong electrolyte is completely ionized in solution and so the number of ions remains almost constant.

At higher concentration, the greater inter-ionic interaction decreases the movement of the ions and therefore, conductance decreases with increasing concentration.

On dilution, the ions are far apart, and therefore inter-ionic attraction decreases and hence, conductance increases and approaches a maximum limiting value at infinite dilution.

It is also observed that the plot for a strong electrolyte becomes linear near high dilution and can be extrapolated to zero concentration to get the value of Λ_m° or Λ_{eq}°. (Conductivity at infinite dilution).

(b) For Weak Electrolytes

The conductance of weak electrolytes is less than that of strong electrolytes at the same concentration since weak electrolytes are not completely ionized. Moreover, the curve for weak electrolytes shows that there is a very large increase in the conductance with dilution near the infinite dilution since on dilution the degree of ionization increases. Thus, an increase in conductance with dilution is due to the increase in the number of ions in the solution. However, it does not reach a limiting value.

For a weak electrolyte, Λ_m or Λ_{eq} increases sharply near high dilution. Hence, an extrapolation at infinite dilution is not possible. Experimentally, it is also not possible to determine the Λ_{eq}° or Λ_m° value for a weak electrolyte because although the ionization is complete but the number of ions per unit volume is so low that the conductivity cannot be measured accurately.

This problem was solved by Kohlrausch who gave a law known as Kohlrausch law of independent migration of ions.

Hot Spot 1

KOHLRAUSCH's Law

It is a very important topic for JEE Main examination. The questions based on this topic are generally numerical type and their level vary from easy to difficult.

According to **Kohlrausch law,** the molar conductivity of an electrolyte at infinite dilution is the sum of molar conductivity of ions produced by the electrolyte at infinite dilution. In other words, we can say that the **sum of molar conductivity of cation and anion at infinite dilution is called molar conductivity of electrolyte,** *e.g.*, if μ_c^∞ and μ_a^∞ are the molar conductivities of cations and anions at infinite dilution then

$$\mu_\infty = n^+ \times \mu_c^\infty + n^- \times \mu_a^\infty$$

where, n^+ and n^- are the number of cations and anions respectively.

(The multiplication of number of ions with molar conductivity of a particular ion is called **molar ionic conductance** of that particular ion.)

In terms of equivalent conductivities, Kohlrausch's law is defined as, **the equivalent conductivity of an electrolyte at infinite dilution is the sum of two values one depending upon the cation and other on anion,** *i.e.,*

$$\Lambda_{eq}^\circ = \lambda_c^\circ + \lambda_a^\circ$$

here, λ_c° and λ_a° are limiting equivalent or ionic conductivities of cation and anion respectively.

Some important applications of Kohlrausch's law are as follows

(a) Calculation of Λ_m° or Λ_{eq}°

This law is helpful in calculation of molar conductance at infinite dilution for weak electrolytes. Suppose, we have to calculate the limiting conductance for CH_3COOH.

Then, according to Kohlrausch's law

$$\mu^\infty_{(CH_3COOH)} = \mu^\infty_{(CH_3COO^-)} + \mu^\infty_{(H^+)} \qquad \text{...(i)}$$

This equation can be obtained by the knowledge of molar conductance at infinite dilution for some strong electrolytes, *i.e.*,

$$\mu^\infty_{(CH_3COO^-Na^+)} = \mu^\infty_{(CH_3COO^-)} + \mu^\infty_{(Na^+)} \qquad \text{...(ii)}$$

$$\mu^\infty_{(HCl)} = \mu^\infty_{(H^+)} + \mu^\infty_{(Cl^-)} \qquad \text{...(iii)}$$

$$\mu^\infty_{(NaCl)} = \mu^\infty_{(Na^+)} + \mu^\infty_{(Cl^-)} \qquad \text{...(iv)}$$

The above Eq. (i) can be obtained by adding Eqs. (ii) and (iii) and subtracting Eq. (iv) from them, *i.e.*,

$$\mu^\infty_{(CH_3COOH)} = \mu^\infty_{(CH_3COONa)} + \mu^\infty_{(HCl)} - \mu^\infty_{(NaCl)}$$

Sample **Problem 6** *Λ_m° for* NaCl, HCl, *and* NaAc *are* 126.4, 425.9, *and* 91.0 *S* cm^2 *mol*$^{-1}$, *respectively. Calculate* Λ° (*S* cm^2 *mol*$^{-1}$) *for* HAc. **[NCERT]**

(*a*) 390.5 (*b*) 180.3 (*c*) 420.2 (*d*) 350.5

Interpret (*a*) $\Lambda^\circ_{m(HAc)} = \Lambda^\circ_{m(HCl)} + \Lambda^\circ_{m(NaAc)} - \Lambda^\circ_{m(NaCl)}$

$$= (425.9 + 91.0 - 126.4)\ \text{S cm}^2\ \text{mol}^{-1}$$

$$= 390.5\ \text{S cm}^2\ \text{mol}^{-1}$$

Sample **Problem 7** 0.1 *M* H_2SO_4 *is diluted to* 0.01 *M* H_2SO_4. *Hence, its molar conductance will be*

(*a*) 10 *times* (*b*) $\frac{1}{10}$ *th*

(*c*) 100 *times* (*d*) 10000 *times*

Interpret (*a*)

$$\lambda_m = \frac{\kappa \times 1000}{M}$$

$$\frac{(\lambda_m)_i}{(\Lambda_m)_f} = \frac{M_f}{M_i}$$

$$\frac{(\Lambda_m)_i}{(\Lambda_m)_f} = \frac{0.01}{0.1}$$

$$(\lambda_m)_i = 0.1 \times (\Lambda_m)_f$$

$$\therefore \quad (\Lambda_m)_f = 10 \times (\Lambda_m)_i$$

(b) Calculation of α

For calculating degree of dissociation, α of weak electrolyte, the formula used is

$$\alpha = \frac{\mu^c}{\mu^\infty}$$

where, α = degree of dissociation

μ^c = molar conductance at any concentration

μ^∞ = molar conductance at infinite dilution

(c) Calculation of K_a

It is helpful in determination of the ionisation constant of a weak electrolyte, as we can calculate α from it.

Sample **Problem 8** *The molar conductivity of* 0.025 *mol* L^{-1} *methanoic acid is* 46.1 *S* cm^2 *mol*$^{-1}$. *Its dissociation constant is* [*Given,* $\lambda^\circ(H^+) = 349.6$ *S* cm^2 *mol*$^{-1}$ *and* $\lambda^\circ(HCOO^-) = 54.6$ *S* cm^2 *mol*$^{-1}$] **[NCERT]**

(*a*) 2.89×10^{-4} (*b*) 1.87×10^{-3}

(*c*) 3.67×10^{-4} (*d*) 4.28×10^{-3}

Interpret (*c*) ***Step I*** **Calculation of degree of dissociation (α) of HCOOH**

$$\Lambda_m^c = 46.1\ \text{S cm}^2\ \text{mol}^{-1}$$

$$\Lambda^\circ_{m(\text{HCOOH})} = \lambda^\circ_{m(\text{HCOO}^-)} + \lambda^\circ_{m(\text{H}^+)}$$

$$= (54.6 + 349.6)\ \text{S cm}^2\ \text{mol}^{-1}$$

$$= 404.2\ \text{S cm}^2\ \text{mol}^{-1}$$

$$\alpha = \frac{\Lambda^c_m}{\Lambda^\circ_m} = \frac{(46.1)\ \text{S cm}^2\ \text{mol}^{-1}}{(404.2)\ \text{S cm}^2\ \text{mol}^{-1}} = 0.1140$$

Step II **Calculation of dissociation constant**

$$\text{HCOOH}(aq) \overset{\text{Water}}{\rightleftharpoons} \text{HCOO}^-(aq) + \text{H}^+(aq)$$

	HCOOH	HCOO⁻	H⁺
Initial conc.	C	0	0
Equilibrium conc.	$C(1-\alpha)$	$C\alpha$	$C\alpha$

$$\text{Dissociation constant, } K_a = \frac{[\text{HCOO}^-][\text{H}^+]}{[\text{HCOOH}]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

$$\text{Placing values } K_a = \frac{(0.025\ \text{mol L}^{-1}) \times (0.114)^2}{(1-0.114)}$$

$$= \frac{(3.249 \times 10^{-4}\ \text{mol L}^{-1})}{(0.886)}$$

$$= 3.67 \times 10^{-4}\ \text{mol L}^{-1}$$

(d) Determination of the Solubility of a Sparingly Soluble Salt

If a salt is very less soluble in the given solvent, its molar or equivalent conductivity at some concentration is taken as its molar or equivalent conductivity at infinite dilution.

$$\text{Thus,}\quad \lim_{c \to 0} \Lambda^c_m = \Lambda^\circ_m \quad \text{and} \lim_{c \to 0} \Lambda^\circ_{\text{eq}} = \Lambda^\circ_{\text{eq}}$$

$$\text{Thus,}\quad \lim_{c \to 0} \Lambda^c_m = \Lambda^\circ_m = \frac{\kappa \times 100}{M} \quad \text{or} \quad \frac{\kappa \times 1000}{S}$$

(S = solubility in mol L^{-1})

$$\lim_{c \to 0} \Lambda^c_{\text{eq}} = \Lambda^\circ_{\text{eq}} = \frac{\kappa \times 1000}{N} \quad \text{or} \quad \frac{\kappa \times 1000}{S}$$

(S = solubility in eq L^{-1})

Λ°_m or $\Lambda^\circ_{\text{eq}}$ can be computed using Kohlrausch's law.

Thus, S can be computed and can be used to calculate the solubility product. For example, for A_xB_y if S mol L^{-1} is the solubility, then

$$K_{\text{sp}} = x^x y^y S^{x+y}$$

Sample **Problem 9** *For a saturated solution of* AgCl *at* $25°$,*C specific conductance is* 3.41×10^{-6} *ohm*$^{-1}$ *cm*$^{-1}$ *and that of water used for preparing the solution was* 1.60×10^{-6} *ohm*$^{-1}$ *cm*$^{-1}$. *The solubility product of* AgCl *is* [$\Lambda^\infty_{\text{eq}}$ (AgCl) = 138.3 *ohm*$^{-1}$ *cm*$^{-1}$ *equiv*$^{-1}$]

(a) 1.31×10^{-5} (b) 1.74×10^{-8}
(c) 1.72×10^{-10} (d) 3.61×10^{-3}

Interpret (c) For AgCl, molarity = normality

Actual specific conductance = (specific conductance of AgCl − specific conductance of water)

$$= (3.41 - 1.60) \times 10^{-6}$$

$$= 1.81 \times 10^{-6}\ \text{ohm}^{-1}\ \text{cm}^{-1}$$

For saturated solution of sparingly soluble salt,

$$\Lambda_{\text{eq}} = \Lambda^\infty_{\text{eq}}, \text{ and solubility = concentration}$$

$$\Lambda^\infty_{\text{eq}} = \frac{1000 \times \text{specific conductance}}{\text{solubility}}$$

$$\therefore \quad 138.3 = \frac{1000 \times 1.81 \times 10^{-6}}{S}$$

$$S\ (\text{mol L}^{-1}) = \frac{1000 \times 1.81 \times 10^{-6}}{138.3}$$

$$= 1.31 \times 10^{-5}\ \text{mol L}^{-1}$$

$$\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$$

$$\therefore \quad K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = S^2$$

$$= (1.31 \times 10^{-5})^2$$

$$= 1.72 \times 10^{-10}\ \text{mol}^2\ \text{L}^{-2}$$

Sample **Problem 10** *Equivalent conductance of* BaCl_2, H_2SO_4 *and* HCl *are* x_1, x_2 *and* x_3 *S cm*^{2} *equiv*$^{-1}$ *at infinite dilution. If specific conductance of saturated* BaSO_4 *solution is* y *S cm*$^{-1}$ *then* K_{sp} *of* BaSO_4 *is*

(a) $\dfrac{10^3 y}{2(x_1 + x_2 - 2x_3)}$ (b) $\dfrac{10^6\, y^2}{(x_1 + x_2 - 2x_3)^2}$

(c) $\dfrac{10^6 y^2}{4(x_1 + x_2 - 2x_3)^2}$ (d) $\dfrac{x_1 + x_2 - 2x_3}{10^6\, y^2}$

Interpret (c) $\Lambda_{\text{BaSO}_4} = \Lambda_{\text{BaCl}_2} + \Lambda_{\text{H}_2\text{SO}_4} - 2 \times \Lambda_{\text{HCl}}$

$$= x_1 + x_2 - 2x_3$$

$$\Lambda_{\text{BaSO}_4} = \frac{1000 \times \kappa}{\text{normality}}$$

$$\therefore \quad \text{Normality} = \frac{10^3 \times y}{x_1 + x_2 - 2x_3}$$

$$\text{Molarity} = \frac{10^3 \times y}{2(x_1 + x_2 - 2x_3)}$$

$$\text{For BaSO}_4, \quad K_{\text{sp}} = (s)^2 = \left[\frac{10^3 \times y}{2(x_1 + x_2 - 2x_3)}\right]^2$$

$$= \frac{10^6 y^2}{4(x_1 + x_2 - 2x_3)^2}$$

Transport Number

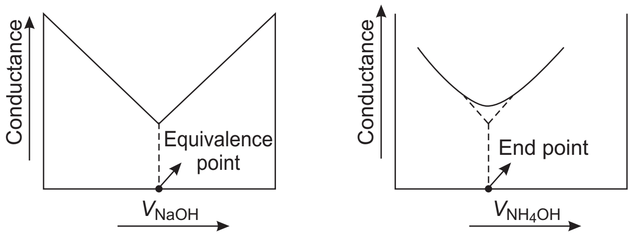
Transport number or transference number is defined as the fraction of the current carried by an ion.

$$\text{Transport number} = \frac{\text{current carried by ion}}{\text{total current carried}}$$

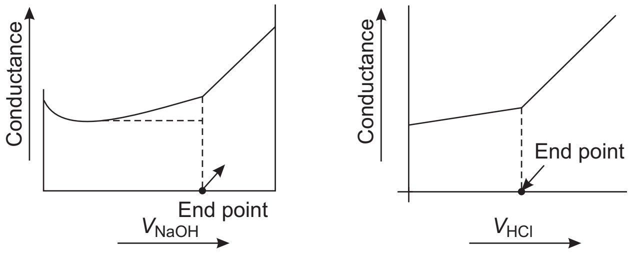
Transport no. of cation + Transport no. of anion = 1

Conductometric Titration

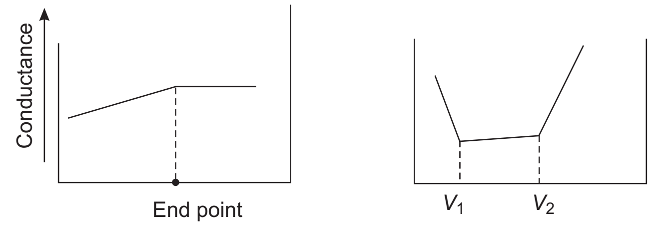
The measurement of conductance of resulting solution from an acid and base titration is used to calculate equivalence point if there is a regular change in the conductance and sharp change at equivalence point. For various titrations, conductometric curves are as follows



(a) For strong acid *vs* strong base (b) For strong acid *vs* weak base



(c) For weak acid *vs* strong base (d) For strong acid *vs* weak base



(e) For weak acid *vs* weak base (f) For a mixture of weak and strong acids *vs* strong base

Fig. 3.3 Titration curves

Check Point 1

1. Solid NaCl does not conduct electricity but an aqueous solution of NaCl or molten NaCl conducts electricity. Explain.
2. At infinite dilution, every ion makes an independent contribution to the total conductivity of solution, why? [**Hints** because of no interionic attraction]
3. Specific conductivity decreases while equivalent conductivity increases with dilution. Explain.
4. Why is it necessary to use AC current for the measurement of the conductivity of the solution?
5. At infinite dilution, the conductance of weak as well as strong electrolytes are same, why?
6. At 50°C, the conductivity of a weak electrolyte is *x* and at 100°C, the conductivity of the same electrolyte is *y*. Find the correct relation between *x* and *y* and also give the appropriate reason.
7. For weak electrolytes, dilution increases equivalence conductance very slowly in higher concentration range but steep rise is observed as concentration approaches to zero-why?

3.3 Electrochemical Cells

Electrochemical cells are the devices in which inter-conversion of electrical energy and chemical energy takes place. *Electrochemical cells are of two basic types*

(i) Electrolytic cell (ii) Galvanic cell

Electrolytic Cell

In an electrolytic cell a chemical reaction is carried out with the help of an external source of electric current. Therefore, in an electrolytic cell, electrical energy is converted into chemical energy. Here a non-spontaneous redox reaction is forces to take place with the help of external current. Like galvanic cell, here also, anode is the site of oxidation and cathode is the site of reduction. An example of non-spontaneous redox reaction which is carried out in an electrolytic cell is

Electrolysis of Molten NaCl

$$\text{NaCl(molten)} \longrightarrow \text{Na}^+ + \text{Cl}^-$$

At anode

$$2\text{Cl}^- + 2\,e^- \longrightarrow \text{Cl}_2\uparrow$$

At cathode

$$2\text{Na}^+ + 2\,e^- \longrightarrow 2\text{Na}(l)$$

Thus, Cl_2 and Na are the products of electrolysis of molten NaCl.

Preferential Discharge Theory

According to this theory if more than one type of ions are attracted towards a particular electrode then the one discharged is the ion which requires least energy. The potential at which the ion is discharged or deposited on the appropriate electrode is termed as the discharge or deposition potential. The values of discharge potential are different for different ions. For example, the discharge potential of H^+ ions is lower than Na^+ ions when platinum or most of the other metals are used as cathodes. Similarly, discharge potential of Cl^- ions is lower than that of OH^- ions. *This can be explained by some examples given below.*

Electrolysis of Aqueous NaCl

In case of aqueous NaCl, H_2O is also present along with Na^+ and Cl^- ions. On passing electricity, the following reactions takes place

At anode

$$2\text{Cl}^-(aq) \longrightarrow \text{Cl}_2(g) + 2\,e^-; \qquad E^\circ = -1.36\text{ V}$$
$$2\text{H}_2\text{O}(l) \longrightarrow \text{O}_2(g) + 4\text{H}^+(aq) + 4\,e^-; \quad E^\circ = -1.23\text{ V}$$

If the solution of NaCl is concentrated, Cl_2 is the main product. However, if it is quite dilute, the product is O_2 instead of Cl_2. This is because of overvoltage.

(From experiments, it was found that the applied voltage required is always higher than that calculated from the standard oxidation and reduction potentials. The additional voltage required is called the overvoltage).

At cathode

$$2Na^+ + 2e^- \longrightarrow 2Na \qquad E^\circ = -2.71\text{ V}$$
$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \quad E^\circ = -0.83\text{ V}$$

Similar to above, in case of dilute NaCl solution, here also, the product is H_2 instead of Na due to overvoltage.

However, if cathode is made up of mercury, Na-Hg is the main product as Na is soluble in Hg and the overpotential of hydrogen is higher on mercury. In such case, on hydrolysis NaOH is obtained as main product.

$$2\text{Na-Hg} + 2H_2O \longrightarrow 2NaOH + 2Hg + H_2$$

Caution Point *When* Hg *is used as a cathode,* Na^+ *ions have lower discharge potential than* H^+ *ions.*

Electrolysis of Aqueous $CuSO_4$ Solution

(i) **With inert electrodes like Pt**

At anode

$$2SO_4^{2-}(aq) \longrightarrow S_2O_8^{2-}(aq) + 2e^-; \quad E^\circ = 1.96\text{ V}$$
$$2H_2O(l) \longrightarrow O_2(g) + 4H^+ + 4e^-; E^\circ = -1.23\text{ V}$$

At cathode

$$2H_2O(l) + 2e^- \longrightarrow H_2 + 2OH^-; \quad E^\circ = -0.83\text{ V}$$
$$2Cu^{2+}(aq) + 4e^- \longrightarrow 2Cu(s); \quad E^\circ = +0.337\text{ V}$$

Thus, the main products of electrolysis of aqueous (dilute) solution of $CuSO_4$ are Cu and O_2.

This reaction follows the principle of electrolysis and due to electrolysis, the blue colour of the $CuSO_4$ solution gradually fades.

(b) **With copper electrodes**

At anode

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-; \quad E^\circ = -0.337\text{ V}$$

At cathode

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s); \qquad E^\circ = +0.337\text{ V}$$

For this process only a very slight voltage is required. The concentration of the solution remains unchanged. This makes the basis of purification of metals, called electrorefining.

Infact, this whole process involves the transference of copper from anode to cathode.

Sample **Problem 11** *A dilute aqueous solution of* H_2SO_4 *is electrolysed using* Pt *electrodes. The products at the anode and cathode are*

(a) O_2, H_2 (b) $S_2O_8^{2-}$, Na (c) O_2, Na (d) $S_2O_8^{2-}$, H_2

Interpret (a) When dilute aqueous solution of H_2SO_4 is subjected to electrolysis following reactions take place at cathode and anode

At anode

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$$
$$2SO_4^{2-} \longrightarrow S_2O_8^{2-} + 2e^-$$

At cathode

$$2H^+ + 2e^- \longrightarrow H_2$$

Thus, O_2 and H_2 are the main products.

Caution Point *When an aqueous solution of a salt is electrolysed if metal has –ve reduction potential less than –0.83 V,* H_2O *is reduced at cathode liberating* $H_2(g)$, *leaving behind metal ion intact in the solution. On the other hand, if anion is nitrate or sulphate,* H_2O *is oxidized at anode liberating* $O_2(g)$.

Faraday's Laws of Electrolysis

Faraday was the first scientist who described the quantitative aspect of electrolysis. He gave two laws of electrolysis, which in their modern combined version may be stated as *"The amount of electricity* (or charge) *required for oxidation or reduction depends upon stoichiometry of the electrode reaction".* However, their previous forms was as follows

Faraday's first law states, "mass of any substance deposited or liberated at any electrode is directly proportional to the quantity of electricity passed" *i.e.,*

$$w = Zit$$

where, w = substance deposited (in gram)
$i \times t$ = electricity passed per unit time
Z = proportionality constant, also called electrochemical equivalent

This electrochemical equivalent is defined as the mass of substance deposited when 1 C electricity is passed through a solution. It can be calculated as

$$Z = \frac{\text{equivalent weight of substance}}{96500}$$

Here, 96500 is called *Faraday's constant.* It is basically the charge on 1 mole of electrons. Its exact value is 96487 and with approximation we take it 96500.

Sample **Problem 12** *If a current of* 0.5 *A flows through a metallic wire for 2 h, then how many electrons would flow through the wire?* **[NCERT]**

(a) 6.022×10^{23} (b) 1.202×10^{22}
(c) 2.246×10^{22} (d) 3.02×10^{24}

Interpret (c)

$$\text{Quantity of charge } (Q) \text{ passed} = \text{Current (C)} \times \text{Time } (t)$$
$$= (0.5\text{A}) \times (2 \times 60 \times 60\text{ s})$$
$$= (3600)\text{ A-s} = 3600\text{ C}$$

Number of electrons flowing through the wire on passing charge of one Faraday (96500 C) $= 6.022 \times 10^{23}$

Number of electrons flowing through the wire on passing a charge of 3600 C

$$= \frac{6.022 \times 10^{23} \times (3600\ \text{C})}{(96500\ \text{C})}$$

$$= 2.246 \times 10^{22}$$

Number of electrons $= 2.246 \times 10^{22}$

Sample Problem 13 10800 *C of electricity on passing through the electrolyte solution deposited* 2.977 g *of metal with atomic mass* 106.4 g mol^{-1}. *The charge on the metal cation is*

(a) +2 (b) +3 (c) +4 (d) +1

Interpret (c) $E = \frac{w \times 96500}{i \times t} = \frac{2.977 \times 96500}{10800}$

$$= 26.6\ \text{g equi}^{-1}$$

$$\therefore \quad \text{Valency} = \frac{\text{at. wt.}}{\text{eq. wt.}} = \frac{106.4}{26.6} = 4$$

Faraday's second law states, "When same quantity of electricity is passed through solutions of different electrolytes connected in series, the weight of substance produced at the electrodes is directly proportional to their equivalent weights" *i.e.,*

$$\frac{\text{Wt. of Cu deposited}}{\text{Wt. of Ag deposited}} = \frac{\text{Eq. wt. of Cu}}{\text{Eq. wt. of Ag}}$$

The above formula can be given when $CuSO_4$ and $AgNO_3$ solutions are connected in series and same quantity of electricity is passed through them.

Now suppose for electrode reactions,

$$Mg^{2+}(l) + 2e^- \longrightarrow Mg(s)$$

$$Al^{3+}(l) + 3e^- \longrightarrow Al(s)$$

the requirement of electrons is 2 moles and 3 moles respectively for completion, *i.e.,* 2 Faraday and 3 Faraday. Similarly for the electrode reaction,

$$Ag^+(aq) + e^- \longrightarrow Ag(s)$$

only 1 mole (1F) of electricity is required for completion. Thus, the requirements of electricity (or charge) is electrode reaction oriented and varies with the change in electrode reactions.

Sample Problem 14 *In an aqueous solution* $AgNO_3$ *and* $CuSO_4$ *are connected in series. If* Ag *deposited at cathode is* 1.08 g *then* Cu *deposited is*

(a) 0.5326 g (b) 0.818 g (c) 0.264 g (d) 0.317 g

Interpret (d) Eq. of Ag = Eq. of Cu

$$\frac{1.08}{108} = \frac{w_{Cu}}{63.5/2}$$

$$W_{Cu} = \frac{63.5 \times 1.08}{2 \times 108} = 0.3175\ \text{g}$$

Current Efficiency

Sometimes the ammeter shows false current due to mechanical fault. In this case,

$$\%\ \text{Current efficiency} = \frac{\text{Actual current}}{\text{Ammeter current}} \times 100$$

Thickness of Coated Layer

Let the dimensions of metal sheet to be coated $= (a\ \text{cm} \times b\ \text{cm})$.

Thickness of coated layer $= c$ cm

Volume of coated layer $= (a \times b \times c)\ \text{cm}^3$

Mass of the deposited substance = volume × density

$$= (a \times b \times c) \times d\ \text{g}$$

$$\therefore \quad (a \times b \times c) \times d = \frac{I \times t \times E}{96500}$$

Using above relation we may calcualte the thickness of coated layer.

Galvanic (Voltaic) Cell

In a galvanic cell, some spontaneous redox reaction takes place producing electric current. Therefore, in galvanic cell, chemical energy is converted into electrical energy. An example of galvanic cell is Daniell cell. *In this cell,*

At cathode $Cu^{2+}(aq) + 2e^- \longrightarrow Cu$ (Reduction)

At anode $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$ (Oxidation)

Overall $Cu^{2+} + Zn(s) \longrightarrow Cu + Zn^{2+}(aq)$

The change of chemical energy to electrical energy causes lowering of free energy, which appears as electrical energy and measured in terms of emf.

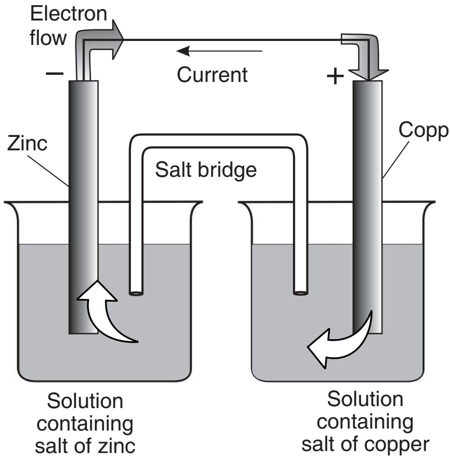


Fig. 3.4 Daniell cell having electrodes of Zn and Cu dipping in the solutions of their respective salts

In galvanic cell, chemical reactions takes place in two compartments, each of which is called a **half-cell** and contains a suitable electrolyte and electrodes.

The solution in two compartments is connected through an inverted U shaped tube containing a mixture of agar-agar jelly and an electrolyte like KCN or KNO_3 or NH_4NO_3 (inert electrolyte) etc. This U tube connecting the two compartments is called **salt bridge.**

The significance of salt bridge includes

1. It connects the solution of two half-cells, thus completes the cell circuit.
2. It prevents transference or diffusion of the solutions from one half-cell to other.
3. It helps in keeping the solution in two half-cells electrically neutral, *i.e.,* it provides negative ions to anodic half-cell, thus preventing the accumulation of extra positive charge in the solution and around anode which normally hinders the flow of electrons from anode. Similarly, in cathodic half-cell, it provides positive ions to prevent the accumulation of extra negative ions in this half.
4. It prevents **liquid-liquid junction potential,** *i.e.,* the potential difference which arises between two solutions when these are in contact with each other due to different movement of ions.

Characteristics of electrolyte used as salt bridge are

1. The electrolyte should be inert and should not react chemically with the electrolyte of either of the two half cells.
2. The cation as well as anion of the electrolyte should have same ionic mobility and almost same transport number, *viz.*, KCl, KNO_3, NH_4NO_3, etc.

The salt bridge can be replaced by a porous partition like a paper strip, clay porous pot, unglazed porcelain or asbestos fibre which allows the migration of ions without allowing the solutions to intermix.

The electrochemical cells may be **reversible** or **irreversible.** A cell is considered as reversible if

(i) The chemical reaction of cell stops when an exactly equal opposing emf is applied.

(ii) The chemical reaction of the cell is reversed and current flows in opposite direction when opposing emf is slightly greater than that of the cell.

Any other cell which does not obey above two conditions is called **irreversible cell,** *e.g.,* a cell consisting of Zn and Cu electrodes dipped in H_2SO_4 is irreversible.

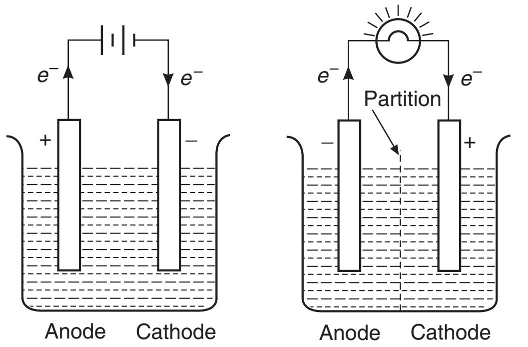
Difference between Electrolytic and Electrochemical Cells

The main points of difference between these two cells are

1. The device in which electrolysis (chemical reaction involving oxidation and reduction) is carried out by using electricity or in which conversion of electrical energy into chemical energy is done is called electrolytic cell while **galvanic** or **voltaic** cell is a device in which **redox** reaction is used to convert chemical energy to electrical energy.
2. In 'electrolytic cell', anode is positive electrode, while cathode is negative electrode. On the other hand, in 'galvanic cell' anode is negative electrode and cathode is positive electrode.

Caution Point *In both the cells anode is always the site of oxidation and cathode is of reduction.*

3. In electrolytic cell, ions are discharged at both the electrodes, while in galvanic cell ions are discharged only at cathode.
4. In electrolytic cell, both the electrodes are fitted in same compartment, while in galvanic cell both the electrodes are fitted in different compartments.



(a) Electrolytic cell (emf is applied to cell)

(b) Voltaic or galvanic cell (emf is generated by cell)

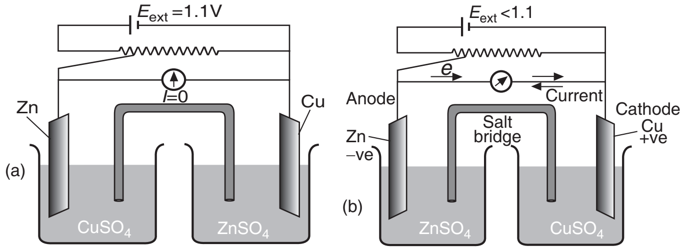
Fig. 19.5

5. Besides salt bridge in both the cells, both the electrodes are connected externally with the help of a wire connected through a voltmeter. Flow of current and electrons occur through this wire.

3.4 Daniell Cell

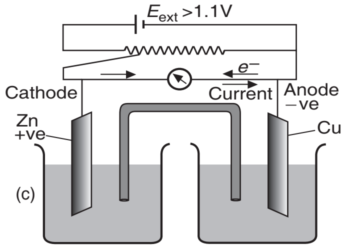
Among the galvanic cells when cell is designed in such a manner to make the use of spontaneous reaction between Zn and Cu ions to produce an electric current, the cell is called **Daniell cell.**

In **Daniell cell,** the anode is made up of Zn rod and dipped in a solution of $ZnSO_4$ (electrolyte). Similarly, the cathode is made up of Cu rod and dipped in the solution of $CuSO_4$.



When E_{ext} =1.1V
(i) No flow of electrons or current
(ii) No chemical reaction.

When E_{ext}<1.1V
(i) Electrons flow from Zn rod to Cu rod, hence current flows from Cu to Zn
(ii) Zn dissolves at anode and copper deposits at cathode.



When E_{ext} >1.1V
(i) Electrons flow from Cu to Zn and current flows from Zn to Cu
(ii) Zinc is deposited at the zinc electrode and copper dissolves at copper electrode.

Fig. 3.6 Functioning of Daniell cell when external voltage (E_{ext}) opposing the cell potential is applied

When the Zn and Cu electrodes are joined by a wire, the following observations are noted :

1. There is a flow of electric current in the external circuit from Cu electrode to Zn electrode *i.e.,* (+)ve electrode to (−)ve electrode.
2. The Zn rod loses its mass, while Cu rod gains its mass.
3. The concentration of $ZnSO_4$ solution increases while that of $CuSO_4$ solution decreases.
4. The solutions in both the compartments remain electrically neutral.

Actually Zn metal is oxidised at Zn electrode and the electrons released travel through the external circuit to Cu electrode where they are used in the reduction of Cu^{2+} ions into metallic Cu which is deposited on the electrode. Thus, the overall redox reaction is,

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

As you know that voltaic or galvanic cell consists of two halves as half-cells. The half-cell in which oxidation occurs is called **oxidation half-cell,** while in which reduction occurs is called **reduction half-cell.**

$$Zn \longrightarrow Zn^{2+} + 2\,e^- \quad \text{(oxidation half-cell)}$$

$$Cu^{2+} + 2\,e^- \longrightarrow Cu \quad \text{(reduction half-cell)}$$

Representation of a Galvanic Cell

The following conventions are used in representing an electrochemical or Galvanic cell

1. The cell representation contains anodic half on the left hand side and cathodic half on the right hand side.
2. The anodic side of the cell is represented by writing metal or solid phase first and then the electrolyte (infact cation of electrolyte).
3. The cathodic side, on the other hand, is represented by writing the electrolyte first (anion) and then the metal or solid phase.
4. Metal and cation are separated by a semicolon (;) or by a vertical line (l).
5. The concentration of electrolyte is also written within brackets after the cation.
6. Salt bridge which separates two half-cells is represented by two vertical lines.

Thus, a complete cell can be represented as,

$$Zn \mid Zn^{2+}\,(1\text{ M}) \,||\, Cu^{2+}\,(1\text{ M}) \mid Cu$$

Caution Point *Here, it may also be noted that a cell can be written by arranging each of the pair i.e., left-right, anode-cathode, oxidation-reduction, negative-positive in an alphabetical order.*

Sample Problem 15 *The cell reaction of galvanic cell*

$Cu(s) \mid Cu^{2+}(aq) \,||\, Hg^{2+}(aq) \mid Hg(l)$ is

(*a*) $Hg + Cu^{2+} \longrightarrow Hg^{2+} + Cu$
(*b*) $Hg + Cu^{2+} \longrightarrow Cu^{+} + Hg^{+}$
(*c*) $Cu + Hg \longrightarrow CuHg$
(*d*) $Cu + Hg^{2+} \longrightarrow Cu^{2+} + Hg$

Interpret (*d*) From the cell, it is clear that

Anode half-reaction is

$$Cu \longrightarrow Cu^{2+} + 2e^-$$

Cathode half-reaction is

$$Hg^{2+} + 2e^- \longrightarrow Hg(l)$$

On adding Eq. (i) and (ii), we get

$$Cu + Hg^{2+} \longrightarrow Cu^{2+} + Hg$$

This is the cell reaction for galvanic cell.

3.5 Electrodes and Their Types

Electrode is the material which conducts electricity in the cell due to movement of electrons. It may be taken in any form like wire, rod, sheet, etc.

Electrodes may be classified further as

1. Inert and Attackable Electrode

The electrode which only conducts electricity is called inert electrode and the electrode which participates in the reaction also, is called attackable electrode.

2. Anode and Cathode

Anode is the electrode at which oxidation occurs and cathode is the electrode at which reduction takes place.

3. Positive and Negative Electrode

In galvanic cells, the electrode at which reduction occurs (cathode) is positive electrode, while the electrode at which oxidation occurs (anode) is negative electrode. However, in the electrolytic cell, the electrode at which cation discharges (cathode) is negative electrode while the electrode at which anions discharges (anode) is positive electrode.

4. Reversible and Irreversible Electrodes

The electrode at which reduction as well as oxidation may take place is called reversible electrode while in irreversible electrodes, reaction occurs only in one direction. *Some of the example of reversible electrodes are as follows*

(a) Metal-metal Salt Electrode

When any metal is immersed in its salt solution, metal atoms have tendency to move in the solution as metal ion (direction of increase in entropy) while the metal ions from solution have tendency to get deposited at the metal surface (direction of decrease in enthalpy).

$$M(s) \rightleftharpoons M^{n+}(aq) + ne^-$$

(b) Metal Insoluble Metal Salt Electrode

In such electrode, normally the metal surface is coated with some of its insoluble salt and the system is immersed in the aqueous solution of some salt having common anion. *e.g.,*

Ag, AgCl | Cl-electrode $Ag(s) + Cl^-(aq) \rightleftharpoons AgCl(s) + e^-$

Calomel electrode $2Hg(l) + 2Cl^-(aq) \rightleftharpoons Hg_2Cl_2(s) + 2e^-$

(c) Gas Electrodes

Any gas in contact with the solution of its corresponding ion also serves as electrode. In this case, Pt-wire is normally used to conduct electricity. *e.g.,*

Hydrogen electrode $H_2(g) \rightleftharpoons 2H^+(aq) + 2e^-$

Oxgen electrode $4OH^-(aq) \rightleftharpoons O_2(g) + 2H_2O(l) + 4e^-$

(d) Redox Electrode

These are the electrodes in which the electrolytic solution contains the same element in two different oxidation states and current is conducted by immersing Pt-wire in the solution. *e.g.,*

$$Fe^{2+}(aq) \rightleftharpoons Fe^{3+}(aq) + e^-$$

$$Sn^{2+}(aq) \rightleftharpoons Sn^{4+}(aq) + 2e^-$$

3.6 Electrode Potential

When a metallic electrode is dipped in its salt solution, a potential difference is developed between the electrode and its salt solution. The reason for the development of such a potential difference is exchange of electrons between the atoms of electrode and cations in its salt solution. Such a potential difference is called *electrode potential. Thus, we can say that the electrode potential is the measure of the tendency of an electrolyte to gain or lose electrons in a half-cell.*

The electrode potential can be of two types

(a) **Oxidation potential** The tendency of an electrode to lose electrons or to get oxidised is called its oxidation potential, (E_{oxi}) *e.g.,*

$$M(s) \rightleftharpoons M^{n+}(aq) + ne^-$$

$$Zn(s) \rightleftharpoons Zn^{2+} + 2e^-$$

$$H_2(g) \rightleftharpoons 2H^+ + 2e^-$$

$$Na(s) \rightleftharpoons Na^+ + e^-$$

Such an electrode is negatively charged with respect to its salt solution.

(b) **Reduction potential** The tendency of an electrode to gain electrons, *i.e.,* to get reduced is called reduction potential (E_{red}), *e.g.,*

$$M^{n+}(aq) + ne^- \rightleftharpoons M(s)$$

$$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$$

Such an electrode is positively charged with respect to its salt solution.

$$E_{oxi} = -E_{red}$$

The half-cell reactions are always written as reduction half reactions and their potential are represented as *reduction potential.*

The electrode potential depends upon

(i) Nature of metal and its ions,
(ii) Concentration of ions in the solution,
(iii) Temperature.

Standard Electrode Potential

The potential difference developed between metal electrode and solution of its ions of unit molarity (1 M) at 1 atm pressure and 25°C (298 K) is called standard electrode potential. The standard electrode potential is denoted by $E°$. *e.g.,* The potential of the galvanic cell,

$$(Pt)\ H_2\ (g\ 1\ atm) \mid H^+(1\ mol\ L^{-1}) \parallel Zn^{2+}(1\ mol\ L^{-1}) \mid Zn(s)$$

at 298 K, is called the standard electrode potential of zinc electrode. This is denoted by $E°_{Zn^{2+}/Zn}$.

$$E°_{Zn^{2+}/Zn} = -0.76\ V$$

Thus, the standard electrode potential of an electrode describes the electrons accepting tendency of the electrode relative to that of a standard hydrogen electrode, under standard conditions, *viz* 298 K, 1 atm pressure and 1 mol L^{-1} concentration.

Measurement of Electrode Potential

The measurement of absolute value of electrode potential is not possible for a single electrode. Only the difference of potentials between two electrodes can be measured experimentally. It is due to the reason that oxidation or reduction cannot occur alone (*i.e.,* oxidation and reduction occur simultaneously). For indirect measurement of potential of an electrode, we couple the electrode with another electrode whose potential is known. This electrode is called **reference electrode.** The emf of resulting cell is measured experimentally. Now, as we know the emf as well as the potential of reference electrode, the potential of other electrode is determined. *Some important reference electrode are as follows*

Normal Hydrogen Electrode (NHE)

Hydrogen electrode is the primary reference electrode as it is used normally to know the electrode potential of a half-cell of galvanic cell. The reason for such a usage is that it can act as a cathode as well as an anode with respect to other electrode, due to following reactions

$$H_2(g) \longrightarrow 2H^+ + 2e^-$$

$$2H^+ \xrightarrow{+2e^-} H_2$$

The electrode potential of NHE is taken as zero. It is represented as

$$\text{Pt} \mid H_2\ (\text{atm}) \mid H^+\ (1\ \text{M})$$

The hydrogen electrode is constructed by bubbling H_2 gas at a certain pressure over platinised platinum sheet immersed in 1 M HCl solution.

Standard Hydrogen Electrode (SHE)

A hydrogen electrode in which the pressure of H_2 gas is maintained at 1 atm and the concentration of H^+ ions in the solution is 1 M, is called standard hydrogen electrode. The emf of SHE is taken as 0.00 V at all temperatures.

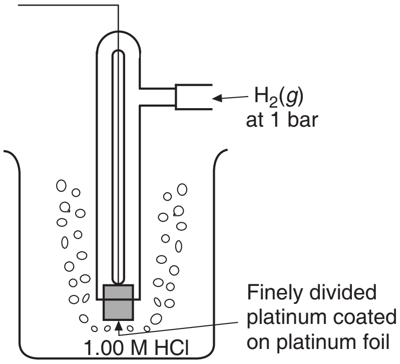


Fig. 3.7 Standard Hydrogen Electrode (SHE)

Caution Point *The use of NHE is not convenient because it is difficult to maintain the* H^+ *ion concentration as 1 M and the pressure of the gas as 1 atm. Hence, it is common to use calomel electrode as the reference electrode.*

Calomel Electrode

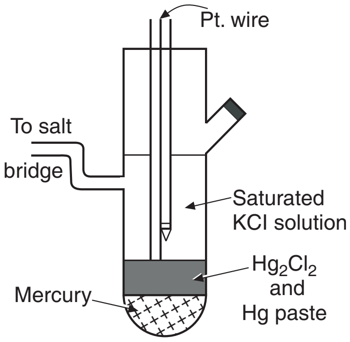


Fig. 3.8 Calomel electrode

It is an another generally used reference electrode but it comes in the category of **secondary reference electrode** (primary reference electrode is standard hydrogen electrode but it is difficult to prepare and maintain it). The electrode consists of Hg at the bottom over which a paste of mercury and mercurous chloride is placed in a tube. The tube is filled with KCl solution over the paste and a glass sealed platinum wire is used for electrical contact. The potential of electrode depends upon KCl solution.

On the basis of concentration of KCl, the calomel electrode is named differently, *e.g.,* If KCl solution is saturated, electrode is called SCE (saturated calomel electrode).

Similarly, if KCl solution is 1 N, the electrode is called NCE (normal calomel electrode) and DNCE (decinormal calomel electrode) for 0.1 N solution of KCl.

The reduction potentials of calomel electrodes on hydrogen scale at 298 K are

for saturated KCl – 0.2415 V
for 1.0 N KCl – 0.2800 V
for 0.1 N KCl – 0.3338 V

Silver-silver Chloride Electrode

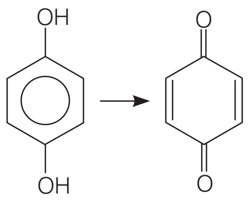
Besides hydrogen and calomel electrodes silver-silver chloride electrode is another widely used secondary reference electrode.

Caution Point *A reading on the voltmeter will be obtained only if the negative terminal of the voltmeter is connected to the negative electrode, i.e., where oxidation occurs and the positive terminal to the positive electrode, i.e., where reduction occurs.*

Various Types of Half-Cells

Various type of half-cells have been used, some as reference half-cells, to make complete cell with spontaneous reaction in forward direction. These half-cells along with half-cell reactions have been summarised in Table 3.2.

Table 3.2 **Various Types of Half-Cells**

S. No.	Type	Example	Half-cell reaction	$Q =$	Reversible to
1.	Gas-ion half-cell	$Pt(H_2) \mid H^+(aq)$	$\frac{1}{2}H_2(g) \longrightarrow H^+(aq) + e^-$	$[H^+]$	H^+ ion
		$Pt(Cl_2) \mid Cl^-(aq)$	$Cl^-(aq) \longrightarrow \frac{1}{2}Cl_2(g) + e^-$	$\frac{1}{[Cl^-]}$	Cl^- ion
2.	Metal-metal ion half-cell	$Ag \mid Ag^+(aq)$	$Ag(s) \longrightarrow Ag^+(aq) + e^-$	$[Ag^+]$	Ag^+ ion
3.	Metal-insoluble salt anion half-cell	$Ag, AgCl \mid Cl^-(aq)$	$Ag(s) + Cl^-(aq) \longrightarrow AgCl(s) + e^-$	$\frac{1}{[Cl^-]}$	Cl^- ion
4.	Calomel electrode	$Hg, Hg_2Cl_2 \mid Cl^-(aq)$	$2Hg(l) + 2Cl^-(aq) \longrightarrow Hg_2Cl_2(s) + 2e^-$	$\frac{1}{[Cl^-]^2}$	Cl^- ion
5.	Metal-metal oxide hydroxide half-cell	$Hg, HgO \mid OH^-(aq)$	$Hg(l) + 2OH^-(aq) \longrightarrow HgO(s) + H_2O(l) + 2e^-$	$\frac{1}{[OH^-]^2}$	OH^- ion
6.	Oxidation-reduction half-cell	$Pt \mid Fe^{2+}(aq), Fe^{3+}(aq)$	$Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^-$	$\frac{[Fe^{3+}]}{[Fe^{2+}]}$	Fe^{2+}, Fe^{3+} ions
7.	Mercury-mercury sulphate half-cell	$Hg, HgSO_4 \mid SO_4^{2-}(aq)$	$SO_4^{2-}(aq) + Hg(l) \longrightarrow HgSO_4(s) + 2e^-$	$\frac{1}{[SO_4^{2-}]}$	SO_4^{2-}
8.	Quinhydrone half-cell	$Pt \mid Quinhydrone \mid H^+(aq)$	 $+ 2H^+ + 2e^-$	$[H^+]^2$	H^+

Hot Spot 2

EMF of Cell

It is an important topic for JEE Main examination point of view. The level of question is easy and a small practice make you able to solve problems of this topic.

In electrochemical cell, the electrodes in different half-cells have different reduction potential. As a result of this, different flow of electrons is seen from the electrode with higher tendency to lose electrons to other electrode. This difference in electrode potential of electrodes is called **electromotive force** or **cell potential** of a cell. This is the driving force for all cell reactions.

We know that reduction occurs at cathode and oxidation occurs at anode, therefore,

EMF = reduction potential of cathode − reduction potential of anode

or, EMF = oxidation potential of anode + reduction potential of cathode

Thus, emf of a cell may also be defined as the potential difference between two electrodes when either no or negligible current is allowed to flow in the circuit.

If the two half cells are selected arbitrarily for the purpose of constructing a galvanic cell, then compare the reduction potentials of two electrodes. The electrode whose reduction potential has greater positive value is made cathode and other electrode is made anode. Alternatively, compare the oxidation potentials of two electrodes. The electrode whose oxidation potential has greater positive value is made anode and the other electrode is made cathode.

Constructing the cell in this manner will always give a positive EMF otherwise sometimes if electrode is choosen wrongly the EMF will be negative. In such cases, if the EMF of the cell is positive, the cell is said to be spontaneous or feasible or exergonic ($\Delta G < 0$). If the EMF of the cell is negative, the cell is said to be non-spontaneous or non-feasible or endergonic ($\Delta G > 0$). Reduction potential is taken as standard potential, *i.e.,* if electrode potential is given (and nothing is mentioned whether it is oxidation or reduction), it is taken as the reduction potential, by default.

Sample Problem 16 *For the given reaction,*

$$2Ce^{4+} + Co \longrightarrow 2Ce^{3+} + Co^{2+}$$

E°_{cell} is 1.89 V. If $E_{Co^{2+}/Co}$ is –0.28 V, what is the value of $E^\circ_{Ce^{4+}/Ce^{3+}}$?

(*a*) 3.78 *V* (*b*) 1.61 *V*
(*c*) 0.94 *V* (*d*) –3.78 *V*

Interpret (*b*) $E^\circ_{cell} = E^\circ_{oxi} + E^\circ_{red}$

$$= E^\circ_{Co/Co^{2+}} + E^\circ_{Ce^{4+}/Ce^{3+}}$$

or $$E^\circ_{cell} = -E^\circ_{Co^{2+}/Co} \,|\, E^\circ_{Ce^{4+}/Ce^{3+}}$$

$$1.89 = -(-0.28) + E^\circ_{Ce^{4+}/Ce^{3+}}$$

$\therefore$ $$E^\circ_{Ce^{4+}/Ce^{3+}} = 1.89 - 0.28 = 1.61 \text{ V}$$

Table 3.3 **Difference between Potential Difference and EMF**

S.N.	Potential difference	EMF
1.	It is the difference between the electrode potentials of the two electrode under any condition.	It is the potential difference between the two electrodes of the cell when no current is flowing in the circuit (*i.e.*, in an open circuit).
2.	It is less than the maximum voltage obtainable from the cell (*i.e.,* EMF of the cell).	It is the maximum voltage obtainable from the cell.
3.	It is measured by a simple voltmeter.	It is measured by potentiometeric method only so that the EMF sent by the potentiometric source is equal and opposite to that of the cell and there is no net current flowing in the circuit. It cannot be measured by voltmeter which draws current.
4.	It is not responsible for the flow of steady current in the circuit.	It is responsible for the flow of steady current in the circuit.

Check Point 2

1. How will the pH of brine (aq. NaCl solution) be affected when it is electrolysed? **[NCERT Exemplar]**
2. Metallic sodium cannot be obtained by electrolysing an aqueous solution of NaCl. Why?
3. Dilute aqueous solution of NaOH, H_2SO_4 and Na_2SO_4 liberate the same products at the electrodes during electrolysis. Explain.
4. The cell potential of a spontaneous reaction is always positive. Explain with appropriate reason.
5. A galvanic cell has electrical potential of 1.1 V. If an opposing potential of 1.1 V is applied to this cell, what will happen to the cell reaction and current flowing through the cell? **[NCERT Exemplar]**

3.7 Electrochemical Series

The arrangement of metals in decreasing order of tendency to lose electrons is called **electrochemical series** or it is the series in which the elements are arranged on the basis of the values of their standard reduction potentials.

Table 3.4 **Standard Electrode Potentials at 25°C "The Electrochemical Series"**

Element	Electrode reaction (reduction)	Standard electrode reduction potential E°, (volt)
Li	$Li^+ + e^- \longrightarrow Li$	– 3.05
K	$K^+ + e^- \longrightarrow K$	– 2.925
Ca	$Ca^{2+} + 2e^- \longrightarrow Ca$	– 2.87
Na	$Na^+ + e^- \longrightarrow Na$	– 2.714
Mg	$Mg^{2+} + 2e^- \longrightarrow Mg$	– 2.37
Al	$Al^{3+} + 3e^- \longrightarrow Al$	– 1.66
Zn	$Zn^{2+} + 2e^- \longrightarrow Zn$	– 0.7628
Cr	$Cr^{3+} + 3e^- \longrightarrow Cr$	– 0.74
Fe	$Fe^{2+} + 2e^- \longrightarrow Fe$	– 0.44
Cd	$Cd^{2+} + 2e^- \longrightarrow Cd$	– 0.403
Ni	$Ni^{2+} + 2e^- \longrightarrow Ni$	– 0.25
Sn	$Sn^{2+} + 2e^- \longrightarrow Sn$	– 0.14
H_2	$2H^+ + 2e^- \longrightarrow H_2$	0.00
Cu	$Cu^{2+} + 2e^- \longrightarrow Cu$	+ 0.337
I_2	$I_2 + 2e^- \longrightarrow 2I^-$	+ 0.535
Ag	$Ag^+ + e^- \longrightarrow Ag$	+ 0.799
Hg	$Hg^{2+} + 2e^- \longrightarrow Hg$	+ 0.885
Br_2	$Br_2 + 2e^- \longrightarrow 2Br^-$	+ 1.08
Cl_2	$Cl_2 + 2e^- \longrightarrow 2Cl^-$	+ 1.36
Au	$Au^{3+} + 3e^- \longrightarrow Au$	+ 1.50
F_2	$F_2 + 2e^- \longrightarrow 2F^-$	+ 2.87

Increasing tendency for reduction
Increasing tendency to accept e^-
Increasing strength as oxidising agent ↓

↑ Increasing strength as reducing agent
Increasing tendency to lose electrons
Increasing tendency for oxidation

In other words we can say that the arrangement of elements in increasing order of their reduction electrode potentials is called **electrochemical series.**

Characteristics of Electrochemical Series

Following characteristics of electrochemical series can be noted.

1. The negative sign of SRP (standard reduction potential) indicates that the electrode when joined with SHE

(standard hydrogen electrode) behaves as anode, *i.e.,* oxidation occurs at that electrode. Similarly, positive sign of SRP suggests behaviour of electrode as cathode when joined with SHE.

2. The above findings suggest that elements which are better reducing agents than hydrogen get their place above hydrogen in this series (such elements have negative value of SRP) while elements which are better oxidising agents than hydrogen get their place below the hydrogen in this series (such elements have (+) ve value of their SRP).
3. Elements which get oxidised easily are good reducing agents (metals) and elements which get reduced easily are good oxidising agents (non-metals).
4. A metal with lower SRP can have the ability to displace metal with higher SRP from their solutions. *Secondly, the reactivity of metals decrease from top to bottom in electrochemical series, i.e.,* metals higher in the series are more active than metals lying lower in the series.

   The elements which are placed above hydrogen in electrochemical series, have the ability to displace hydrogen from any protic solution (any solution containing H^+) .

Hot Spot 3

NERNST Equation

It is the most important topic of the chapter for JEE Main examination. The questions asked were generally numerically type. The level of question is easy to average.

A relationship between electrode potential and concentration of solution is called **Nernst equation.** For a general reduction half reaction, *i.e.,*

$$M^{n+}(aq) + ne^- \longrightarrow M(s)$$

This equation can be given as,

$$E_{(M^{n+}\mid M)} = E^\circ_{(M^{n+}\mid M)} - \frac{RT}{nF}\ln\frac{[M(s)]}{[M^{n+}(aq)]}$$

or

$$E_{(M^{n+}\mid M)} = E^\circ_{(M^{n+}\mid M)} - \frac{2.303RT}{nF}\log\frac{[M(s)]}{[M^{n+}(aq)]}$$

$$(\text{as } \log_e 10 = 2.303 \log 10)$$

where, $E_{(M^{n+}\mid M)}$ = electrode potential, *i.e.*, E

$E^\circ_{(M^{n+}/M)}$ = standard electrode potential, *i.e.*, E°

R = gas constant

T = temperature

F = Faraday constant

n = number of electrons gained during electrode reaction

$[M^{n+}(aq)]$ = concentration of ions

$[M(s)]$ = concentration of metal

Since, the concentration of solid phase is taken as unity, the Nernst equation will become

$$E_{(M^{n+}/M)} = E^\circ_{(M^{n+}/M)} - \frac{2.303RT}{nF}\log\frac{1}{[M^{n+}(aq)]}$$

For a hypothetical redox reaction,

$$M' + M^{n+} \longrightarrow M'^{n+} + M$$

the electrode potentials for two half-cells are given as,

$$E_{(M'^{n+}/M')} = E^\circ_{M'^{n+}/M'} + \frac{2.303RT}{nF}\log\frac{1}{[M'^{n+}(aq)]}$$

$$E_{(M^{n+}/M)} = E^\circ_{(M^{n+}/M)} - \frac{2.303RT}{nF}\log\frac{1}{[M^{n+}(aq)]}$$

In oxidation half-cell reaction,

(i) If $[M^{n+}]$ increases, E_{oxi} decreases.

(ii) If temperature increases at constant $[M^{n+}]$, E_{oxi} decreases.

In reduction half-cell reaction,

(i) If $[M^{n+}]$ increases, E_{red} increases.

(ii) If temperature increases at constant $[M^{n+}]$, E_{red} increases.

We know that, the cell potential,

$$E_{\text{cell}} = E_{(M^{n+}/M)} - E_{(M'^{n+}/M')} \quad [\because\ E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}]$$

$$= E^\circ_{(M^{n+}/M)} - \frac{2.303RT}{nF}\log\frac{1}{[M^{n+}(aq)]} - [E^\circ_{[M'^{n+}/M']} + \frac{2.303RT}{nF}\log\frac{1}{[M'^{n+}]}]$$

$$= E^\circ_{(M^{n+}/M)} - E^\circ_{(M'^{n+}/M')} - \frac{2.303RT}{nF}\log\frac{1}{[M^{n+}(aq)]} - \log\frac{1}{[M'^{n+}(aq)]}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{2.303RT}{nF}\log\frac{[M'^{n+}(aq)]}{[M^{n+}(aq)]} \qquad \text{...(i)}$$

If in both the half-cells, the number of electrons are not same,

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{2.303RT}{nF}\log\frac{[M'^{n+}(aq)]^x}{[M^{n+}(aq)]^y}$$

where, x and y = stoichiometric coefficients of M' and M in balanced equation.

Now, if the values of R, T and F, *i.e.*, 8.314 $\text{JK}^{-1}\ \text{mol}^{-1}$ for R, 298 K for T and 96500 for F, are substituted in Nernst equation we get,

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n}\log\frac{[M'^{n+}(aq)]^{x}}{[M^{n+}(aq)]^{y}}$$

Sample **Problem 17** *Calculate the emf of the cell in which the following reaction takes place*

$$\text{Ni}(s) + 2\ \text{Ag}^{+}(0.002\ \text{M}) \longrightarrow \text{Ni}^{2+}\ (0.160\ \text{M}) + 2\text{Ag}(s)$$

Given that $E^{\circ}_{\text{cell}} = 1.05\,V$ **[NCERT]**

(*a*) 0.61 *V* (*b*) 0.91 *V*
(*c*) 0.82 *V* (*d*) 0.023 *V*

Interpret (*b*) From the given cell reaction and Nernst equation,

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n}\log\frac{[\text{Ni}^{2+}]}{[\text{Ag}^{+}]^{2}}$$

$$= 1.05\text{V} - \frac{0.0591}{2}\log\frac{[0.160]}{[0.002]^{2}}$$

$$= 1.05 - \frac{0.0591}{2}\log(4\times 10^{4})$$

$$= 1.05 - \frac{0.0591}{2}(4.6021)$$

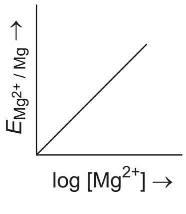
$$= 1.05 - 0.14 = 0.91\text{V}$$

$$E_{\text{cell}} = 0.91\text{V}$$

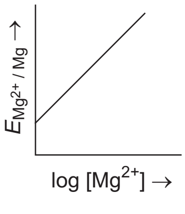
Sample **Problem 18** *Electrode potential for* Mg *electrode varies according to the equation* **[NCERT Exemplar]**

$E_{\text{Mg}^{2+}/\text{Mg}} = E^{\circ}_{\text{Mg}^{2+}/\text{Mg}} - \dfrac{0.059}{2}\log\dfrac{1}{[\text{Mg}^{2+}]}$. *The graph of* $E_{\text{Mg}^{2+}/\text{Mg}}$ *vs* $\log[\text{Mg}^{2+}]$ *is*

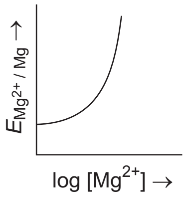
(a)



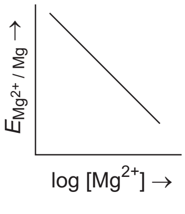
(*b*)



(*c*)



(*d*)



Interpret (*b*) The given equation is of $y = mx + c$ type which is equation of straight line. So, graph of $E_{\text{Mg}^{2+}\mid\text{Mg}}(y)$ *vs* $\log[\text{Mg}^{2+}](x)$ is a straight line with slope $\dfrac{0.059}{2}$ and intercept $E^{\circ}_{\text{Mg}^{2+}\mid\text{Mg}}$.

Determination of the pH of a Solution

Using a suitable reference half-cell, pH of the unknown solution can be determined.

$$\text{Pt}(\text{H}_2)\ |\ \text{H}^{+}\ (\text{pH} = x)\ ||\ \text{Cl}^{-}(1\ \text{M})\ |\ \underset{\text{Calomel}}{\text{Hg}_2\text{Cl}_2}, \text{Hg}$$

LHS half-cell $\quad \text{H}_2(g) \longrightarrow 2\text{H}^{+}(aq) + 2e^{-} \qquad E^{\circ}_{\text{ox}} = 0.00\ \text{V}$

RHS half-cell

$$\text{Hg}_2\text{Cl}_2(s) + 2e^{-} \longrightarrow 2\text{Hg}(l) + 2\text{Cl}^{-}(aq);\quad E^{\circ}_{\text{red}} = 0.2676\ \text{V}$$

Net : $\quad \text{H}_2(g) + \text{Hg}_2\text{Cl}_2(s) \longrightarrow 2\text{H}^{+}(aq) + 2\text{Hg}(l) + 2\text{Cl}^{-}(aq);$

$$E^{\circ}_{\text{cell}} = 0.2676\ \text{V}$$

$$Q = [\text{Cl}^{-}]^{2}[\text{H}^{+}]^{2}$$

$$= [\text{H}^{+}]^{2} \qquad (\text{since } [\text{Cl}^{-}] = 1\ \text{M})$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{2}\log[\text{H}^{+}]^{2} = E^{\circ}_{\text{cell}} + 0.0591\ \text{pH}$$

$$\therefore \qquad \text{pH} = \frac{E_{\text{cell}} - E^{\circ}_{\text{cell}}}{0.0591}$$

In general, $\quad \text{pH} = \dfrac{E_{\text{cell}} - [E^{\circ}_{\text{reference}} + E^{\circ}_{\text{SHE}}]}{0.0591}$

$$\text{pH} = \frac{E_{\text{cell}} - E^{\circ}_{\text{reference}}}{0.0591}$$

In this case reference half-cell is calomel electrode.

Sample **Problem 19** *Calculate the potential of hydrogen electrode in contact with a solution whose* pH *is* 10. **[NCERT]**

(*a*) 0.0591 V (*b*) – 0.0591 V
(*c*) 0.591 V (*d*) – 0.591 V

Interpret (*d*) For hydrogen electrode, $\text{H}^{+} + e^{-} \longrightarrow \frac{1}{2}\text{H}_2$

Applying Nernst equation,

$$E_{(\text{H}^{+}/1/2\text{H}_2)} = E^{\circ}_{(\text{H}^{+}/1/2\text{H}_2)} - \frac{0.0591}{n}\log\frac{1}{[\text{H}^{+}]}$$

$$= 0 - \frac{0.0591}{1}\log\frac{1}{(10^{-10})}$$

$$[\text{pH} = 10\ ; [\text{H}^{+}] = 10^{-10}\text{M}]$$

$$= 0 - \frac{0.0591}{1}\times(10\log 10) = -\ 0.591\ \text{V}$$

$$E_{(\text{H}^{+}/1/2\text{H}_2)} = -0.591\text{V}$$

Nernst Equation for Concentration Cells

The cells in which both the electrodes are of the same type but the electrolytic solution have different concentration, are called concentration cells.

(a) When Electrode is Reversible with Respect to Cation

e.g., $\quad \text{Zn}\ |\ \text{Zn}^{2+}\ (C_1)\ ||\ \text{Zn}^{2+}(C_2)\ |\ \text{Zn}$

$$\begin{array}{llll} \text{At anode} & Zn \longrightarrow Zn^{2+}(C_1) + 2e^- & & E^\circ = 0.76\ V \\ \text{At cathode} & Zn^{2+}(C_2) + 2e^- \longrightarrow Zn & & E^\circ = -0.76\ V \\ \hline & Zn^{2+}(C_2) \longrightarrow Zn^{2+}(C_1) & & E^\circ = 0.00\ V \\ \hline \end{array}$$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{C_1}{C_2}$$

or
$$E_{cell} = 0 - \frac{0.0591}{2} \log \frac{C_1}{C_2}$$

or
$$E_{cell} = \frac{0.0591}{2} \log \frac{C_2}{C_1}$$

Thus, for this reaction to be spontaneous, $C_2 > C_1$.

(b) When Electrode is Reversible with Respect to Anion

$$\underset{1\text{ atm}}{Pt(Cl_2)} \mid Cl^-(C_1) \parallel Cl^-(C_2) \mid \underset{1\text{ atm}}{Pt(Cl_2)}$$

$$E_{cell} = \frac{0.0591}{1} \log \frac{C_1}{C_2}$$

For such cases, cell reaction is spontaneous in forward reaction, if $C_1 > C_2$.

(c) When Electrodes at Different Concentration are Dipped into Same Electrolytes

$$\underset{\text{at } p_1}{Pt(H_2)} \mid \underset{1\text{ M}}{HCl} \mid \underset{\text{at } p_2}{Pt(H_2)}$$

Two half-cells are joined by two salt-bridges since they have common electrolyte.

$$\begin{array}{lll} \text{At anode} & H_2(p_1) \longrightarrow \underset{1\text{ M}}{2H^+} + 2e^- & \\ \text{At cathode} & \underset{1\text{ M}}{2H^+} + 2e^- \longrightarrow H_2(p_2) & \\ \text{Net reaction} & \overline{\underline{H_2(p_1) \longrightarrow H_2(p_2)}} & E^\circ_{cell} = 0.00 \end{array}$$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \frac{p_2}{p_1} = \frac{0.0591}{2} \log \frac{p_1}{p_2}$$

Cell reaction is spontaneous in forward direction, if p_1 (LHS) $> p_2$(RHS).

Sample **Problem 20** *The emf of the following cell is 0.086 V.*

Ag | $AgNO_3$ (0.0093 *M*) || $AgNO_3$ (*xM*) | Ag. *The value of x will be*

(a) 0.295 (b) 0.642

(c) 0.359 (d) 0.266

Interpret (d)
$$E = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

$$0.086 = \frac{0.0591}{1} \log \frac{x}{0.0093}$$

$$\frac{0.086}{0.059} = \log \frac{x}{0.0093}$$

$$\frac{x}{0.0093} = 28.7$$

$$\therefore \quad x = 0.266\ M$$

Equilibrium Constant from Nernst Equation

For a general electrochemical reaction,

$$aA + bB \longrightarrow cC + dD$$

the Nernst equation can be written as,

$$E_{cell} = E^\circ{}_{cell} - \frac{RT}{nF} \ln \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

or
$$E_{cell} = E^\circ{}_{cell} + \frac{RT}{nF} \ln \frac{[A]^a[B]^b}{[C]^c[D]^d}$$

At equilibrium, $E_{cell} = 0$

and
$$\frac{[C]^c[D]^d}{[A]^a[B]^b} = K_c$$

Thus, Nernst equation may also be used to calculate the equilibrium constant for a cell reaction through the formula

$$E^\circ{}_{cell} = \frac{0.0591}{n} \log K_c$$

where, K_c = equilibrium constant

Sample **Problem 21** *Calculate the equilibrium constant of the reaction :* **[NCERT]**

$$Cu(s) + 2Ag^{\oplus}(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s) \qquad E^\ominus_{cell} = 0.46\ V$$

(a) 4×10^{15} (b) 3×10^{16}

(c) 2×10^{13} (d) 1.56×10^{16}

Interpret (a)
$$E^\ominus_{cell} = \frac{0.059\ V}{2} \log K_c$$

$$0.46\ V = \frac{0.059\ V}{2} \log K_c$$

$$\therefore \quad \log K_c = \frac{0.46\ V \times 2}{0.059\ V} = 15.6$$

$$K_c = \text{Antilog } (15.6) = 3.98 \times 10^{15}$$

Sample **Problem 22** *Consider the following half-cells.*

$Cl^-(1M) \mid Hg_2Cl_2(s) \mid Hg(l)$; $E^\circ = 0.270$ V

Cl^-(saturated) | $Hg_2Cl_2(s) \mid Hg(l)$, $E = 0.244$ V

What is the concentration of Cl^- *in saturated solution?*

(a) 10.25 *M* (b) 3.84 *M* (c) 2.75 *M* (d) 4.24 *M*

Interpret (c) Half-cell reaction is

$$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^- \text{ (saturated)}$$

$$K_c = [Cl^-]^2$$

For saturated Cl^- solution, $E = 0.244$ V and for saturated 'half cell, $E^\circ = 0.270$ V

$$\therefore \quad E = E^\circ - \frac{0.0591}{2} \log [Cl^-]^2$$

$$0.244 = 0.270 - 0.0591 \log [Cl^-]$$

$$\log [Cl^-] = \frac{0.026}{0.0591} = 0.4399$$

$$[Cl^-] = 2.754\ M$$

Relationship between Cell Potential and Gibbs Energy Change (ΔG)

In an electrochemical cell, maximum work done (ΔG) is given by

$$\Delta G = nF \times E_{\text{cell}}$$

where, $F =$ Faraday's constant

$n =$ number of moles of electrons transferred.

A galvanic cell does electrical work by transferring electrical charge through an external circuit. When small amount of current is drawn from the cell then

$$-\Delta G = W_{\text{elec.}}$$

(i) If ΔG of the system is positive then the process would be possible only if the surrounding do electrical work on the system (as in electrolysis).

(ii) If ΔG of the system is negative then the system does electric work on the surroundings (as in galvanic cells). For a voltaic cell, the work is done on the surroundings, thus given a negative sign. Hence,

$$\Delta G = W_{\max} = -\,nFE_{\text{cell}}$$

and the standard free energy (ΔG°) is given by,

$$\Delta G^\circ = -\,nFE^\circ_{\text{cell}}$$

Sample Problem 23 *The standard electrode potential for Daniell cell is* 1.1 *V. Calculate the standard Gibbs energy for the reaction.* **[NCERT]**

$$\text{Zn}(s) + \text{Cu}^{2+}(aq) \longrightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s)$$

(a) 2.12 *kJ mol*$^{-1}$ (b) 21.2 *kJ mol*$^{-1}$

(c) 212.2 *kJ mol*$^{-1}$ (d) 2122 *kJ mol*$^{-1}$

Interpret (c) $\Delta_r G^\ominus = -\,nFE^\ominus_{\text{cell}}$

n in the above equation is, $F = 96487\ \text{C mol}^{-1}$ and $E^\ominus_{\text{cell}} = 1.1\ \text{V}$,

$$\therefore \quad \Delta_r G^\ominus = -2 \times 96487\ \text{C mol}^{-1} \times 1.1\ \text{V}$$

$$= -212271\ \text{J mol}^{-1}$$

$$= -212.27\ \text{kJ mol}^{-1}$$

Relation Between Cell Potential (E°_{cell}), Free Energy (ΔG°) and K

The relation between cell potential (E°_{cell}), free energy (ΔG°) and equilibrium constant (K_c) is given by,

$$\Delta G^\circ = -\,2.303RT \log K_c$$

as $\Delta G^\circ = nFE^\circ_{\text{cell}}$ and $E^\circ_{\text{cell}} = \dfrac{2.303\,RT}{nF} \log K_c$

where, n is the number of moles of electrons transferred in the balanced equation for the process to which you apply the Nernst equation.

Relation Between Standard Potentials of Half-cells Containing a Metal in different Oxidation State

If two half-reactions having potentials E_1° and E_2° are combined to give a third half-reaction having a potential E_3°, then

$$\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$$

or
$$-\,n_3FE_3^\circ = -\,n_1FE_1^\circ - n_2FE_2^\circ$$

or
$$n_3E_3^\circ = n_1E_1^\circ + n_2E_2^\circ$$

or
$$E_3^\circ = \frac{n_1E_1^\circ + n_2E_2^\circ}{n_3}$$

Sample Problem 24 *If for the half-cell reactions, E° values are given,*

$$\text{Cu}^{2+} + e^- \longrightarrow \text{Cu}^+; \quad E^\circ = 0.15\ V$$

$$\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}; \quad E^\circ = 0.34\ V$$

Calculate E° of the half-cell reaction,

$$\text{Cu}^+ + e^- \longrightarrow \text{Cu}$$

(a) +0.53 *V* (b) −0.53 *V*

(c) − 0.80 *V* (d) −0.28 *V*

Interpret (a) $\text{Cu}^{2+} + e^- \longrightarrow \text{Cu}^+, \quad E^\circ = 0.15\ \text{V}$

(i) $\text{Cu}^+ \longrightarrow \text{Cu}^{2+} + e^- \quad E_1^\circ = -0.15\ \text{V}, n_1 = 1$

(ii) $\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}, \quad E_2^\circ = 0.34\ \text{V}, n_2 = 2$

From Eqs. (i) and (ii)

$$\text{Cu}^+ + e^- \longrightarrow \text{Cu} \quad E_3^\circ = ?, n_3 = 1$$

$$\therefore \quad \Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$$

$$-n_3E_3^\circ = -n_1E_1^\circ - n_2E_2^\circ$$

$$E_3^\circ = \frac{1 \times (-0.15) + 2 \times (0.34)}{1}$$

$$= +\ 0.53\ \text{V}$$

Variation of EMF (E_{cell}) with Temperature

Using Gibbs Helmholtz equation, the temperature coefficient of the EMF of the cell is written as :

$$\Delta G = \Delta H + T\left[\frac{d(\Delta G)}{dT}\right]_p \quad \text{(at constant pressure)} \qquad \text{...(i)}$$

(since $\Delta G = -\,nFE_{\text{cell}}$)

$$\Rightarrow \quad -nFE_{\text{cell}} = \Delta H + T\left[\frac{d(-nFE_{\text{cell}})}{dT}\right]_p$$

$$= \Delta H - nFT\left(\frac{dE_{\text{cell}}}{dT}\right)_p$$

$$\Rightarrow \quad \left(\frac{dE_{\text{cell}}}{dT}\right)_p = \frac{\Delta H}{nFT} + \frac{E_{\text{cell}}}{T} \qquad \text{...(ii)}$$

Enthalpy change from Eq. (i)

$$\Delta H = -nFE_{\text{cell}} + nFT\left(\frac{dE_{\text{cell}}}{dT}\right)_p$$

$$= -nF\left[E_{\text{cell}} - T\left(\frac{dE_{\text{cell}}}{dT}\right)_p\right]$$

Enthalpy change can be determined by comparing Eq. (i) with $\Delta G = \Delta H - T\Delta S$.

$$\Delta S = -\left(\frac{d(\Delta G)}{dT}\right)_p$$

$$= -\left[\frac{d}{dT}(-nFE_{\text{cell}})_p\right]$$

$$= nF\left(\frac{dE_{\text{cell}}}{dT}\right)_p$$

3.8 Battery

A cell or a **battery** (arrangement of 1 or more cells connected in series) is basically a galvanic cell and used where the chemical energy of redox reaction is converted into electrical energy.

An electrochemical cell to be used as a commercial cell must fulfil the following two requirements

1. It should have the compactness, lightness, and ruggedness for portability.
2. Its voltage should not drop much during use, *i.e.,* drop in voltage should be negligible over the small interval of time during which it is being put to use.

Different applications require batteries with different properties. The battery required to start a car, for example, must be capable of delivering a large electrical currrent for a short time period. The battery that powers a heart pacemaker, on the other hand, must be very small and capable of delivering a small but steady current over an extended time period.

The batteries are of two types basically

Primary Batteries

The primary batteries are those in which the cell reaction occurs only once and the battery becomes dead after use over a period of time and cannot be reused again, *e.g.,* dry cells like Leclanche cell, mercury cell etc.

(a) Leclanche Cell

The electrode reaction for Leclanche cell is

Anode $\mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+} + 2e^-$

Cathode $\mathrm{MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3}$

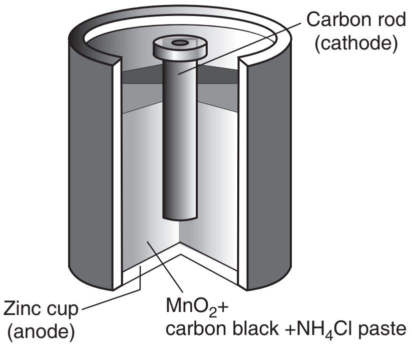


Fig. 3.9 (Leclanche cell) A commercial dry cell containing a graphite (carbon) cathode in a zinc container; the latter acts as the anode

NH_3 formed in the reaction at cathode combines with Zn^{2+} to form the complex like $[\mathrm{Zn(NH_3)_4}]^{2+}$. The cell has a potential of nearly 1.5 V.

(b) Mercury Cell

It shows following electrode reactions :

Anode $\mathrm{Zn(Hg) + 2OH^- \longrightarrow ZnO}(s) + \mathrm{H_2O} + 2e^-$

Cathode $\mathrm{HgO + H_2O} + 2e^- \longrightarrow \mathrm{Hg}(l) + 2\mathrm{OH}^-$

With the overall reaction,

$$\mathrm{Zn(Hg) + HgO}(s) \longrightarrow \mathrm{ZnO}(s) + \mathrm{Hg}(l)$$

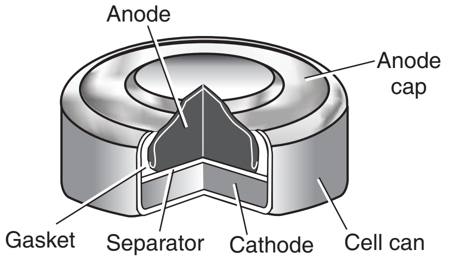


Fig. 3.10 Mercury cell. Here, the reducing agent is zinc and the oxidising agent is mercury (II) oxide

The cell potential is approximately 1.35 V and remains constant throughout its life since overall reaction does not involve any ion, the concentration of which can change during its life-time.

Secondary Batteries

A secondary battery can be recharged by passing current through it in opposite direction, so that it can be used again.

(a) Lead Storage Battery

The most important secondary cell is lead storage battery, commonly used in **automobiles** and **invertors.** A 12 V lead storage battery or lead accumulator generally consists of six cells each producing 2 V. Here 38% solution of H_2SO_4 is used as electrolyte.

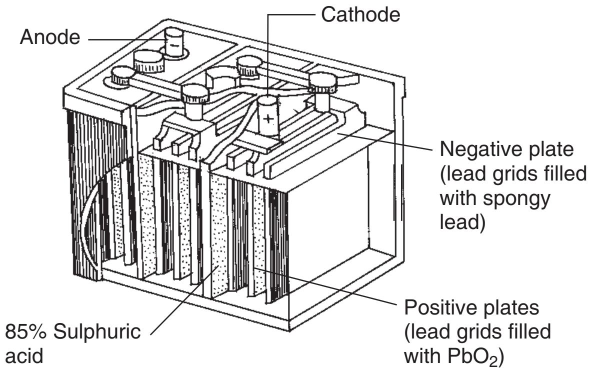


Fig. 3.11 Lead storage battery

The overall reaction for lead stroage battery during discharging (*i.e.*, when cell is in the use) is,

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$$

Reverse reaction occurs when cell is charged.

$$\begin{array}{l} PbSO_4 + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq) \\ PbSO_4(s) + 2H_2O \longrightarrow PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \\ \hline PbSO_4(s) + 2H_2O \longrightarrow Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \\ \hline \end{array}$$

(b) Nickel Cadmium Battery

Another important secondary battery is Ni-Cd battery with longer life but more expensive.

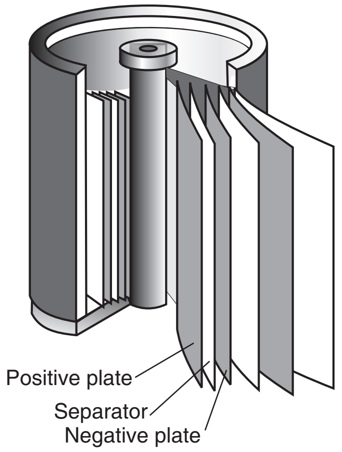


Fig. 3.12 A nickel cadmium battery in a jelly roll arrangement and separated by a layer soaked in moist sodium or potassium hydroxide

The overall reaction for Ni-Cd battery is,

$$Cd(s) + 2Ni(OH)_3(s) \longrightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O(l)$$

3.9 Fuel Cells

Galvanic cells which use energy of combustion of fuels like H_2, CH_4, CH_3OH, etc., as the source to produce electrical energy are called **fuel cells.** One of the most successful fuel cells use reaction of H_2 and O_2 in gaseous state to form water.

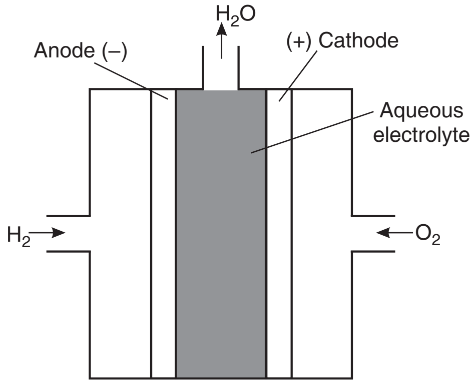


Fig. 3.14 H_2-O_2 Fuel cell

The electrode reactions for the cell are

Cathode $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4HO^-(aq)$

Anode $2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$

With overall reaction being

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

Advantages of Fuel Cell

1. Due to continuous supply of gases, such cell never becomes dead.
2. Usually operated at 70–140°C.
3. High efficiency than other power plants. (≈ 70%)
4. Pollution free.

Caution Point *Theoretically thermodynamics efficiency* (η)

$$h = \frac{\Delta G}{\Delta H} - \frac{-nEF}{\Delta H}$$

Disadvantages of Fuel Cell

1. Electrolyte causes corrosion.
2. Difficult to make contact between gaseous fuel, the liquid electrolyte and the solid catalyst.
3. High cost of catalyst.
4. Gaseous fuels are difficult to handle at low temperature and high pressure.

Check Point 3

1. The solution of $AgNO_3$ turns blue when a copper rod is immersed in it. Explain, why?
2. HgO on heating decomposes while ZnO does not decompose. Explain
3. Why does a cell stop working after sometime?
4. Unlike dry cell, the mercury cell has a constant cell potential throughout its life, why? **[NCERT Exemplar]**

WORKED OUT Examples

Example 1 *The equivalent conductance of silver nitrate solution at 250°C for an infinite dilution was found to be* $133.3\ ohm^{-1}\ cm^2\ equiv^{-1}$. *The transport number of* Ag^+ *ions in very dilute solution of* $AgNO_3$ *is 0.464. Calculate the equivalent conductance of* NO_3^- *(in* $\Omega^{-1}\ cm^2\ equiv^{-1}$*) at infinite dilution.*

(*a*) 61.9
(*b*) 195.2
(*c*) 133.3
(*d*) 71.4

Solution (*d*) $\lambda^\infty(Ag^+) = \text{transport number of } Ag^+ \times \Lambda^\infty\ (AgNO_3)$

$$\lambda^\infty\ (Ag^+) = n_{Ag^+} \times \Lambda^\infty\ (AgNO_3)$$
$$= 0.464 \times 133.3$$
$$= 61.9\ \text{ohm}^{-1}\ \text{cm}^2\ \text{equiv}^{-1}$$

By Kohlrausch's law,

$$\Lambda^\infty(AgNO_3) = \lambda^\infty(Ag^+) + \lambda^\infty(NO_3^-)$$
$$\therefore \quad \lambda^\infty(NO_3^-) = \Lambda^\infty(AgNO_3) - \lambda^\infty(Ag^+)$$
$$= 133.3 - 61.9$$
$$= 71.4\ \text{ohm}^{-1}\ \text{cm}^2\ \text{equiv}^{-1}$$

Example 2 *EMF of the cell,*
$Ag\,|\,AgNO_3\ (0.1M)\,||\,KBr\ (1N), AgBr(s)\,|\,Ag$ *is* $-0.6\ V$ *at* $298\ K$. $AgNO_3$ *is 80% and* KBr *is 60% dissociated.* K_{sp} *of AgBr at 298 K is*

(*a*) $7 \times 10^{-7}\ M$
(*b*) $6.82 \times 10^{-6}\ M$
(*c*) $4.8 \times 10^{-7}\ M$
(*d*) $1.23 \times 10^{-8}\ M$

Solution (*a*) The above cell is a concentration cell.

$$\therefore \quad E^\ominus_{\text{cell}} = 0.0\ \text{V}$$

The half cell reactions are

Anode reaction

$$Ag\ (\text{anode}) \rightleftharpoons Ag^\oplus(0.1M) + e^-$$

Cathode reaction

$$Ag^\oplus(\text{cathode}) + e^- \rightleftharpoons Ag(s)(\text{cathode})$$

Cell reaction

$$Ag^\oplus(\text{cathode}) \rightleftharpoons Ag^\oplus(0.1M)_{\text{anode}}$$

Since, $AgNO_3$ is 80% ionized.

$$\therefore \quad [Ag^\oplus]_a = 0.1 \times \frac{80}{100} = 0.08\ \text{M}$$

$$\therefore \quad E_{\text{cell}} = E^\ominus_{\text{cell}} - \frac{0.06}{1} \log \frac{[Ag^\oplus]_a}{[Ag^\oplus]_c} \qquad (\text{Take } 0.059 \approx 0.06)$$

$$-0.6\ \text{V} = 0 - 0.06 \log \frac{0.08}{[Ag^\oplus]_c}$$

$$\log\ [Ag^\oplus]_c = \log 0.08 - 10 = (\log 2^3 - \log 100) - 10$$
$$= 0.9 - 2 - 10 = -11.1$$

$$\therefore \quad [Ag^\oplus]_c = \text{Antilog}\ (-11.1) = \text{Antilog}\ (\overline{12}.9) = 0.79 \times 10^{-12}$$
$$\approx 0.8 \times 10^{-12}\ \text{M}$$

Since, KBr is 60% dissociated,

$$\therefore \quad [Br^\ominus] = 1 \times \frac{60}{100} = 0.6\ \text{M}$$

$$\therefore \quad K_{sp} = [Ag^\oplus][Br^\ominus]$$
$$= 0.8 \times 10^{-12} \times 0.6 = 0.48 \times 10^{-12}\ \text{M}^2$$

$$\text{Solubility } (S) = \sqrt{K_{sp}} = \sqrt{0.48} \times 10^{-6}\ \text{M}$$
$$= 0.6928 \times 10^{-6}\ \text{M}$$
$$\approx 0.7 \times 10^{-6}\ \text{M} = 7 \times 10^{-7}\ \text{M}$$

Example 3 *How many electrons per second do pass through a cross-section of a copper wire carrying* $10^{-16}\ A$*?*

(*a*) $555\ e^-/s$
(*b*) $624\ e^-/s$
(*c*) $725\ e^-/s$
(*d*) $433\ e^-/s$

Solution (*b*) $10^{-16}\ \text{A} = 10^{-16}\ \text{C/s}$

Charge on one electron $= 1.603 \times 10^{-19}\ \text{C}/e^-$

$$\therefore \quad \text{Rate} = \frac{10^{-16}}{1.603 \times 10^{-19}}$$
$$= 624\ e^-/s$$

Example 4 *Arrange the following oxidising agents in order of increasing strength under standard state conditions*

Given,

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 6Cr^{3+} + 7H_2O; \qquad E_1^\circ = 1.33\ V$$
$$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq); \qquad E_2^\circ = 1.06\ V$$
$$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq); \qquad E_3^\circ = 0.77\ V$$

(*a*) $Fe^{3+} < Br_2 < Cr_2O_7^{2-}$
(*b*) $Br_2 < Fe^{3+} < Cr_2O_7^{2-}$
(*c*) $Fe^{3+} < Cr_2O_7^{2-} < Br_2$
(*d*) $Cr_2O_7^{2-} < Br_2 < Fe^{3+}$

Solution (*a*) Since, the order of standard reduction potential is

$$E_1^\circ > E_2^\circ > E_3^\circ$$

Higher the value of standard reduction potential, higher is the ease to get reduced. The species which readily gets reduced, is a better oxidising agent. Thus, the order of strength of oxidising agent is

$$Fe^{3+} < Br_2 < Cr_2O_7^{2-}$$

Example 5 *A certain current liberates 0.500 g of* H_2 *in 2.00 hr. How many gram of oxygen can be liberated by the same current in the same time?*

(*a*) 0.500 *g* (*b*) 8.00 *g* (*c*) 4.00 *g* (*d*) 16.00 *g*

Solution (*c*) According to Faraday's first law,

$$w = Z \cdot it$$

Given, *it* is same for H_2 and O_2.

$$\frac{w_{H_2}}{w_{O_2}} = \frac{Z_{H_2}}{Z_{O_2}}$$

$$\frac{w_{H_2}}{w_{O_2}} = \frac{E_{H_2}}{E_{O_2}}$$

$$\frac{0.500}{w_{O_2}} = \frac{2}{16}$$

$$w_{O_2} = 4.00 \text{ g}$$

Example 6 *The reversible reduction potential of pure water is* –0.413 *V under* 1.00 *atm* H_2 *pressure. If the reduction is considered to be* $2H^+ + 2e^- \longrightarrow H_2$, *calculate the pH of pure water.*

(*a*) 4 (*b*) 5 (*c*) 6 (*d*) 7

Solution (*d*) $2H^+ + 2e^- \longrightarrow H_2 \qquad Q = \dfrac{1}{[H^+]^2}$

$$E = E^\circ_{SHE} - \frac{0.0591}{2}\log\frac{1}{[H^+]^2}$$

$$-0.413 = 0 + \frac{0.0591}{2}\log[H^+]^2$$

$$0.413 = -0.0591 \log[H^+]$$

$$= 0.0591 \text{ pH} \qquad [\because -\log[H^+] = \text{pH}]$$

$$\text{pH} = \frac{0.413}{0.0591} = 7$$

Example 7 *The value of the reaction quotient, Q, for the cell,* $Ni(s)\,|\,Ni^{2+}(0.19\,M)\,||\,Cl^-(0.40\,M)\,|\,Cl_2$ (g 0.10 *atm*), Pt(*s*), *is*

(*a*) 3.0×10^{-2} (*b*) 3.0×10^{-3}

(*c*) 3.0×10^{-1} (*d*) 2.5×10^{-2}

Solution (*c*) The half-cell reactions and overall reaction are

$$Ni \longrightarrow Ni^{2+} + 2e^-$$

$$Cl_2 + 2e^- \longrightarrow 2Cl^-$$

$$Ni + Cl_2 \longrightarrow Ni^{2+} + 2Cl^-$$

$$\therefore \qquad Q = \frac{[Ni^{2+}][Cl^-]^2}{[p_{Cl_2}]} = \frac{0.19 \times (0.4)^2}{0.1} = 0.30$$

Example 8 *Calculate* E_{cell} *of the following cell*

$$\underset{\ominus}{Pt}\,|\,Fe^{2+}(0.10\,M), Fe^{3+}(0.20\,M)\,||\,Ag^+(1.0\,M)\,|\,\underset{\oplus}{Ag}.$$

Given, $E^\circ_{Fe^{3+}, Fe^{2+}/Pt} = 0.770$ *V and* $E^\circ_{Ag^+/Ag} = 0.800$ *V.*

(*a*) 0.0254 *V* (*b*) 0.0186 *V*

(*c*) 0.1460 *V* (*d*) 0.0122 *V*

Solution (*d*) At anode,

$$Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^- \qquad E^\circ_{oxi} = -0.77 \text{ V}$$

At cathode $\quad Ag^+ + e^- \longrightarrow Ag(s) \qquad E^\circ_{red} = 0.80$ V

Overall cell reaction,

$$Fe^{2+}(aq) + Ag^+(aq) \longrightarrow Fe^{3+}(aq) + Ag(s)$$

$$E^\circ_{cell} = E^\circ_{oxi} + E^\circ_{red} = -0.77 + 0.80 = 0.03 \text{ V}$$

$$K_c = \frac{[Fe^{3+}][Ag]}{[Fe^{2+}][Ag^+]} = \frac{[Fe^{3+}]}{[Fe^{2+}][Ag^+]} = \frac{0.20}{(0.10)(1)} = 2$$

Using Nernst equation,

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log K_c$$

$$E_{cell} = 0.03 - \frac{0.0591}{1}\log 2$$

$$= 0.0122 \text{ V.}$$

Example 9 *The EMF of the cell,*

$$Cd\,|\,CdCl_2 \text{ (solution) (1 atm)}\,|\,AgCl(s)\,|\,Ag$$

is 0.675 *at* 25°C. *The temperature coefficient of the cell is* -6.5×10^{-4} *V degree*$^{-1}$. *Find the change in heat content* (*kJ mol*$^{-1}$) *and entropy* (*V deg*$^{-1}$) *for the electrochemical reaction that occurs when* 1 *F of electricity is drawn for it.*

(*a*) 78.34, 83.83 (*b*) + 62.73, – 83.83

(*c*) –62.73, –83.83 (*d*) –78.34, +83.83

Solution (*c*) $E_{cell} = 0.675$ V

Cell reaction is

Anode reaction

$$\frac{1}{2}Cd(s) \longrightarrow \frac{1}{2}Cd^{2+}(aq) + e^-$$

Cathode reaction

$$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^{\ominus}(aq)$$

Cell reaction

$$\frac{1}{2}Cd(s) + AgCl \rightleftharpoons Ag(s) + \frac{1}{2}Cd^{2+}(aq) + Cl^{\ominus}(aq)$$

Temperature coefficient of the cell, *i.e.*,

$$\left(\frac{\partial E}{\partial T}\right)_P = -6.5 \times 10^{-4} \text{ V deg}^{-1}$$

$$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_p \qquad (n_{cell} = 1)$$

$$= 1 \times 96500 \times (-6.5 \times 10^{-4})$$

$$= -62.73 \text{ V deg}^{-1}$$

$$E = -\frac{\Delta H}{nF} + T\left(\frac{\partial E}{\partial T}\right)_p$$

$$0.675\ \text{V} = \frac{-\Delta H}{1\times 96500} + 298\,(-6.5\times 10^{-4})$$

$$\Delta H = -83829.55\ \text{J} \approx -83.83\ \text{kJ mol}^{-1}$$

Example 10 *At 25°C, the free energy of formation of* $H_2O(l)$ *is –56,700 cal mol*$^{-1}$. *The free energy of ionization of water to* $H^{\oplus}$ *and* $\overset{\ominus}{O}H$ *is 19050 cal mol*$^{-1}$. *What is the reversible EMF of the following cell at 25°C ?*

$$H_2(g)\ (1\ atm)\,|\,H^{\oplus}\,|\,\overset{\ominus}{O}H,\ O_2(g),\ 1\ atm$$

(*a*) 0.625 *V* (*b*) 0.305 *V*

(*c*) 0.534 *V* (*d*) 0.405 *V*

Solution (*d*) Given;

$$H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(l) \qquad \text{...(i)}$$

$$H_2O \rightleftharpoons H^{\oplus} + \overset{\ominus}{O}H \qquad \text{...(ii)}$$

$\Delta G_1 = -56700\ \text{cal mol}^{-1}, \Delta G_2 = 19050\ \text{cal mol}^{-1}$

Cell reaction

$$H_2 \rightleftharpoons 2H^{\oplus} + 2e^-$$

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightleftharpoons 2\overset{\ominus}{O}H$$

$$H_2 + \frac{1}{2}O_2 + H_2O \rightleftharpoons 2H^{\oplus} + 2\overset{\ominus}{O}H$$

Multiply Eq. (ii) by 2 and adding Eq. (i), we get

$$H_2 + \frac{1}{2}O_2 + H_2O \rightleftharpoons 2H^{\oplus} + 2\overset{\ominus}{O}H$$

$$\begin{aligned}\therefore \quad \Delta G &= \Delta G_1 + 2\Delta G_2\\ &= -56700 + 2\times 19050\\ &= -18600\ \text{cal mol}^{-1}\\ &= -18600\times 4.2\ \text{J mol}^{-1}\end{aligned}$$

(1 cal = 4.184 J ≈ 4.2 J)

$$= -078120\ \text{J mol}^{-1}$$

$$\Delta G = -nFF_{\text{cell}}$$

$$-78120\ \text{J mol}^{-1} = -2\times 96500\ \text{C}\times E_{\text{cell}}$$

$$\therefore \quad E_{\text{cell}} = 0.405\ \text{V}.$$

Example 11 *The EMF of the cell,* $\text{Pt}\,|\,\text{Ce}^{4+}(90\%),\ \text{Ce}^{3+}(10\%)\,|$ *Normal calomel electrode is 1.464 V at 25°C. Find the value of equilibrium constant of the reaction :*

$$2Ce^{3+} + 2H^{\oplus} \longrightarrow 2Ce^{4+} + H_2$$

The electrode potential of the normal calomel electrode is + 0.28 V.

(*a*) 2.38×10^{38} (*b*) 1.08×10^{42}

(*c*) 1.67×10^{39} (*d*) 3.24×10^{44}

Solution (*b*) $E_{\text{cell}} = E_c - E_a = 1.464\ \text{V}$

$$E_{Ce^{4+}\,|\,Ce^{3+}} = E^{\ominus}_{Ce^{4+}\,|\,Ce^{3+}} - \frac{0.059}{1}\log\frac{[Ce^{3+}]}{[Ce^{4+}]}$$

$$= E^{\ominus}_{Ce^{4+}\,|\,Ce^{3+}} - \frac{0.059}{1}\log\frac{10}{90}$$

$$E_{\text{cell}} = E_{\text{calo}} - E_{Ce^{4+}\,|\,Ce^{3+}}$$

$$1.464 = E_{\text{calo}} - \left[\left(E^{\ominus}_{Ce^{4+}\,|\,Ce^{3+}} - 0.059\log\frac{1}{8}\right)\right]$$

$$1.464 = 0.28 - \left(E^{\ominus}_{Ce^{4+}\,|\,Ce^{3+}} - 0.059\log\frac{1}{8}\right)$$

$$E^{\ominus}_{Ce^{4+}\,|\,Ce^{3+}} = -1.24\ \text{V}$$

Now, $2Ce^{3+} + 2H^{\oplus} \rightleftharpoons 2Ce^{4+} + H_2$

At Eq. $E_{\text{cell}} = 0$.

$$\therefore \quad E^{\ominus} = \frac{0.059}{2}\log K$$

At anode $2Ce^{3+} \longrightarrow 2Ce^{4+} + 2e^-$ (Oxidation)

At cathode $2H^{\oplus} + 2e^- \longrightarrow H_2$ (Reduction)

Cell reaction $2Ce^{3+} + 2H^{\oplus} \longrightarrow 2Ce^{4+} + H_2$

$$\begin{aligned}E^{\ominus}_{\text{cell}} &= E^{\ominus}_{\text{red (cathode)}} - E^{\ominus}_{\text{red (anode)}}\\ &= E^{\ominus}_{\text{red}\,(H_2)} - E^{\ominus}_{\text{red}\,(Ce^{4+}\,|\,Ce^{3+})}\\ &= 0 - (-1.24) = 1.24\end{aligned}$$

$$\therefore \quad E^{\ominus} = \frac{0.059}{2}\log K$$

$$1.24 = \frac{0.059}{2}\log K$$

$$\log K = 42.03 \Rightarrow K = 1.08\times 10^{42}$$

Start Practice for JEE Main

Round I (Topically Divided Problems)

Conduction and Electrolytic Conductance

1. Electrolytes when dissolved in water dissociates into ions because
(a) they are unstable
(b) the water dissolves it
(c) the force of repulsion increases
(d) the force of electrostatic attraction are broken down by water

2. The conductivity of strong electrolyte
(a) increases on dilution slightly
(b) decreases on dilution
(c) does not change with dilution
(d) depends upon density of electrolyte itself

3. Which of the statements about solutions of electrolytes is not correct? **[NCERT Exemplar]**
(a) Conductivity of solution depends upon size of ions
(b) Conductivity depends upon viscosity of solution
(c) Conductivity does not depend upon solvation of ions present in solution
(d) Conductivity of solution increases with temperature

4. The conductivity of a 0.01 N solution is found to be $0.005\ \text{ohm}^{-1}\ \text{cm}^{-1}$. The equivalent conductivity of the solution will be
(a) $5\times 10^{-2}\ \text{ohm}^{-1}\ \text{cm}^2\ \text{equiv}^{-1}$
(b) $5.00\times 10^{-3}\ \text{ohm}^{-1}\ \text{cm}^2$
(c) $500\ \text{ohm}^{-1}\ \text{cm}^2\ \text{equiv}^{-1}$
(d) $0.5\ \text{ohm}^{-1}\ \text{cm}^2\ \text{equiv}^{-1}$

5. The equivalent conductivity of a solution containing 2.54 g of $CuSO_4$ per L is $91.0\,\Omega^{-1}\ \text{cm}^2\ \text{eq}^{-1}$. Its conductivity would be
(a) $2.9\times 10^{-3}\ \Omega^{-1}\ \text{cm}^{-1}$
(b) $1.8\times 10^{-2}\ \Omega^{-1}\ \text{cm}^{-1}$
(c) $2.4\times 10^{-4}\ \Omega^{-1}\ \text{cm}^{-1}$
(d) $3.6\times 10^{-3}\ \Omega^{-1}\ \text{cm}^{-1}$

6. Conductivity (unit Siemen) is directly proportional to the area of vessel and the concentration of the solution in it and is inversely proportional to the length of the vessel. Then, the units of the constant of proportionality is
(a) $S^2\ m^2\ mol$
(b) $S^2\ m^2\ mol^{-2}$
(c) $S\ m^2\ mol^{-1}$
(d) $S\ m\ mol^{-1}$

7. The cell constant of a conductivity cell …… . **[NCERT Exemplar]**
(a) changes with change of electrolyte
(b) changes with change of concentration of electrolyte
(c) changes with temperature of electrolyte
(d) remains constant for a cell

8. The specific conductance of 0.1 N KCl solution at 23°C is $0.012\ \text{ohm}^{-1}\ \text{cm}^{-1}$. The resistance of cell containing the solution at the same temperature was found to be 55 ohm. The cell constant will be
(a) $0.66\ \text{cm}^{-1}$
(b) $1.12\ \text{cm}^{-1}$
(c) $0.918\ \text{cm}^{-1}$
(d) $1.66\ \text{cm}^{-1}$

9. $\Lambda^0_{m\,[NH_4OH]}$ is equal to …… . **[NCERT Exemplar]**
(a) $\Lambda^0_{m(NH_4OH)} + \Lambda^0_{m(NH_4Cl)} - \Lambda^0_{m(HCl)}$
(b) $\Lambda^0_{m(NH_4Cl)} + \Lambda^0_{m(NaOH)} - \Lambda^0_{m(NaCl)}$
(c) $\Lambda^0_{m(NH_4Cl)} + \Lambda^0_{m(NaCl)} - \Lambda^0_{(NaOH)}$
(d) $\Lambda^0_{m(NaOH)} + \Lambda^0_{m(NaCl)} - \Lambda^0_{m(NH_4Cl)}$

10. Given the limiting molar conductivity as

$$\Lambda^\infty_m(\text{HCl}) = 425.9\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$
$$\Lambda^\infty_m(\text{NaCl}) = 126.4\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$
$$\Lambda^\infty_m\ (\text{CH}_3\text{COONa}) = 91\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

The molar conductivity, at infinite dilution, of acetic acid (in $\Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$) will be
(a) 481.5
(b) 390.5
(c) 299.5
(d) 516.9

11. The limiting molar conductivities Λ° for NaCl, KBr and KCl are 126, 152 and 150 S cm^2 mol^{-1} respectively. The Λ° for NaBr is

(a) 128 S cm^2 mol^{-1}
(b) 248 S cm^2 mol^{-1}
(c) 328 S cm^2 mol^{-1}
(d) 348 S cm^2 mol^{-1}

12. The resistance of a conductivity cell filled with 0.1 M KCl solution is 100 Ω. If R of the same cell when filled with 0.02 M KCl solution is 520 Ω, calculate the molar conductivity of 0.02 M KCl solution. The conductivity of 0.1 M KCl solution is 1.29 S m^{-1}. **[NCERT]**

(a) 124 S m^2 mol^{-1}
(b) 124×10^{-2} S m^2 mol^{-1}
(c) 124×10^{-4} S m^2 mol^{-1}
(d) 124×10^{-3} S m^2 mol^{-1}

13. Conductivity of 0.00241 M acetic acid is 7.896×10^{-5} S cm^{-1}. If Λ_m° for acetic acid is 390.5 S cm^2 mol^{-1}, what is its dissociation constant? **[NCERT]**

(a) 1.85×10^{-5} mol L^{-1}
(b) 2.68×10^{-5} mol L^{-1}
(c) 8.4×10^{-4} mol L^{-1}
(d) 3.98×10^{-4} mol L^{-1}

Electrolysis

14. During electrolysis, the species discharged at cathode are

(a) anion
(b) cation
(c) ions
(d) All of these

15. Electrolysis involves oxidation and reduction respectively at

(a) anode and cathode
(b) cathode and anode
(c) at both the electrodes
(d) None of these

16. In the electrolysis of aqueous sodium chloride solution which of the half cell reaction will occur at anode? **[NCERT Exemplar]**

(a) $Na^+(aq) + e^- \longrightarrow Na(s);\quad E^\ominus_{cell} = -2.71\,V$
(b) $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-;\quad E^\ominus_{cell} = 1.23\,V$
(c) $H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g);\quad E^\ominus_{cell} = 0.00\,V$
(d) $Cl^-(aq) \longrightarrow \frac{1}{2}Cl_2(g) + e^-;\quad E^\ominus_{cell} = 1.36\,V$

17. During the electrolysis of fused NaCl, which reaction occurs at anode?

(a) Chloride ions are oxidised
(b) Sodium ions are oxidised
(c) Chloride ions are reduced
(d) Sodium ions are reduced

18. Use of electrolysis is

(a) electrorefining
(b) electroplating
(c) Both (a) and (b)
(d) None of these

19. For which of the following highest charge is required? **[NCERT]**

(a) 1 mole of Al^{3+} to Al
(b) 1 mole of Cu^{2+} to Cu
(c) 1 mole of MnO_4^- to Mn^{2+}
(d) Same for all

20. The quantity of charge required to obtain one mole of aluminium from Al_2O_3 is **[NCERT Exemplar]**

(a) 1 F
(b) 6 F
(c) 3 F
(d) 2 F

21. The number of Faraday's needed to reduce 4 g-equivalents of Cu^{2+} to Cu metal will be

(a) 1
(b) 2
(c) 4
(d) 8

22. During the electrolysis of an electrolyte, the number of ions produced is directly proportional to the

(a) time consumed
(b) mass of electrons
(c) quantity of electricity passed
(d) electrochemical equivalent of electrolytes

23. The number of coulombs required to reduce 12.3 g of nitrobenzene to aniline, is

(a) 96500 C
(b) 5790 C
(c) 95700 C
(d) 57900 C

24. On passing 3 A of electricity for 50 min, 1.8 g metal deposits. The equivalent mass of metal is

(a) 9.3
(b) 19.3
(c) 38.3
(d) 39.9

25. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 A for 20 min. What mass of Ni is deposited at the cathode? (Atomic mass of Ni = 58.7) **[NCERT]**

(a) 5.87 g
(b) 1.82 g
(c) 3.97 g
(d) 2.22 g

26. When 9.65 C of electricity is passed through a solution of silver nitrate (atomic weight of Ag = 107.87 taking as 108), the amount of silver deposited is

(a) 5.8 mg
(b) 10.8 mg
(c) 15.8 mg
(d) 20.8 mg

27. An electric current is passed through silver nitrate solution using silver electrodes. 10.79 g of silver was found to be deposited on the cathode. If the same amount of electricity is passed through copper sulphate solution using copper electrodes, the weight of copper deposited on the cathode is

(a) 1.6 g
(b) 2.3 g
(c) 3.2 g
(d) 6.4 g

Galvanic Cell and the Nernst's Equation

28. Which of the following statements is correct? Galvanic cell converts
(a) chemical energy into electrical energy
(b) electrical energy into chemical energy
(c) metal from its elemental state to the combined state
(d) electrolyte into individual ions

29. In a galvanic cell, the electrons flow from
(a) anode to cathode through the external circuit
(b) anode to cathode through the solution
(c) cathode to anode through the external circuit
(d) cathode to anode through the solution

30. What flows in the internal circuit of a galvanic cell?
(a) Ions (b) Electrons
(c) Electricity (d) Atoms

31. Which cell will measure standard electrode potential of copper electrode? **[NCERT Exemplar]**
(a) $\mathrm{Pt}(s)\,|\,\mathrm{H_2}(g, 0.1\text{ bar})\,|\,\mathrm{H^+}(aq, 1\text{ M})\,||\,\mathrm{Cu^{2+}}(aq, 1\text{ M})\,|\,\mathrm{Cu}$
(b) $\mathrm{Pt(s)}\,|\,\mathrm{H_2}(g, 1\text{ bar})\,|\,\mathrm{H^+}(aq, 1\text{ M})\,||\,\mathrm{Cu^{2+}}(aq, 2\text{ M})\,|\,\mathrm{Cu}$
(c) $\mathrm{Pt(s)}\,|\,\mathrm{H_2}(g, 1\text{ bar})\,|\,\mathrm{H^+}(aq, 1\text{ M})\,||\,\mathrm{Cu^{2+}}\,(aq, 1\text{ M})\,|\,\mathrm{Cu}$
(d) $\mathrm{Pt}(s)\,|\,\mathrm{H_2}(g, 1\text{ bar})\,|\,\mathrm{H^+}(aq, 0.1\text{ M})\,||\,\mathrm{Cu^{2+}}(aq, 1\text{ M})||\,\mathrm{Cu}$

32. The standard potential at 25°C for the following half-reactions are given against them

$$\mathrm{Zn^{2+}} + 2e^- \longrightarrow \mathrm{Zn}; \quad E^\circ = -\,0.762\text{ V}$$
$$\mathrm{Mg^{2+}} + 2e^- \longrightarrow \mathrm{Mg}; \quad E^\circ = -\,2.37\text{ V}$$

When zinc dust is added to the solution of $\mathrm{MgCl_2}$,
(a) $\mathrm{ZnCl_2}$ is formed
(b) Mg is precipitated
(c) Zn dissolves in the solution
(d) No reaction takes place

33. Arrange the following metals in the order in which they displace each other from the solution of their salts. Al, Cu, Fe, Mg and Zn. **[NCERT]**
(a) Mg > Zn > Al > Fe > Cu (b) Mg > Fe > Al > Zn > Cu
(c) Mg > Al > Zn > Fe > Cu (d) Mg > Al > Fe > Zn > Cu

34. If a salt bridge is removed from the two half cells, the voltage
(a) drops to zero
(b) does not change
(c) increase gradually
(d) increases rapidly

35. An electrochemical cell can behave like an electrolytic cell when …… . **[NCERT Exemplar]**
(a) $E_{\text{cell}} = 0$ (b) $E_{\text{cell}} > E_{\text{ext}}$
(c) $E_{\text{ext}} > E_{\text{cell}}$ (d) $E_{\text{cell}} = E_{\text{ext}}$

36. Using the data given below find out the correct order of reducing tendency **[NCERT Exemplar]**

$$E^{\ominus}_{\mathrm{Cr_2O_7^{2-}/Cr^{3+}}} = 1.33\text{ V};\; E^{\ominus}_{\mathrm{Cl_2/Cl^-}} = 1.36\text{ V}$$
$$E^{\ominus}_{\mathrm{MnO_4^-/Mn^{2+}}} = 1.51\text{ V};\; E^{\ominus}_{\mathrm{Cr^{3+}/Cr}} = -0.74\text{ V}$$

(a) $\mathrm{Cr^{3+} < Cl^- < Mn^{2+} < Cr}$
(b) $\mathrm{Mn^{2+} < Cl^- < Cr^{3+} < Cr}$
(c) $\mathrm{Cr^{3+} < Cl^- < Cr_2O_7^{2-} < MnO_4^-}$
(d) $\mathrm{Mn^{2+} < Cr^{3+} < Cl^- < Cr}$

37. Use the data given in Q. 36 and find out which of the following is the strongest oxidising agent? **[NCERT Exemplar]**
(a) $\mathrm{Cl^-}$ (b) $\mathrm{Mn^{2+}}$
(c) $\mathrm{MnO_4^-}$ (d) $\mathrm{Cr^{3+}}$

38. The platinum electrodes were immersed in a solution of cupric sulphate and electric current was passed through the solution. After sometime, it was found that colour of copper sulphate disappeared with evolution of gas at the electrode. The colourless solution contains
(a) copper sulphate (b) copper hydroxide
(c) platinum sulphate (d) sulphuric acid

39. Saturated solution of $\mathrm{KNO_3}$ is used to make 'salt-bridge' because
(a) velocities of both $\mathrm{K^+}$ and $\mathrm{NO_3^-}$ are nearly the same
(b) velocity of $\mathrm{K^+}$ is greater than that of $\mathrm{NO_3^-}$
(c) velocity of $\mathrm{NO_3^-}$ is greater than that of $\mathrm{K^+}$
(d) $\mathrm{KNO_3}$ is highly soluble in water

40. Standard electrode potential of NHE at 298 K is
(a) 0.05 V (b) 0.10 V
(c) 0.50 V (d) 0.00 V

41. Which of the following statement is not correct about an inert electrode in a cell? **[NCERT Exemplar]**
(a) It does not participate in the cell reaction
(b) It provides surface either for oxidation or for reduction reaction
(c) It provides surface for conduction of electrons
(d) It provides surface for redox reaction

42. For a cell reaction involving a two electron change, the standard emf of the cell is found to be 0.295 V at 25°C. The equilibrium constant of the reaction, at 25°C, will be
(a) 10 (b) 1×10^{10}
(c) 1×10^{-10} (d) 10×10^{-2}

43. A cell constructed by coupling a standard copper electrode and a standard magnesium electrode has emf of 2.7 V. If the standard reduction potential of copper electrode is +0.34 V then that of the magnesium electrode is

(a) + 2.36 V (b) – 2.36 V
(c) + 3.26 V (d) – 3.26 V

44. $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O;\ E° = 1.51\ V$
$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O;\ E° = 1.23\ V$

$E°_{MnO_4^- \mid MnO_2}$ is

(a) 1.70 V (b) 0.91 V
(c) 1.37 V (d) 0.548 V

45. The standard reduction potential for Fe^{2+}/Fe and Sn^{2+}/Sn electrodes are -0.44 and -0.14 V respectively. For the given cell reaction, $Fe^{2+} + Sn \longrightarrow Fe + Sn^{2+}$, the standard emf is

(a) 0.42 V (b) – 0.42 V
(c) – 0.30 V (d) – 1.10 V

46. For the electrochemical cell,

$H_2(g)$ 1 atm | H^+(1 M) || Cu^{2+} (1 M) | Cu(s)

which one of the following statements is true?

(a) H_2 is anode, Cu is cathode
(b) Cu is anode, H_2 is cathode
(c) Oxidation occurs at Cu electrode
(d) Reduction occurs at H_2 electrode

47. Standard electrode potential of cell $H_2\ |H^+\ ||\ Ag^+\ |Ag$ is (Given, $E°_{Ag^+/Ag} = 0.80$ V)

(a) 0.4 V (b) 0.8 V
(c) 1.4 V (d) 1.8 V

48. The hydrogen electrode is dipped in a solution of pH = 3 at 25°C. The potential of the cell would be (the value of $\frac{2.303RT}{T}$ is 0.059 V)

(a) 0.059 V (b) 0.088 V
(c) 0.178 V (d) –0.177 V

49. $I_2(s)$ | I^-(0.1 M) half-cell is connected to a $H^+(aq)$ | H_2 (1 bar) | Pt half-cell and emf is found to be 0.7714 V. If $E°_{I_2/I^-} = 0.535$ V, find the pH of H^+/H_2 half-cell.

(a) 1 (b) 2
(c) 3 (d) 5

50. If the standard electrode potential of Cu^{2+}/Cu electrode is 0.34 V, what is the electrode potential at 0.01 M concentration of Cu^{2+}? ($T = 298$ K)

(a) 0.399 V (b) 0.281 V
(c) 0.222 V (d) 0.176 V

51. The standard reduction potential, $E°$ for the half-reactions are as

$$Zn \rightleftharpoons Zn^{2+} + 2e^-, \qquad E° = +0.76\ V$$
$$Fe \rightleftharpoons Fe^{2+} + 2e^-, \qquad E° = +0.41\ V$$

The $E°_{cell}$ for the cell formed by these two electrodes is

(a) – 0.35 V (b) – 1.17 V
(c) + 0.35 V (d) + 1.17 V

52. Which of the following statements is correct?
[NCERT Exemplar]

(a) E_{cell} and $\Delta_r G$ of cell reaction both are extensive properties
(b) E_{cell} and $\Delta_r G$ of cell reaction both are intensive properties
(c) E_{cell} is an intensive property while $\Delta_r G$ of cell reaction is an extensive property
(d) E_{cell} is an extensive property while $\Delta_r G$ of cell reaction is an intensive property

53. If the ΔG of a cell reaction $AgCl + e^- \longrightarrow Ag + Cl^-$ is –21.20 kJ, the standard emf of cell is

(a) 0.239 V (b) 0.220 V
(c) –0.320 V (d) – 0.110 V

54. What will be the emf for the given cell Pt | $H_2(p_1)$ | $H^+(aq)$ || $H_2(p_2)$ | Pt?

(a) $\frac{RT}{2F}\log_e\frac{p_1}{p_2}$ (b) $\frac{RT}{F}\log_e\frac{p_1}{p_2}$
(c) $\frac{RT}{F}\log_e\frac{p_2}{p_1}$ (d) None of these

Batteries

55. When a lead storage battery is charged, it acts as

(a) a primary cell
(b) a galvanic cell
(c) a concentration cell
(d) an electrolytic cell

56. While charging the lead stroage battery
[NCERT Exemplar]

(a) $PbSO_4$ anode is reduced to Pb
(b) $PbSO_4$ cathode is reduced to Pb
(c) $PbSO_4$ cathode is oxidised to Pb
(d) $PbSO_4$ anode is oxidised to PbO_3

57. On the basis of electrochemical theory of aqueous corrosion, the reaction occurring at the cathode is

(a) $O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$
(b) $H_2(g) + 2OH^-(aq) \longrightarrow 2H_2O(l) + 2e^-$
(c) $Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$
(d) $Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^-$

58. Which of the following statements is true for fuel cells?
(a) They are more efficient
(b) They are free from pollution
(c) They run till reactants are active
(d) All of the above

59. Which of the following reactions is used to make a fuel cell?
(a) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$
(b) $2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l)$
(c) $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + H_2O(l)$
(d) $Cd(s) + 2Ni(OH)_3(s) \longrightarrow CdO(s) + 2Ni(OH)_2 + 2H_2O(l)$

60. When an acid cell is charged, then
(a) voltage of cell increases
(b) resistance of cell increases
(c) electrolyte of cell dilutes
(d) None of the above

Round II (Mixed Bag)

1. Λ_{eq} of 0.10 N solution of CaI_2 is 100.0 S cm^2 eq^{-1} at 298 K. G^* of the cell $= 0.25\ cm^{-1}$. How much current will flow when the potential difference between the electrode is 5 V?
(a) 0.2 A
(b) 0.1 A
(c) 0.4 A
(d) 0.8 A

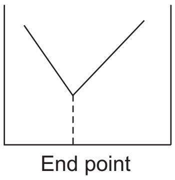
2. The resistance of a solution A is $50\,\Omega$ and that of solution B is $100\,\Omega$. Both the solutions are taken in same conductivity cell. If equal volumes of solution A and B are mixed, what is the resistance of the mixture using the same cell? (Assume there is no change or increase in the α of A and B on mixing.)
(a) $33.4\,\Omega$
(b) $66.7\,\Omega$
(c) $14.7\,\Omega$
(d) $77.8\,\Omega$

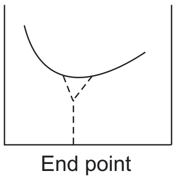
3. Conductivity of a saturated solution of $Co_2[Fe(CN)_6]$ is 2.0×10^{-6} S cm^{-1}. The conductivity water used to prepare the solution has conductivity 8.0×10^{-7} S cm^{-1}. If the ionic molar conductivities of Co^{2+} and $[Fe(CN)_6]^{4-}$ are 80.0 and 440.0 S cm^2 mol^{-1}, respectively, calculate the solubility product (K_{sp}) of $Co_2[Fe(CN)_6]$, assuming 100% ionization of the complex.
(a) 8×10^{-16}
(b) 3.2×10^{-16}
(c) 32×10^{-18}
(d) 3.2×10^{-18}

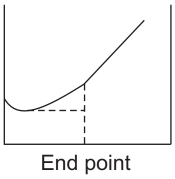
4. The electrical conductivity of a solution serves as a means of determining the end point in a chemical reaction, involved in the titration of acids, bases, or precipitation. Which of the following conductometric titrations represent the curve of HCl *vs* NH_4OH?

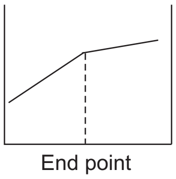
x-axis ⇒ Volume of alkali added

y-axis ⇒ Conductivity

(a)


(b)


(c)


(d)


5. A solution of sodium sulphate in water is electrolysed using inert electrodes. The products at the cathode and anode are respectively
(a) H_2, O_2
(b) O_2, H_2
(c) O_2, Na
(d) O_2, SO_2

6. When 1 F of electricity is passed through acidulated water, O_2 evolved is
(a) 1.0 dm^3
(b) 5.6 dm^3
(c) 11.2 dm^3
(d) 22.4 dm^3

7. The reaction,

$$\frac{1}{2}H_2(g) + AgCl(s) \longrightarrow H^+(aq) + Cl^-(aq) + Ag(s)$$

occurs in the galvanic cell
(a) $Pt/H_2(g)$ KCl(sol) || $AgCl(s)$ | Ag
(b) $Pt/H_2(g)$ HCl(sol) || $AgNO_3$(sol) | Ag
(c) $Pt/H_2(g)$ HCl(sol) || $AgCl(s)$ | Ag
(d) Ag/$AgCl(s)$ KCl(sol) || $AgNO_3$ | Ag

8. A gas X at 1 atm is bubbled through a solution containing a mixture of 1 M y^- and 1 M z^- at 25°C. If the order of reduction potential is $z > y > x$ then
(a) y will oxidise x and not z
(b) y will oxidise x and z
(c) y will oxidise z and not x
(d) y will reduce both x and z

9. A solution containing one mole per litre of each $Cu(NO_3)_2$, $AgNO_3$, $Hg_2(NO_3)_2$ and $Mg(NO_3)_2$ is being electrolysed by using inert electrodes. The values of standard electrode potentials in volts (reducing potentials) are $Ag / Ag^+ = +0.80$, $2Hg / Hg^{2+} = +0.79$, $Cu / Cu^{2+} = +0.34$, $Mg / Mg^{2+} = -2.37$. With increasing voltage, the sequence of deposition of metals on the cathode will be

(a) Ag, Hg, Cu
(b) Cu, Hg, Ag
(c) Ag, Hg, Cu, Mg
(d) Mg, Cu, Hg, Ag

10. An electrochemical cell is set up as follows

$Pt(H_2, 1\text{ atm}) \mid 0.1\text{ M HCl} \parallel 0.1\text{ M}$ acetic acid $\mid (H_2, 1\text{ atm})Pt$

Emf of this cell will not be zero because

(a) the pH of 0.1 M HCl and 0.1 M acetic acid is not the same
(b) acids used in two compartments are different
(c) emf of a cell depends on the molarities of acids used
(d) the temperature is constant

11. On passing 1 F of electricity through the electrolytic cells containing Ag^+, Ni^{2+} and Cr^{3+} ions solution, the deposited Ag (at. wt. = 108), Ni (at. wt. = 59) and Cr (at. wt. = 52) is

	Ag	Ni	Cr
(a)	108 g	29.5 g	17.3 g
(b)	108 g	59.5 g	52.0 g
(c)	108 g	108 g	108 g
(d)	108 g	117.5 g	166 g

12. Which of the following will form a cell with the highest voltage?

(a) 0.1 M Ag^+, 2 M Co^{2+}
(b) 2 M Ag^+, 2 M Co^{2+}
(c) 1 M Ag^+, 1 M Co^{2+}
(d) 2 M Ag^+, 0.1 M Co^{2+}

13. The Edison storage cell is represented as

$$Fe(s), FeO(s) \mid KOH(aq) \mid Ni_2O_3(s) \mid NiO(s)$$

The half reactions are

$$Ni_2O_3(s) + H_2O(l) + 2e^- \longrightarrow 2NiO(s) + 2OH^-; \quad E^\circ = +0.40\text{ V}$$

$$FeO(s) + H_2O(l) + 2e^- \longrightarrow Fe(s) + 2OH^-; \quad E^\circ = -0.87\text{ V}$$

Choose the incorrect statement.

(a) E_{anode} increases with increase in concentration of OH^-
(b) $E_{cathode}$ decreases with increase in concentration of OH^-
(c) $E^\circ_{cell} = 1.27$ V
(d) E_{cell} increases with increase in concentration of FeO

14. 1.05 g of lead ore containing impurity of Ag was dissolved in HNO_3 and the volume was made 350 mL. An Ag electrode was dipped in the solution.

$$Pt(H_2) \mid H^+ (1\text{ M}) \parallel Ag^+ \mid Ag$$

The E_{cell} is 0.503 V at 298 K. The per cent of Ag in the ore is ($E^\circ_{Ag^+Ag} = 0.80$ V)

(a) 0.033%
(b) 0.050%
(c) 0.066%
(d) 0.13%

15. Given, standard electrode potentials

$$Fe^{2+} + 2e^- \longrightarrow Fe, \quad E^\circ = -0.440\text{ V}$$

$$Fe^{3+} + 3e^- \longrightarrow Fe, \quad E^\circ = -0.036\text{ V}$$

The standard electrode potential (E°) for

$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \text{ is}$$

(a) + 0.771 V
(b) – 0.771 V
(c) + 0.417 V
(d) – 0.417 V

16. The emf of the cell, $Zn \mid Zn^{2+}\ (0.01\text{ M}) \parallel Fe^{2+}(0.001\text{ M}) \mid Fe$ at 298 K is 0.2905. The value of equilibrium constant for the cell reaction is

(a) $10^{\frac{0.32}{0.0295}}$
(b) $e^{\frac{0.32}{0.0295}}$
(c) $10^{\frac{0.32}{0.0591}}$
(d) $10^{\frac{0.26}{0.0295}}$

17. Consider the following disproportionation reaction,

$$2ClO_3^- \rightleftharpoons ClO_2^- + ClO_4^-$$

If the initial concentration of perchlorate ion is 0.1 M what it would be at equilibrium at 298 K?

($E^\circ_{ClO_4^-/ClO_3^-} = 0.36$ V and $E^\circ_{ClO_3^-/ClO_2^-} = 0.33$ V)

(a) 0.1 M
(b) 0.06 M
(c) 0.07 M
(d) 0.19 M

18. The standard emf for the given cell reaction, $Zn + Cu^{2+} \longrightarrow Cu + Zn^{2+}$ is 1.10 V at 25°C. The emf for the cell reaction, when 0.1 M Cu^{2+} and 0.1 M Zn^{2+} solutions are used, at 25°C, is

(a) 1.10 V
(b) – 1.10 V
(c) 2.20 V
(d) – 2.20 V

19. By how much is the oxidising power of $Cr_2O_7^{2-}/Cr^{3+}$ couple decreased if the H^+ concentration is decreased from 1 M to 10^{-3} M at 25°C?

(a) 0.207 V
(b) 0.414 V
(c) 0.001 V
(d) 0.287 V

20. The emf of a Daniell cell at 298 K is E_1, $Zn \mid \underset{(0.01\text{ M})}{ZnSO_4} \parallel \underset{(1.0\text{ M})}{CuSO_4} \mid Cu$. When the concentration of $ZnSO_4$ is 1.0 M and that of $CuSO_4$ is 0.01 M, the emf changed to E_2. What is the relationship between E_1 and E_2?

(a) $E_1 = E_2$
(b) $E_1 > E_2$
(c) $E_1 < E_2$
(d) $E_2 = 0 \neq E_1$

21. Cu^+ ion is not stable in aqueous solution because of disproportionation reaction. E° value for disproportionation of Cu^+ is

(given, $E^\circ_{Cu^{2+}/Cu^+} = 0.15, E^\circ_{Cu^{2+}/Cu} = 0.34$ V)

(a) + 0.38 V (b) − 0.38 V

(c) + 0.49 V (d) − 0.49 V

22. Consider the following reaction :

$$2Ag^+ + C_6H_{12}O_6 + H_2O \longrightarrow 2Ag(s) + C_6H_{12}O_7 + 2H^+$$

When ammonia is added to the solution, pH is raised to 11. Which half-cell reaction is affected by pH and by how much?

$$Ag^+ + e^- \longrightarrow Ag; \qquad E^\circ_{red} = 0.8 \text{ V}$$

$$C_6H_{12}O_6 + H_2O \longrightarrow C_6H_{12}O_7 + 2H^+ + 2e^-; \quad E^\circ_{red} = -0.05 \text{ V}$$

$$Ag(NH_3)_2^+ + e^- \longrightarrow Ag(s) + 2NH_3; \; E^\circ_{red} = 0.337 \text{ V}$$

(a) $E^\circ_{oxid.}$ will increase by a factor of 0.65 from $E^\circ_{oxid.}$

(b) $E^\circ_{oxid.}$ will decrease by a factor of 0.65 from $E^\circ_{oxid.}$

(c) $E^\circ_{red.}$ will increase by a factor of 0.65 from $E^\circ_{red.}$

(d) $E^\circ_{red.}$ will decrease by a factor of 0.65 from $E^\circ_{red.}$

23. EMF of which of the following cells at 298 K is highest? **[NCERT]**

Given,

$$E^\circ_{(Mg^{2+}/Mg)} = -2.37\text{V};$$

$$E^\circ_{(Cu^{2+}/Cu)} = +0.34\text{V};$$

$$E^\circ_{(Fe^{2+}/Fe)} = -0.44\text{V};$$

$$E^\circ_{(Sn^{2+}/Sn)} = -0.14\text{V};$$

$$E^\circ_{(1/2Br_2/Br^-)} = +1.08\text{V}.$$

(a) $Mg(s)|Mg^{2+}(0.001M)||\,Cu^{2+}(0.0001M)|Cu(s)$

(b) $Fe(s)|Fe^{2+}(0.001M)||H^+(1M)|H_2(g)$ (1 bar)$|Pt(s)$

(c) $Sn(s)|Sn^{2+}(0.050\text{ M})\;||H^+(0.020\text{ M})\;|H_2(g)$ (1 bar)$|Pt(s)$

(d) $Pt(s)|Br_2(l)|Br^-(0.010\text{ M})\;||\;H^+(0.030M)|H_2(g)$ (1bar) $|Pt(s)$

24. Using the following data, for the electrode potentials calculate ΔG°, in kJ, for the indicated reaction.

$$5Ce^{4+}(aq) + Mn^{2+}(aq) + 4H_2O(l) \longrightarrow 5Ce^{3+}(aq) + MnO_4^-(aq) + 8H^+(aq)$$

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l) \quad E^\circ = +1.51 \text{ V}$$

$$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq); E^\circ = +\,1.61 \text{ V}$$

(a) −36.24 (b) − 48.25

(c) −31.54 (d) −19.65

25. The value of K_w can be determined from emf data. If the standard half-reaction potentials are 0.00 V for $H^+(1\,M)\,|\,Pt(H_2)$ and −0.8277 V for the half reaction

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$$

K_w is

(a) 1.01×10^{-14} (b) 1.01×10^{-7}

(c) 2.36×10^{-8} (d) 5.55×10^{-7}

26. $E^\circ_{Cu^{2+}/Cu} = 0.34$ V. Calculate reduction potential at pH = 14 for the Cu^{2+}/Cu couples. K_{sp} of $Cu(OH)_2 = 1.0 \times 10^{-19}$.

(a) 0.22 V (b) − 0.22 V

(c) 0.44 V (d) − 0.44 V

27. The reversible reduction potential of pure water is − 0.413 V under 1.00 atm H_2 pressure. If the reduction is cosidered to be $2H^+ + 2e^- \longrightarrow H_2$, pH of pure water is

(a) 3 (b) 7

(c) 8 (d) 6.85

More than One Correct Option

28. Molar conductivity of ionic solution depends on …… **[NCERT Exemplar]**

(a) temperature

(b) distance between electrodes

(c) concentration of electrolytes in solution

(d) surface area of electrodes

29. What will happen during the electrolysis of aqueous solution of $CuSO_4$ in the presence of Cu electrodes? **[NCERT Exemplar]**

(a) Copper will deposit at cathode

(b) Copper will dissolve at anode

(c) Oxygen will be released at anode

(d) Copper will deposit at anode

30. $E^\ominus_{cell} = 1.1$ V for Daniell cell. Which of the following expressions are correct description of state of equilibrium in this cell? **[NCERT Exemplar]**

(a) $1.1 = K_c$ (b) $\dfrac{2.303RT}{2F} \log K_c = 1.1$

(c) $\log K_c = \dfrac{2.2}{0.059}$ (d) $\log K_c = 1.1$

31. How can the oxidation potential of a hydrogen electrode be decreased?

(a) Increasing the p_{H_2}

(b) Increasing the $[H^+]$

(c) Decreasing the p_{H_2}

(d) Decreasing the pOH of the solution

32. Which of the following conditions will increase the voltage of the cell represented by the following equation?

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

(a) Decrease in temperature
(b) Increase in pressure
(c) Decrease in the concentration of $Zn^{2+}(aq)$ ions
(d) Increase in the concentration of $Cu^{2+}(aq)$ ions

Assertion and Reason

Directions (Q. Nos. 33 to 37) *Each of these questions contains two statements : Statement* I (*Assertion*) *and Statement* II (*Reason*). *Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes* (*a*), (*b*), (*c*), (*d*) *given below :*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

33. **Statement I** Mercury cell does not give steady potential.

Statement II In the cell reaction, ions are not involved in solution. **[NCERT Exemplar]**

34. **Statement I** On increasing dilution, the specific conductance keep on increasing.

Statement II On increasing dilution, degree of ionisation of weak electrolyte increases and molality of ions also increases.

35. **Statement I** $E_{Ag^+/Ag}$ increases with increase in concentration of Ag^+ ions.

Statement II $E_{Ag^+/Ag}$ has a positive value. **[NCERT Exemplar]**

36. **Statement I** If an aqueous solution of NaCl is electrolysed using inert electrodes, chlorine gas is produced at the anode, and H_2 gas is produced at the cathode.

Statement II Electrolysis of aqueous solutions containing metal ion that is a weaker oxidising agent than $H^+(aq)$, will produce H_2 gas at cathode.

37. **Statement I** E_{cell} should have a positive value for the cell to function.

Statement II $E_{cathode} < E_{anode}$ **[NCERT Exemplar]**

Comprehension Based Questions

Directions (Q. Nos. 38 and 39) The concentration of potassium ions inside a biological cell is at least 20 times higher than outside. The resulting potential difference across the cell is important in several processes such as transmission of nerve impulses and maintaining the ion balance. A simple model for a concentration cell involving a metal M is

$$M(s) \mid M^{\oplus}(aq; 0.05\,\text{molar}) \mid\mid M^{\oplus}(aq; 1\,\text{molar}) \mid M(s)$$

For the above electrolytic cell, the magnitude of the cell potential is $|E_{cell}| = 70$ mV.

38. For the above cell

(a) $E_{cell} < 0; \Delta G > 0$	(b) $E_{cell} > 0; \Delta G < 0$
(c) $E_{cell} > 0; \Delta G > 0$	(d) $E_{cell} < 0; \Delta G < 0$

39. If the 0.05 molar solution of $M^{\oplus}$ is replaced by a 0.0025 molar $M^{\oplus}$ solution then the magnitude of the cell potential would be

(a) 35 mV	(b) 70 mV
(c) 140 mV	(d) 700 mV

Directions (Q. Nos. 40 to 42) A fuel cell is continuously supplied with an oxidant and a reductant so that it can deliver a current indefinitely. Fuel cell offer the possibility of achieving high thermodynamic efficiency in the conversion of Gibbs energy into mechanical work. Internal combustion engines at best convert only the fraction $\frac{(T_2 - T_1)}{T_2}$ of the heat of combustion into mechanical work. While the thermodynamic efficiency of the fuel cell is given by $\eta = \frac{\Delta G}{\Delta H}$, where ΔG is the Gibbs energy change for the cell reaction and ΔH is the enthalpy change of the cell reaction,

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \quad E^\circ = 1.2288\text{ V}$$

40. For a hydrogen-oxygen fuel cell if $\Delta H_f^\circ(H_2O, l) = -285$ kJ/mol then what will be its thermodynamic efficiency under standard conditions?

(a) 0.64	(b) 0.46
(c) 0.83	(d) 0.59

41. If 560 mL of H_2 gas at STP is fed into and is consumed by the fuel cell in 10 min then what is the current output of the fuel cell?

(a) 2	(b) 4
(c) 12	(d) 8

42. The advantage of using fuel cell in a motor car could be

(a) low initial cost	(b) emissionless operation
(c) light weight	(d) freedom from refueling

Previous Years' Questions

43. The standard reduction potentials for Zn^{2+}/Zn, Ni^{2+}/Ni and Fe^{2+}/Fe are – 0.76, – 0.23 and – 0.44 V respectively. The reaction $X + Y^{2+} \longrightarrow X^{2+} + Y$ will be spontaneous when **[AIEEE 2013]**

(a) $X = Ni, Y = Fe$ (b) $X = Ni, Y = Zn$
(c) $X = Fe, Y = Zn$ (d) $X = Zn, Y = Ni$

44. The reduction potential of hydrogen half-cell will be negative if **[AIEEE 2011]**

(a) $p(H_2) = 1$ atm and $[H^+] = 2.0$ M
(b) $p(H_2) = 1$ atm and $[H^+] = 1.0$ M
(c) $p(H_2) = 2$ atm and $[H^+] = 1.0$ M
(d) $p(H_2) = 2$ atm and $[H^+] = 2.0$ M

45. Resistance of 0.2 M solution of an electrolyte is 50 Ω. The specific conductance of the solution is 1.3 S m^{-1}. If resistance of the 0.4M solution of the same electrolyte is 260 Ω, its molar conductivity is **[AIEEE 2011]**

(a) $6250 \text{ S m}^2 \text{ mol}^{-1}$
(b) $6.25 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$
(c) $625 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$
(d) $62.5 \text{ S m}^2 \text{ mol}^{-1}$

46. The Gibbs energy for the decomposition of Al_2O_3 at 500°C is as follows

$$\frac{2}{3} Al_2O_3 \longrightarrow \frac{4}{3} Al + O_2; \ \Delta_r G = +966 \text{ kJ mol}^{-1}$$

The potential difference needed for electrolytic reduction of Al_2O_3 at 500°C is at least **[AIEEE 2010]**

(a) 4.5 V (b) 3.0 V
(c) 2.5 V (d) 5.0 V

47. Given, $E^\circ_{Cr^{3+}/Cr} = -0.72 \text{ V}, E^\circ_{Fe^{2+}/Fe} = -0.42 \text{ V}.$

The potential for the cell $Cr \mid Cr^{3+} (0.1M) \parallel Fe^{2+} (0.01M) \mid Fe$ is **[AIEEE 2008]**

(a) 0.26 V (b) 0.399 V
(c) – 0.339 V (d) – 0.26 V

48. The equivalent conductances of two strong electrolytes at infinite dilution in H_2O (where ions move freely through a solution) at 25°C are given below

$$\Lambda^\circ_{CH_3COONa} = 91.0 \text{ S cm}^2 / \text{equiv}$$
$$\Lambda^\circ_{HCl} = 426.2 \text{ S cm}^2 / \text{equiv}$$

What additional information/quantity one needs to calculate Λ° of an aqueous solution of acetic acid ? **[AIEEE 2007]**

(a) Λ° of NaCl
(b) Λ° of CH_3COOK
(c) The limiting equivalent conductance of H^+ ($\lambda^\circ_{H^+}$)
(d) Λ° of chloroacetic acid ($ClCH_2COOH$)

49. The cell, $Zn \mid Zn^{2+} (1 \text{ M}) \parallel Cu^{2+} (1 \text{ M}) \mid Cu$ ($E^\circ_{cell} = 1.10$ V), was allowed to be completely discharged at 298 K. The relative concentration of Zn^{2+} to Cu^{2+} $\left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right)$ is **[AIEEE 2007]**

(a) antilog (24.08) (b) 37.3
(c) $10^{37.3}$ (d) 9.65×10^4

50. The molar conductivities Λ°_{NaOAc} and Λ°_{HCl} at infinite dilution in water at 25°C are 91.0 and 426.2 S cm²/mol respectively. To calculate Λ°_{HOAc}, the additional value required is **[AIEEE 2006]**

(a) $\Lambda^\circ_{H_2O}$ (b) Λ°_{KCl}
(c) Λ°_{NaOH} (d) Λ°_{NaCl}

51. Given the data at 25°C,

$$Ag + I^- \longrightarrow AgI + e^-; \quad E^\circ = 0.152 \text{ V}$$
$$Ag \longrightarrow Ag^+ + e^-; \quad E^\circ = -0.800 \text{ V}$$

What is the value of $\log K_{sp}$ for AgI ?

$\left(2.303 \frac{RT}{F} = 0.059 \text{ V}\right)$ **[AIEEE 2006]**

(a) – 8.12 (b) + 8.612
(c) – 37.83 (d) – 16.13

52.

Electrolyte	KCl	KNO_3	HCl	NaOAC	NaCl
Λ^∞ (S cm² mol⁻¹)	149.9	145.0	426.2	91.0	126.5

Calculate Λ^∞_{HOAc} using appropriate molar conductances of the electrolytes listed above at infinite dilution in H_2O at 25°C. **[AIEEE 2005]**

(a) 217.5 (b) 390.7
(c) 552.7 (d) 517.2

53. Aluminium oxide may be electrolysed at 1000°C to furnish aluminium metal (atomic mass = 27 u; 1 Faraday = 96500 C). The cathode reaction is

$$Al^{3+} + 3e^- \longrightarrow Al^0$$

To prepare 5.12 kg of aluminium metal by this method would require **[AIEEE 2005]**

(a) 5.49×10^1 C of electricity
(b) 5.49×10^4 C of electricity
(c) 1.83×10^7 C of electricity
(d) 5.49×10^7 C of electricity

54. In a hydrogen-oxygen fuel cell, combustion of hydrogen occurs to **[AIEEE 2004]**

(a) generate heat
(b) create potential difference between the two electrodes
(c) produce high purity water
(d) remove adsorbed oxygen from electrode surfaces

55. The $E^\circ_{M^{3+}/M^{2+}}$ values for Cr, Mn, Fe and Co are –0.41, + 1.57, + 0.77 and + 1.97 V respectively. For which one of these metals the change in oxidation state from + 2 to + 3 is easiest ? **[AIEEE 2004]**

(a) Cr (b) Mn
(c) Fe (d) Co

56. In a cell that utilises the reaction

$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

addition of H_2SO_4 to cathode compartment will **[AIEEE 2004]**

(a) lower the E and shift equilibrium to the left
(b) lower the E and shift the equilibrium to the right
(c) increase the E and shift the equilibrium to the right
(d) increase the E and shift the equilibrium to the left

57. Standard reduction electrode potentials of three metals A, B and C are + 0.5 V, – 3.0 V and – 1.2 V respectively. The reducing power of these metals are **[AIEEE 2003]**

(a) $B > C > A$ (b) $A > B > C$
(c) $C > B > A$ (d) $A > C > B$

Answers

Round I

1. (d)	**2.** (a)	**3.** (c)	**4.** (c)	**5.** (a)	**6.** (c)	**7.** (d)	**8.** (a)	**9.** (b)	**10.** (b)
11. (a)	**12.** (c)	**13.** (a)	**14.** (b)	**15.** (a)	**16.** (b)	**17.** (a)	**18.** (c)	**19.** (c)	**20.** (c)
21. (c)	**22.** (c)	**23.** (d)	**24.** (b)	**25.** (b)	**26.** (b)	**27.** (c)	**28.** (a)	**29.** (a)	**30.** (a)
31. (c)	**32.** (d)	**33.** (c)	**34.** (a)	**35.** (c)	**36.** (b)	**37.** (c)	**38.** (d)	**39.** (a)	**40.** (d)
41. (d)	**42.** (b)	**43.** (b)	**44.** (a)	**45.** (c)	**46.** (a)	**47.** (b)	**48.** (d)	**49.** (c)	**50.** (b)
51. (c)	**52.** (c)	**53.** (b)	**54.** (a)	**55.** (d)	**56.** (a)	**57.** (a)	**58.** (d)	**59.** (a)	**60.** (a)

Round II

1. (a)	**2.** (b)	**3.** (c)	**4.** (b)	**5.** (a)	**6.** (b)	**7.** (c)	**8.** (a)	**9.** (a)	**10.** (a)
11. (a)	**12.** (d)	**13.** (d)	**14.** (a)	**15.** (a)	**16.** (a)	**17.** (b)	**18.** (a)	**19.** (b)	**20.** (b)
21. (a)	**22.** (a)	**23.** (a)	**24.** (b)	**25.** (a)	**26.** (b)	**27.** (b)	**28.** (a,c)	**29.** (a,b)	**30.** (b,c)
31. (b,c)	**32.** (c,d)	**33.** (d)	**34.** (d)	**35.** (b)	**36.** (a)	**37.** (c)	**38.** (b)	**39.** (c)	**40.** (c)
41. (d)	**42.** (b)	**43.** (d)	**44.** (c)	**45.** (b)	**46.** (c)	**47.** (a)	**48.** (a)	**49.** (c)	**50.** (d)
51. (d)	**52.** (b)	**53.** (d)	**54.** (b)	**55.** (a)	**56.** (c)	**57.** (a)			

the Guidance

Round I

3. Conductivity also depends upon the solvation of ions.

4. $$\Lambda^\circ_{eq} = \kappa \times \frac{1000}{\text{normality}}$$

$$= \frac{0.005 \times 1000}{0.01} = 500 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$$

5. $$\kappa = \Lambda_{eq} \cdot C$$

$$= (91 \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}) \left(\frac{2.54}{159/2 \times 1000} \text{ eq} \cdot \text{cm}^{-3} \right)$$

$$= 2.9 \times 10^{-3} \ \Omega^{-1} \text{ cm}^{-1}$$

8. $$\kappa = \frac{1}{R} \times \text{cell constant}$$

$$\therefore \ \text{Cell constant} = \kappa \times R = 0.012 \times 55 = 0.66 \text{ cm}^{-1}$$

9. From Kohlrausch's law,

$$\Lambda^0_{m(NH_4OH)} = \Lambda^0_{m(NH_4Cl)} + \Lambda^0_{m(NaOH)} - \Lambda^0_{(NaCl)}$$

10. Sum of molar conductivity of reactants = sum of molar conductivity of producs

Therefore, for the reaction

$$CH_3COOH + NaCl \longrightarrow CH_3COONa + HCl$$

$$\Lambda_m^0\ \mathrm{CH_3COOH} = \Lambda_m^0\mathrm{CH_3COONa} + \Lambda_m^0\mathrm{HCl} - \Lambda_m^0\mathrm{NaCl}$$
$$= 91 + 425.9 - 126.4$$
$$= 390.5\ \Omega^{-1}\ \mathrm{cm^2\ mol^{-1}}$$

11. $(126\ \mathrm{S\ cm^2\ mol^{-1}})\Lambda^\infty_{\mathrm{NaCl}} = \Lambda^\infty_{\mathrm{Na^+}} + \Lambda^\infty_{\mathrm{Cl^-}}$ ...(i)

$(152\ \mathrm{S\ cm^2\ mol^{-1}})\ \Lambda^\infty_{\mathrm{KBr}} = \Lambda^\infty_{\mathrm{K^+}} + \Lambda^\infty_{\mathrm{Br^-}}$ ...(ii)

$(150\ \mathrm{S\ cm^2\ mol^{-1}})\ \Lambda^\infty_{\mathrm{KCl}} = \Lambda^\infty_{\mathrm{K^+}} + \Lambda^\infty_{\mathrm{Cl^-}}$ ...(iii)

By Eqs. (i) + (ii) – (iii)

$$\because \quad \Lambda^\infty_{\mathrm{NaBr}} = \Lambda^\infty_{\mathrm{Na^+}} + \Lambda^\infty_{\mathrm{Br^-}}$$
$$= 126 + 152 - 150$$
$$= 128\ \mathrm{S\ cm^2\ mol^{-1}}$$

12. Cell constant, $G^* =$ Conductivity × Resistance

$$= 1.29\ \mathrm{S\ m^{-1}} \times 100\ \Omega$$
$$= 129\ \mathrm{m^{-1}} = 1.29\ \mathrm{cm^{-1}}$$

Conductivity (κ) of 0.02 M KCl solution $= \dfrac{G^*}{R}$

$$= \frac{129\ \mathrm{m^{-1}}}{520\ \Omega} = 0.248\ \mathrm{m^{-1}}$$

Concentration $= 0.02\ \mathrm{M} = 1000 \times 0.02\ \mathrm{mol\ m^{-3}}$

$$= 20\ \mathrm{mol\ m^{-3}}$$

Molar conductivity $(\Lambda_m) = \dfrac{\kappa}{c} = \dfrac{0.248\ \mathrm{S\ m^{-1}}}{20\ \mathrm{mol\ m^{-3}}}$

$$= 124 \times 10^{-4}\ \mathrm{S\ m^2\ mol^{-1}}$$

13. Calculation of molar conductivity (Λ^c_m)

$$\kappa = 7.896 \times 10^{-5}\ \mathrm{S\ cm^{-1}};$$
$$C = 0.00241 \mathrm{mol\ L^{-1}} = \frac{0.00241}{10^3}\ \mathrm{mol\ cm^{-3}}$$
$$= 241 \times 10^{-8} \mathrm{mol\ cm^{-3}}$$
$$\Lambda^c_m = \frac{\kappa}{C} = \frac{(7.896 \times 10^{-5}\ \mathrm{S\ cm^{-1}})}{(241 \times 10^{-8}\ \mathrm{mol\ cm^{-3}})}$$
$$= 32.76\ \mathrm{S\ cm^2\ mol^{-1}}$$

Calculation of degree of dissociation of $\mathrm{CH_3COOH}$ (α)

$$\alpha = \frac{\Lambda^c_m}{\Lambda^\circ_m} = \frac{(32.76\ \mathrm{S\ cm^2\ mol^{-1}})}{(390.5\ \mathrm{S\ cm^2\ mol^{-1}})}$$
$$= 0.084 = 8.4 \times 10^{-2}$$

Calculation of dissociation constant (K_a)

$$K_a = \frac{[\mathrm{CH_3COO^-}]\ [\mathrm{H^+}]}{[\mathrm{CH_3COOH}]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$
$$= \frac{(0.00241\ \mathrm{mol\ L^{-1}}) \times (0.084)^2}{(1 - 0.084)}$$
$$= 0.0000185\ \mathrm{mol\ L^{-1}}$$
$$= 1.85 \times 10^{-5}\ \mathrm{mol\ L^{-1}}$$

16. Anode is always the site of oxidation. Thus, the reaction where oxidation occurs, *i.e.*, electron releases occurs at anode. Moreover H_2O is oxidised more readily as compared to $\mathrm{Cl^-}$.

17. During the electrolysis of fused NaCl, chloride ions are oxidised at anode and this process is called oxidation.

19. (i) **1 mol of $\mathbf{Al^{3+}}$ to Al**

electrode reaction : $\underset{1\,\mathrm{mol}}{\mathrm{Al^{3+}}(aq)} + \underset{3\,\mathrm{mol}}{3e^-} \longrightarrow \mathrm{Al}(s)$

Quantity of charge required for reduction of 1 mole of $\mathrm{Al^{3+}} = 3$ Faraday $= 3 \times 96500\ \mathrm{C} = 289500\ \mathrm{C}$

$$= 2.896 \times 10^5\ \mathrm{C}$$

(ii) **1 mol $\mathbf{Cu^{2+}}$ to Cu**

Electrode reaction : $\underset{1\mathrm{mol}}{\mathrm{Cu^{2+}}(aq)} + \underset{2\mathrm{mol}}{2\,e^-} \longrightarrow \mathrm{Cu}(s)$

Quantity of charge required for reducing 1 mole $\mathrm{Cu^{2+}}$ to Cu = 2 F = 2 × 96500 C = 193000 C = 1.93×10^5C

(iii) **1 mol $\mathbf{MnO_4^-}$ to $\mathbf{Mn^{2+}}$**

Electrode reaction : $\underset{\substack{(\text{ox.no.}\\ \text{of Mn} = 7)\\ 1\ \text{mol}}}{\mathrm{MnO_4^-}} + \underset{5\text{mol}}{5e^-} \longrightarrow \underset{\substack{(\text{ox.no.of}\\ \text{Mn} = 2)}}{\mathrm{Mn^{2+}}}$

Quantity of charge required for reducing 1 mole $\mathrm{MnO_4^-}$ to $\mathrm{Mn^{2+}}$ = 5 F = 5 × 96500 = 482500 C = 4.825×10^5C

21. Number of g-equivalent = number of faraday pass

$$4\ \mathrm{g} = 4\,\mathrm{F}$$

22. According to Faraday law, number of ions produced ∝ quantity of electricity passed.

23. $\mathrm{C_6H_5NO_2} + 6\mathrm{H^+} + 6e^- \longrightarrow \mathrm{C_6H_5NH_2} + 2\mathrm{H_2O}$

1 mol (= 123 g) nitrobenzene requires 6 moles of electrons

$$= 6 \times 96500\ \mathrm{C\ charge}$$

∴ 12.3 g nitrobenzene will require charge

$$= \frac{6 \times 96500 \times 12.3}{123}$$
$$= 6 \times 9650 = 57900\mathrm{C}$$

24. $w_{\text{metal}} = \dfrac{E \times i \times t}{96500} = \dfrac{E \times 3 \times 50 \times 60}{96500}$

$$\therefore \quad E = \frac{96500 \times w}{3 \times 50 \times 60} = \frac{96500 \times 1.8}{3 \times 50 \times 60} = 19.3$$

25. Quantity of electricity used = current in amperes × time in second

$$= 5\mathrm{A} \times (20 \times 60)\ \mathrm{s} = 6000\ \mathrm{C}$$

Chemical equation for the reaction during electrolysis :

$$\mathrm{Ni(NO_3)_2}(aq) + 2\mathrm{H^+} + \underset{2\mathrm{F}}{2e^-} \longrightarrow \underset{58.7\mathrm{g\ mol^{-1}}}{\mathrm{Ni}} + 2\mathrm{HNO_3}$$

Charge Q on n moles of electrons is given by : $Q = nF$

Charge required to deposit 1 mole nickel

$$= 2\,F = 2 \times 96500\ \text{C} = 1.93 \times 10^5\ \text{C}$$

Molar mass of nickel = 58.7g mol^{-1}

1.93×10^5 C of charge produces nickel = 58.7g

$$6000\ \text{C of charge produces nickel} = \frac{(58.7\text{g}) \times (6000\ \text{C})}{(1.93 \times 10^5\text{C})}$$

$$= 1.825\ \text{g}$$

26. $w_{\text{Ag}} = \dfrac{E_{\text{Ag}} \times Q}{96500} = \dfrac{108 \times 9.65}{96500} = 1.08 \times 10^{-2}\ \text{g} = 10.8\ \text{mg}$

27. Number of equivalents of silver formed

= number of equivalents of copper formed

In $AgNO_3$, Ag is in +1 oxidation state.

In $CuSO_4$, Cu is in +2 oxidation state.

$$\text{Equivalent weight of Ag} = \frac{108}{1} = 108\ \text{g equi}^{-1}$$

$$\text{Equivalent weight of Cu} = \frac{63.6}{2} = 31.8\ \text{g equi}^{-1}$$

$$\frac{w_1}{w_2} = \frac{E_1}{E_2}$$

$$\therefore \qquad \frac{10.79}{w_{\text{Cu}}} = \frac{108}{31.8}$$

$$\text{or} \qquad w_{\text{Cu}} = \frac{10.79 \times 31.8}{108} = 3.2\ \text{g}$$

31. $\text{Pt}(s)\,|\,H_2(g, 1\text{bar})\,|\,H^+(aq, 1\text{M})\,||\,Cu^{2+}(aq, 1\text{M})\,|\,Cu$

will be use to measure standard electrode potential of copper electrode.

32. $Zn + MgCl_2 \longrightarrow$ no reaction

This type of reaction does not occur because

$Mg^{2+} E^\circ = -\,2.37$ V, while $Zn^{2+} E^\circ = -\,0.76$ V

33. $Mg > Al > Zn > Fe > Cu$

It means that every metal on the left side can displace the next one (s) from its salt solution.

34. When the salt bridge is removed, potential drops to zero.

35. When $E_{\text{ext}} > E_{\text{cell}}$, the cell behaves like an electrolytic cell.

36. More negative or less positive is the value of reduction potential, stronger is the reducing agent.

Thus, the order of reducing tendency is

$$\underset{(1.51)}{Mn^{2+}} < \underset{(1.36)}{Cl^-} < \underset{(1.33)}{Cr^{3+}} < \underset{(-0.74)}{Cr}$$

37. Higher the value of reduction potential, stronger is the oxidising agent. Thus, MnO_4^- is the strongest oxidising agent.

38. During electrolysis of $CuSO_4$, Cu^{2+} gets discharged at cathode and OH^- at anode. Thus, solution becomes acidic due to excess of H^+ and SO_4^{2-} or H_2SO_4 (sulphuric acid).

39. Velocities of both K^+ and NO_3^- are nearly the same in KNO_3, so it is used to make salt-bridge.

40. Standard electrode potential of NHE is taken as 0.00 V at 298 K.

42. We know that, $\Delta G^\circ = -\,nFE^\circ$

$$\Delta G^\circ = -\,2.303\,RT \log K_c$$

$$\therefore \qquad nFE^\circ = 2.303\,RT \log K_c$$

$$\log K_c = \frac{nFE^\circ}{2.303\,RT}$$

$$= \frac{2 \times 96500 \times 0.295}{2.303 \times 8.314 \times 298}$$

$$\log K_c = 9.97$$

$$\therefore \qquad K_c = 1 \times 10^{10}$$

43. Mg lies above Cu in electrochemical series and hence, Cu electrode acts as cathode.

$$E^\circ_{\text{cell}} = E^\circ_{Cu^{2+}/Cu} - E^\circ_{Mg^{2+}/Mg}$$

$$\therefore \qquad 2.70\ \text{V} = 0.34 - E^\circ_{Mg^{2+}/Mg}$$

$$\therefore \qquad E^\circ_{Mg^{2+}/Mg} = -2.36\ \text{V}$$

44. For the reaction,

$$MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O$$

$$-E_3 = \frac{-1.51 \times 5 + 2 \times 1.23}{3}$$

$$\therefore \qquad E_3 = 1.70\ \text{V}$$

45. For the cell reaction, Fe acts as cathode and Sn as anode. Hence,

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$= -\,0.44 - (-\,0.14) = -\,0.30\ \text{V}$$

The negative emf suggests that the reaction goes spontaneously in reversed direction.

46. H_2 is anode because oxidation takes place. Cu is cathode because reduction takes place.

47. $\frac{1}{2}H_2\ |\ H^+\,||\,Ag^+\,|\ Ag$

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$= E^\circ_{Ag^+/Ag} - E^\circ_{H^+/\frac{1}{2}H_2}$$

$$= (0.80) - (0.0) = 0.80\ \text{V}$$

48. Reduction potential of hydrogen electrode,

$$E_H = -\,\frac{2.303RT}{F} \log \frac{1}{[H^+]}$$

$$= -\,0.059\ \text{pH} = -\,0.059 \times 3$$

$$= -\,0.177\ \text{V}$$

49. The cell reaction is

$$H_2(g) + I_2(s) \rightleftharpoons 2H^+(aq) + 2I^-(aq)$$

$$0.7714 = 0.535 - \frac{0.0591}{2} \log \frac{[H^+]^2[I^-]^2}{p_{H_2}}$$

$$\therefore \qquad pH = 3$$

50. $Cu^{2+} + 2e^- \longrightarrow Cu$

$$E = E° - \frac{0.0591}{2} \log \frac{1}{[Cu^{2+}]}$$

$$= 0.34 - \frac{0.0591}{2} \log 100$$

$$= 0.34 - 0.0591 = 0.281 \text{ V}$$

51. In this reaction,

$$\underbrace{Fe^{2+} + \underbrace{Zn \longrightarrow Zn^{2+}}_{\text{Oxidation}} + Fe}_{\text{Reduction}}$$

$$\text{EMF} = E_{\text{cathode}} - E_{\text{anode}}$$

$$= -0.41 - (-0.76) = +0.35 \text{ V}$$

52. E_{cell} is an intensive property whereas $\Delta_r G$ for a cell reaction is an extensive property.

53. We know that, $\Delta G° = -nFE°$

$$-21.2 \times 10^3 = -1 \times 96500 \times E$$

$$E = \frac{21.2 \times 10^3}{96500} = 0.220 \text{ V}$$

54. Anode reaction $H_2(p_1) \longrightarrow 2H^+$

Cathode reaction $2H^+ \longrightarrow H_2(p_2)$

$$E_{\text{cathode}} = -\frac{RT}{2F} \ln \frac{p_2}{[H^+]^2}$$

$$E_{\text{anode}} = -\frac{RT}{2F} \ln \frac{[H^+]^2}{p_1}$$

$$E_{\text{cell}} = E_{\text{anode}} + E_{\text{cathode}}$$

$$= -\frac{RT}{2F} \ln \frac{[H^+]^2}{p_1} - \frac{RT}{2F} \ln \frac{p_2}{[H^+]^2}$$

$$= -\frac{RT}{2F} \ln \frac{p_2}{p_1}$$

$$= \frac{RT}{2F} \ln \frac{p_1}{p_2}$$

56. During charging of lead storage battery the reaction occurring is

$$2PbSO_4(s) + 2H_2O \longrightarrow Pb(s) + PbO_2(s) + 2H_2SO_4(aq)$$

57. At cathode $2H^+(aq) + 2e^- \longrightarrow 2H$

$$2H + \frac{1}{2}O_2 \longrightarrow H_2O$$

$$\overline{\underline{2H^+ + \frac{1}{2}O_2 + 2e^- \longrightarrow H_2O}}$$

Round II

1. $\Lambda_{eq} = \dfrac{\kappa \times 1000}{N}$, $\kappa = \dfrac{\Lambda_{eq} \times N}{1000} = \dfrac{100 \times 0.1}{1000} = 0.01 \text{ S cm}^{-1}$

$$G(\text{conductance}) = \frac{\kappa}{G^*(\text{cell constant})}$$

$$= \frac{0.01}{0.25} = 0.04\ \Omega^{-1} \text{ or S}$$

$$R = \frac{1}{G} = \frac{1}{0.04} = 25\ \Omega$$

$$\text{Current in ampere} = \frac{\text{potential difference (by Ohms's law)}}{\text{resistance (ohm)}}$$

$$= \frac{5}{25} = 0.2 \text{ A}$$

2. For solution A,

$$\text{Conductivity } (\kappa_A) = G(\text{Conductance}) \times G^*(\text{cell constant})$$

$$= \frac{1}{50} \times G^* \qquad \ldots(i)$$

For solution B,

$$\text{Conductivity } (\kappa_B) = \frac{1}{100} \times G^* \qquad \ldots(ii) \qquad \left(\begin{array}{l} \because G^* \text{ is same} \\ \text{for } A \text{ and } B \end{array}\right)$$

When equal volumes of A and B are mixed, dilution becomes doubled in both the solutions. Hence, their individual contribution towards the conductivity of the mixture will be $\kappa_A/2$ and $\kappa_B/2$, respectively, and conductivity of the mixture will be $\left(\dfrac{\kappa_A + \kappa_B}{2}\right)$.

$$\text{For the mixture : } \left(\frac{\kappa_A + \kappa_B}{2}\right) = \frac{1}{R} \times G^* \qquad \ldots(iii)$$

From Eqs. (i), (ii) and (iii), we get

$$R = 66.67\ \Omega$$

3. $\Lambda^{\circ}_{m\,(\text{complex solution})} = 2\lambda^{\circ}_{Co^{2+}} + \lambda^{\circ}_{[Fe(CN)_6]^{4-}}$

$$= 2 \times 80 + 440$$

$$= 600 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\kappa_{\text{complex}} = \kappa_{\text{solution}} - \kappa_{H_2O}$$

$$= 2 \times 10^{-6} - 8 \times 10^{-7}$$

$$= 2 \times 10^{-6} - 0.8 \times 10^{-6}$$

$$= 1.2 \times 10^{-6} \text{ S cm}^{-1}$$

If S mol L^{-1} is the solubility of complex, then,

$$\Lambda_m^\circ = \Lambda_m = \frac{\kappa \times 1000}{S}$$

$$600 \text{ S cm}^2 \text{ mol}^{-1} = \frac{1.2 \times 10^{-6} \text{ S cm}^{-1} \times 1000 \text{ cm}^3}{S \text{ mol L}^{-1}}$$

$$\therefore \quad S = \frac{1.2 \times 10^{-6} \times 1000 \text{ cm}^3}{600} = 2 \times 10^{-6} \text{ mol L}^{-1}$$

$$\underset{}{Co_2[Fe(CN)_6] + aq} \rightleftharpoons \underset{2S}{2Co^{2+}} + \underset{S}{[Fe(CN)_6]^{4-}}$$

$$\therefore \quad K_{sp} = [Co^{2+}]^2[Fe(CN)_6^{4-}]$$

$$= (2S)^2 \times S = 4S^3$$

$$= 4 \times (2 \times 10^{-6})^3$$

$$= 3.2 \times 10^{-17} \text{ M}^3$$

4. Curve (b) is the conductimetric curve for strong acid and weak base.

5. **At cathode** $2\,H^+ + 2\,e^- \longrightarrow H_2$

At anode $2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2\,e^-$

6. Reaction for electrolysis of water is

$$2H_2O \rightleftharpoons 4H^+ + 2O^{2-}$$

$$2O^{2-} \longrightarrow O_2 + 4e^-$$

$$4e^- + 4H^+ \longrightarrow 2H_2$$

$\because$ $n = 4$,

So, 4 F charge liberates = 1 mol = 22.4 dm^3 oxygen.

$\therefore$ 1 F charge will liberate $= \frac{22.4}{4} = 5.6$ dm^3 oxygen

7. H_2 undergoes oxidation and $AgCl(Ag^+)$ undergoes reduction.

Hence, the cell is representing as

$$Pt\,|\,H_2(g), HCl(sol)\,||\,AgCl(s)\,|\,Ag$$

8. Since the order of reduction poential is

$$z > y > x$$

so z can oxidise x as well as y.

y can oxidise x but not z

x can reduce z as well as y.

9. A cation having highest reduction potential will be reduced first and so on. However, Mg^{2+} in aqueous solution will not be reduced ($E^\circ_{Mg^{2+}/Mg} < E_{H_2O/\frac{1}{2}H_2 + OH^-}$). Instead water would be reduced in preference.

Thus, the sequence of deposition of metals on the cathode is Ag, Hg, Cu.

10. The pH of 0.1 M HCl and 0.1 M acetic acid is not the same, because HCl is a strong acid, so its pH is less and CH_3COOH is a weak acid, so its pH is most.

11. Weight of Ag deposited = eq. wt. of Ag = 108 g

Weight of Ni deposited = eq. wt. of Ni = 29.5 g

Weight of Cr deposited = eq. wt. of Cr = 17.3 g

12. Cobalt is anode, *i.e.*, oxidation takes place on cobalt electrode *i.e.*, cell reaction is

$$Co + 2Ag^+ \longrightarrow Co^{2+} + 2Ag$$

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\ln\frac{[Co^{2+}]}{[Ag^+]^2}$$

Thus, less is the factor $\frac{[Co^{2+}]}{[Ag^{3+}]}$, greater is the E_{cell}.

13. $E^\circ_{cell} = 0.87 + 0.40 = 1.27$ V

Cell reaction : $Fe + Ni_2O_3 \longrightarrow FeO + 2NiO$

E_{cell} remains unaffected from the concentration of FeO.

14. Cell reaction : $\frac{1}{2}H_2(g) + Ag^+(x) \rightleftharpoons Ag(x) + H^+(1M)$

$$E = E^\circ - \frac{0.0591}{n}\log\frac{[H^+]}{[Ag^+]}$$

$$0.503 = 0.80 - \frac{0.0591}{1}\log\frac{1}{x}$$

$$x = 9.43 \times 10^{-6} \text{ M}$$

Number of moles of Ag^+ in 350 mL

$$= \frac{9.43 \times 10^{-6} \times 350}{1000} = 3.3 \times 10^{-6}$$

Mass of Ag $= 3.3 \times 10^{-6} \times 108 = 3.56 \times 10^{-4}$ g

Percentage of Ag in the ore $= \frac{3.56 \times 10^{-4}}{1.05} \times 100$

$$= 0.0339\%$$

15. We know that,

$$\Delta G^\circ = -\,nFE^\circ$$

$$Fe^{2+} + 2\,e^- \longrightarrow Fe$$

$$\Delta G^\circ = -\,2 \times F \times (-\,0.440 \text{ V}) = 0.880 \text{ F} \qquad \text{...(i)}$$

$$Fe^{3+} + 3\,e^- \longrightarrow Fe$$

$$\Delta G^\circ = -\,3 \times F \times (-\,0.036) = 0.108 \text{ F} \qquad \text{...(ii)}$$

On subtracting Eqs. (i) from (ii), we get

$$Fe^{3+} + e^- \longrightarrow Fe^{2+}$$

$$\Delta G^\circ = 0.108 \text{ F} - 0.880 \text{ F} = -\,0.772 \text{ F}$$

E° for the reaction $= -\frac{\Delta G^\circ}{nF} = -\frac{(-\,0.772 \text{ F})}{1 \times \text{F}} = +\,0.772$ V

16. For the given cell, reaction is

$$Zn + Fe^{2+} \longrightarrow Zn^{2+} + Fe$$

$$E = E^\circ - \frac{0.0591}{n}\log\frac{C_1}{C_2}$$

or, $$E^\circ = E + \frac{0.0591}{n}\log\frac{C_1}{C_2}$$

$$= 0.2905 + \frac{0.0591}{2}\log\frac{10^{-2}}{10^{-3}} = 0.32\text{ V}$$

$$E^\circ = \frac{0.0591}{2}\log K_c$$

$$\therefore \quad \log K_c = \frac{0.32 \times 2}{0.0591} = \frac{0.32}{0.0295}$$

$$K_c = 10^{\frac{0.32}{0.0295}}$$

17. Oxidation half-cell

$$\text{ClO}_3^- \longrightarrow \text{ClO}_4^- + 2e^-; \qquad E^\circ_{\text{cell}} = -0.36\text{ V}$$

Reduction half-cell

$$\text{ClO}_3^- + 2e^- \longrightarrow \text{ClO}_2^-; \qquad E^\circ_{\text{cell}} = 0.33\text{ V}$$

$$E^\circ_{\text{cell}} = 0.33 - 0.36 = -0.03 = \frac{RT}{2F}\ln K$$

or $$-0.03 = \frac{0.059}{2}\log K \quad \text{or} \quad K = 0.1$$

$$\underset{0.1-2x}{2\text{ClO}_3^-} \rightleftharpoons \underset{x}{\text{ClO}_4^-} + \underset{x}{\text{ClO}_2^-}$$

$$\frac{x^2}{(0.1-2x)^2} = 0.1$$

or $$x = 1.94 \times 10^{-2}$$

$$C = 0.1 - 2 \times 1.94 \times 10^{-2}$$

$$= 0.06$$

18. $$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n}\log\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$= 1.10 - \frac{0.059}{2}\log\frac{0.1}{0.1}$$

$$= 1.10\text{ V}$$

19. Half-cell reaction is

$$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$$

$$E_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} - E^\circ_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}}$$

$$= -\frac{0.0591}{n}\log\frac{[\text{Cr}^{3+}]^2}{[\text{Cr}_2\text{O}_7^{2-}][\text{H}^+]^{14}}$$

$$= \frac{0.0591}{6}\log[10^{-3}]^{14} = -0.414\text{ V}$$

20. $$E_1 = E_0 - \frac{0.0591}{2}\log\frac{0.01}{1} = E_0 + \frac{0.0591}{2} \times 2$$

$$E_2 = E_0 - \frac{0.0591}{2}\log\frac{1}{0.01}$$

$$= E_0 - \frac{0.0591}{2} \times 2$$

$$\therefore \quad E_1 > E_2$$

21. The required reaction ($\text{Cu}^{2+} + \text{Cu} \longrightarrow 2\text{Cu}^+$) can be obtained by using the following reactions

$$\text{Cu}^{2+} + e^- \longrightarrow \text{Cu}^+, \quad E^\circ_{\text{Cu}^{2+}/\text{Cu}^+} = 0.15\text{ V} \qquad \text{...(i)}$$

$$\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}, \quad E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34\text{ V} \qquad \text{...(ii)}$$

Multiplying Eq. (i) by 2, we get

$$2\text{Cu}^{2+} + 2e^- \longrightarrow 2\text{Cu}^+,$$

$$\Delta G_1 = -nFE = -2 \times F \times 0.15 \qquad \text{...(iii)}$$

$$\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$$

$$\Delta G_2 = -nFE = -2 \times F \times 0.34 \qquad \text{...(iv)}$$

Subtract the Eq. (iv) from Eq. (iii)

$$\text{Cu}^{2+} + \text{Cu} \longrightarrow 2\text{Cu}^+$$

$$\Delta G_3 = -nFE = -1 \times F \times E^\circ$$

Also, $$\Delta G_3 = \Delta G_1 - \Delta G_2$$

$$\therefore \quad -1FE^\circ = (-2F \times 0.15) - (-2F \times 0.34)$$

$$E^\circ = -0.38$$

This is the value for the reaction

$$\text{Cu}^{2+} + \text{Cu} \longrightarrow 2\text{Cu}^+$$

But the given reaction is just reverse of it.

$\therefore$ E_{cell} for given reaction $= +\ 0.38$ V

22. As ammonia is added the concentration of H^+ decreases thus oxidation potential increases by 0.65.

23. (i) Cell equation : $\text{Mg}(s) + \text{Cu}^{2+}(aq) \longrightarrow \text{Mg}^{2+}(aq) + \text{Cu}(s)$ $(n = 2)$

$$\text{Nernst equation : } E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2}\log\frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]}$$

$$\text{EMF of the cell, } E_{\text{cell}} = [0.34 - (-2.37)] - \frac{0.0591}{2}\log\frac{[10^{-3}]}{[10^{-4}]}$$

$$= 2.71 - 0.02955 = 2.68\text{V}$$

$$\text{EMF} = 2.68\text{V}$$

(ii) Cell equation : $\text{Fe}(s) + 2\text{H}^+(aq) \longrightarrow \text{Fe}^{2+}(aq) + \text{H}_2(g)$ $(n = 2)$

$$\text{Nernst equation : } E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2}\log\frac{[\text{Fe}^{2+}]}{[\text{H}^+]^2}$$

$$\text{EMF of the cell, } E_{\text{cell}} = [0 - (-0.44)] - \frac{0.0591}{2}\log\frac{[10^{-3}]}{[1]^2}$$

$$= 0.44 - \frac{0.591}{2} \times (-3)$$

$$= 0.44 + 0.0887$$

$$= 0.5287\text{ V} \approx 0.53\text{ V}$$

$$\text{EMF} = 0.53\text{V}$$

(iii) Cell equation : $\text{Sn}(s) + 2\text{H}^+(aq) \longrightarrow \text{Sn}^{2+}(aq) + \text{H}_2(g)$ $(n = 2)$

$$\text{Nernst equation : } E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2}\log\frac{[\text{Sn}^{2+}]}{[\text{H}^+]^2}$$

EMF of the cell,

$$E_{\text{cell}} = [0 - (-0.14)] - \frac{0.0591}{2}\log\frac{[0.05]}{[0.02]^2}$$

$$= 0.14 - \frac{0.0591}{2} \times (2.097)$$

$$= 0.14 - 0.0620 \approx 0.08 \text{ V}$$

$$\text{EMF} = 0.08 \text{ V}$$

(iv) Cell equation : $2Br^-(l) + 2H^+(aq) \longrightarrow Br_2(l) + H_2(g)$ $(n = 2)$

Nernst equation : $E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{1}{[Br^-]^2[H^+]^2}$

EMF of the cell,

$$E_{cell} = [0 - 1.08] - \frac{0.0591}{2} \log \frac{1}{(0.01)^2 \times (0.03)^2}$$

$$= -1.08 - \frac{0.0591}{2} \log(1.111 \times 10^7)$$

$$= -1.08 - \frac{0.0591}{2} (7.0457)$$

$$= -1.08 - 0.208 = -1.288 \text{ V}$$

$$\text{EMF} = -1.288 \text{ V}$$

(∴ Oxidation will occur at hydrogen electrode and reduction at Br_2 electrode.)

Thus, emf is highest for Mg-Cu cell.

24. $E^\circ_{cell} = E^\circ_{(RHS)} - E^\circ_{(LHS)} = 1.61 - 1.51 = 0.10$ V

$$\Delta G^\circ = -nFE^\circ$$

$$= -5 \times 96500 \times 0.10 \text{ J}$$

$$\Delta G^\circ = -48.25 \text{ kJ}$$

25. We can write cell reaction to make H^+ and OH^- on RHS

$$H_2(g) \longrightarrow 2H^+(aq) + 2e^- \qquad E^\circ = 0.00 \text{ V}$$

$$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq) \qquad E^\circ = -0.8277 \text{ V}$$

$$2H_2O \longrightarrow 2H^+ + 2OH^-, n = 2 \quad E^\circ_{cell} = -0.8277 \text{ V}$$

$$\therefore \qquad Q = [H^+]^2[OH^-]^2 = K_w^2$$

or $\qquad H_2O \longrightarrow H^+ + OH^-,$

$$Q = [H^+][OH^-] = K_w \text{ for } n = 1$$

$$\therefore \qquad E_{cell} = 0.00 \text{ V (at equilibrium)}$$

$$\therefore \qquad E^\circ_{cell} = \frac{0.0591}{n} \log Q$$

$$-0.8277 = \frac{0.0591}{1} \log K_w \qquad \text{(if we use } n = 1)$$

$$-0.8277 = \frac{0.0591}{2} \log K_w^2 \qquad \text{(if we use } n = 2)$$

$$\log K_w = -14.0051$$

$$K_w = 1.012 \times 10^{-14}$$

26. $pH = 14 \quad \therefore \quad pOH = 0, [OH^-] = 1M$

$$\therefore \qquad [Cu^{2+}][OH^-]^2 = K_{sp} = 1.0 \times 10^{-19}$$

$$\therefore \qquad [Cu^{2+}] = 1 \times 10^{-19} \text{ M}$$

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

$$\therefore \qquad E_{Cu^{2+}/Cu} = E^\circ_{Cu^{2+}/Cu} - \frac{0.0591}{2} \log \frac{1}{[Cu^{2+}]}$$

$$= 0.34 - \frac{0.0591}{2} \log 10^{19}$$

$$= 0.34 - \frac{0.0591 \times 19}{2}$$

$$= 0.34 - 0.56 = -0.22 \text{ V}$$

27. $2H^+ + 2e^- \longrightarrow H_2 \qquad Q = \frac{1}{[H^+]^2}$

$$E = E^\circ_{SHE} - \frac{0.0591}{2} \log \frac{1}{[H^+]^2}$$

$$-0.413 = 0 + \frac{0.0591}{2} \log [H^+]^2$$

$$0.413 = -0.0591 \log [H^+], \quad [\text{since}, -\log [H^+] = pH]$$

$$= 0.0591 pH$$

$$\therefore \qquad pH = \frac{0.413}{0.0591} = 7$$

28. Molar conductivity depends upon the concentration of electrolyte solution and temperature.

29. When aqueous solution of $CuSO_4$ is electrolysed by using copper electrodes, copper will dissolve from anode and gets deposited at cathode.

30. Nernst equation is

$$E = E^\circ - \frac{2.303RT}{nF} \log Q_c$$

At equilibrium,

$$E = 0 \quad \text{and} \quad Q_c = K_c$$

$$\therefore \qquad E^\circ = \frac{2.303\, RT}{nF} \log K_c$$

$$1.1 = \frac{2.303RT}{2F} \log K_c$$

or $\qquad 1.1 = \frac{0.059}{2} \log K_c$

$$\frac{2.2}{0.059} = \log K_c$$

$$K_c \text{ or } \log K_c \neq 1.1$$

31. In the given case,

$$E_{oxi} = -\frac{0.059}{1} \log \frac{[H^+]}{\sqrt{p_{H_2}}}$$

∴ Increase $[H^+]$ or decrease p_{H_2}, to decrease E_{oxi}

32. $E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln \frac{[Zn^{2+}]}{[Cu^{2+}]}$. Decrease in $[Zn^{2+}]$ or increase in $[Cu^{2+}]$ will increase E_{cell}.

33. Since, ions are not involved in solution in case of mercury cell, its potential is steady.

34. The specific conductivity decreases while equivalent and molar conductivities increase with dilution.

35. $E_{Ag^+/Ag}$ has positive value.

For $E_{Ag^+/Ag}$

$$E = E° - \frac{0.0591}{1}\log\frac{1}{[Ag^+]}$$

$$= E° + 0.051 \log [Ag^+]$$

Thus, $E_{Ag^+/Ag}$ increases with increase in the concentration of Ag^+ ions.

36. Na metal is not produced at the cathode (instead H_2 is formed) because water contains H_3O^+ ions or H^+ ions which are stronger oxidising agent than Na^+, and are therefore more easily reduced.

37. For a cell to function, $E_{cell} = +\text{ ve}$

$$E_{cell} = E_{cathode} - E_{anode}$$

So, $\quad E_{cathode} > E_{anode}$

38. $M(s) + M^{\oplus}(1 M) \longrightarrow M^{\oplus}(0.5 M) + M(s)$

$$E^{\ominus}_{cell} = 0 \qquad \text{(for concentration cell)}$$

$$E_{cell} = E^{\ominus}_{cell} - \frac{2.303RT}{F}\log\frac{[M^{\oplus}]_{(0.05\,M)}}{[M^{\oplus}]_{(1\,M)}}$$

$$= 0 - \frac{2.303RT}{F}\log(5 \times 10^{-2}) \qquad \text{...(i)}$$

$$= +\text{ ve}$$

Hence, $|E_{cell}| = E_{cell} = 70$ mV and $\Delta G < 0$ for the feasibility of the reaction.

39. Substituting the value of $E_{cell} = 70$ mV in Eq. (i) in Q. 38, we get the value of $\frac{2.303RT}{F} = 0.0538$.

So, $$E_{cell} = E^{\ominus}_{cell} - \frac{0.0538}{1}\log(0.0025)$$

$$= 0 - \frac{0.0538}{1}(\log 5^2 + \log 10^{-4})[\log 5 \approx 0.7]$$

$$= -0.0538\,(2 \times 0.7 - 4)$$

$$= -0.0538 \times -2.6$$

$$= 0.1398 \text{ V} \approx 0.140 \text{ V} \approx 140 \text{ mV}$$

40. $$\Delta G° = -nE°_{cell}F$$

$$= -2 \times 96500 \times 1.2288$$

$$= -237.1584 \text{ kJ / mol}$$

So, thermodynamic efficiency $= \frac{237.1584}{285} = 0.83$

41. 560 mL of H_2 gas $= \frac{560}{11200}$ mol H_2 gas

$$= 0.05 \text{ mol}$$

$$= 0.05 \times 96500 \text{ C}$$

$$= 4825 \text{ C}$$

So, electric current $= \frac{4825}{600} = 8.04$ A

42. For the emissionless operation, the fuel cell is used in the motor car.

43. A cell reaction is spontaneous if $\Delta G° < 0$.

Since, $\quad \Delta G° = -nFE°_{cell}$

Thus, $\quad E°_{cell} > 0$

$$E°_{cell} = E°_{ox} + E°_{red}$$

$$\overbrace{X + Y^{2+} \longrightarrow X^{2+} + Y}^{\text{red}}$$
$$\underbrace{X + Y^{2+} \longrightarrow X^{2+}}_{\text{ox}}$$

(a) $\quad X = \text{Ni}, \; Y = \text{Fe}$

$$\text{Ni} + \text{Fe}^{2+} \longrightarrow \text{Ni}^{2+} + \text{Fe}$$

$$E°_{Ni/Ni^{2+}} = +0.23 \text{ V}$$

$$E°_{Fe^{2+}/Fe} = -0.44 \text{ V}$$

Thus, $\quad E°_{cell} = E°_{Ni/Ni^{2+}} + E°_{Fe^{2+}/Fe}$

$$= -0.21 \text{ V}$$

$$E°_{cell} < 0$$

(b) $\quad X = \text{Ni}, \; Y = \text{Zn}$

$$\text{Ni} + \text{Zn}^{2+} \longrightarrow \text{Ni}^{2+} + \text{Zn}$$

$$E°_{Ni/Ni^{2+}} = 0.23 \text{ V}$$

$$E°_{Zn^{2+}/Zn} = -0.76 \text{ V}$$

$\therefore \quad E°_{cell} = -0.53 \text{ V}$

$$E°_{cell} < 0$$

(c) $\quad X = \text{Fe}, \; Y = \text{Zn}$

$$\text{Fe} + \text{Zn}^{2+} \longrightarrow \text{Fe}^{2+} + \text{Zn}$$

$$E°_{cell} = E°_{Fe/Fe^{2+}} + E°_{Zn^{2+}/Zn}$$

$$= 0.44 - 0.76 = -0.32 \text{ V}$$

$$E°_{cell} < 0$$

(d) $\quad X = \text{Zn}, \; Y = \text{Ni}$

$$\text{Zn} + \text{Ni}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Ni}$$

$$E°_{cell} = E°_{Zn/Zn^{2+}} + E°_{Ni^{2+}/Ni}$$

$$= 0.76 - 0.23$$

$$= 0.53 \text{ V}$$

$$E°_{cell} > 0$$

Thus, this reaction (d) is spontaneous.

44. Reduction hydrogen half-cell is

$$H^+\ (xM)\ \underset{+\ \text{Pressure}\ p_{H_2}}{|}\quad Pt(H_2)$$

Half-cell reaction is

$$2H^+\ (aq) + 2e^- \longrightarrow H_2(g)$$

Reaction quotient, $Q = p_{H_2}/[H^+]^2$, $n = 2$

$$E_{\text{red}} = E^\circ_{\text{red}} - \frac{0.0591}{n}\log Q$$

$$= 0 - \frac{0.0591}{2}\log Q$$

	p_{H_2}	$[H^+]$	Q	E_{red}
(a)	1 atm	2.0 M	0.25	+ve
(b)	1 atm	1.0 M	1.0	0
(c)	2 atm	1.0 M	2.0	–ve
(d)	2 atm	2.0 M	0.50	+ ve

[$E^\circ_{\text{red}} = 0.00$ V for standard hydrogen electrode]

If $Q > 1$, then $E_{\text{red}} = -$ ve.

45. Specific conductance = conductance × cell constant

$$1.3\ \text{Sm}^{-1} = \frac{1}{50}\ \text{S} \times \text{cell constant}$$

$$\therefore\ \text{Cell constant} = 1.3 \times 50\ \text{m}^{-1}$$

$$= 65\ \text{m}^{-1}$$

$$= (65/100)\ \text{cm}^{-1}$$

Molar conductivity

$$= \frac{1000 \times \text{conductance} \times \text{cell constant}}{\text{molarity}}$$

$$= \frac{1000}{0.4} \times \frac{1}{260} \times \frac{65}{100}$$

$$= 6.25\ \text{S cm}^2\ \text{mol}^{-1}$$

$$= 6.25 \times 10^{-4}\ \text{S m}^2\ \text{mol}^{-1}$$

46. $\frac{2}{3}\ Al_2O_3 \longrightarrow \frac{4}{3}\ Al + O_2$

$$\Delta G = +966\ \text{kJ mol}^{-1} = 966 \times 10^3\ \text{J mol}^{-1}$$

$$\Delta G = -nFE_{\text{cell}}$$

$$966 \times 10^3 = -4 \times 96500 \times E_{\text{cell}}$$

$$E_{\text{cell}} = 2.5\ \text{V}$$

47. Cr | Cr^{3+} (0.1 M) || Fe^{2+} (0.01 M) | Fe

Oxidation half cell

$$Cr \longrightarrow Cr^{3+} + 3e^-] \times 2$$

Reduction half cell

$$Fe^{2+} + 2e^- \longrightarrow Fe] \times 3$$

Net cell reaction

$$2Cr + 3Fe^{2+} \longrightarrow 2Cr^{3+} + 3Fe;\ n = 6$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{oxid}} + E^\circ_{\text{red}}$$

$$= 0.72 - 0.42 = 0.30\text{V}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n}\log\frac{[Cr^{3+}]^2}{[Fe^{2+}]^3}$$

$$= 0.30 - \frac{0.0591}{6}\log\frac{(0.1)^2}{(0.01)^3}$$

$$= 0.30 - \frac{0.0591}{6}\log\frac{10^{-2}}{10^{-6}}$$

$$= 0.30 - \frac{0.0591}{6}\log 10^4$$

$$E_{\text{cell}} = 0.2606\ \text{V}$$

48. We know from Kohlrausch's law

$$\Lambda^\circ_{CH_3COOH} = \Lambda^\circ_{CH_3COONa} + \Lambda^\circ_{HCl} - \Lambda^\circ_{NaCl}$$

49. Cell is completely discharged, it means equilibrium gets established, $E_{\text{cell}} = 0$

$$Zn \mid Zn^{2+}\ (1\ M)\ \|\ Cu^{2+}\ (1\ M) \mid Cu$$

Cell reaction : $Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$

$$K_{eq} = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

We know,

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n}\log K_{eq}$$

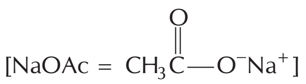
$$E^\circ_{\text{cell}} = \frac{0.0591}{n}\log K_{eq}$$

or $$1.10 = \frac{0.0591}{2}\log K_{eq}$$

$$K_{eq} = \frac{[Zn^{2+}]}{[Cu^{2+}]} = \text{antilog}\frac{2.20}{0.0591}$$

$$= \text{antilog } 37.3$$

50. According to Kohlrausch's law



$$[\text{NaOAc} = CH_3\overset{\overset{\displaystyle O}{\|}}{C}-O^-Na^+]$$

$$\Lambda^\circ_{CH_3COOH} = \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{H^+} \qquad \text{...(i)}$$

$$\Lambda^\circ_{HCl} = \lambda^\circ_{H^+} + \lambda^\circ_{Cl^-} \qquad \text{...(ii)}$$

$$\Lambda^\circ_{CH_3COONa} = \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{Na^+} \qquad \text{....(iii)}$$

Thus, on adding Eqs (ii) and (iii) if $\lambda^\circ_{Na^+}$ and $\lambda^\circ_{Cl^-}$ are subtracted we can obtained the value of Λ°_{HOAc}. Thus, additional value required is Λ°_{NaCl}.

51. $AgI(s) + e^- \rightleftharpoons Ag\ (s) + I^-$; $E^\circ = -\ 0.152$ N

$$\underline{Ag(s) \longrightarrow Ag^+ + e^- \quad ; \quad E^\circ = -\ 0.8\ \text{V}}$$

$$AgI(s) \longrightarrow Ag^+ + I^- \quad ; \quad E^\circ = -\ 0.952$$

$$E^\circ_{\text{cell}} = \frac{0.059}{n}\log K_{sp}$$

$$-0.952 = \frac{0.059}{1}\log K_{sp}$$

$$\log K_{sp} = \frac{-0.952}{0.059} = -16.135$$

52. $\Lambda^{\infty}_{AcOH} = \Lambda^{\infty}_{AcONa} + \Lambda^{\infty}_{HCl} - \Lambda^{\infty}_{NaCl}$

$$= 91.0 + 426.2 - 126.5 = 390.7$$

53. $Al^{3+} + 3e^{-} \rightarrow Al$

$$w = zQ$$

where, w = amount of metal

$$= 5.12 \text{ kg} = 5.12 \times 10^{3} \text{ g}$$

z = electrochemical equivalent

$$= \frac{\text{equivalent weight}}{96500}$$

$$= \frac{\text{atomic mass}}{\text{electrons} \times 96500}$$

$$= \frac{27}{3 \times 96500}$$

$$5.12 \times 10^{3} = \frac{27}{3 \times 96500} \times Q$$

$$Q = \frac{5.12 \times 10^{3} \times 3 \times 96500}{27} \text{ C}$$

$$= 5.49 \times 10^{7} \text{ C}$$

54. Any cell (like fuel cell), works when potential difference is developed.

55.

$$E^{\circ}_{Cr^{3+}/Cr^{2+}} = -0.41 \text{ V}$$

$$E^{\circ}_{Mn^{3+}/Mn^{2+}} = +1.57 \text{ V}$$

$$E^{\circ}_{Fe^{3+}/Fe^{2+}} = +0.77 \text{ V}$$

$$E^{\circ}_{Co^{3+}/Co^{2+}} = +1.97 \text{ V}$$

More negative value of E°_{red} indicates better reducing agent, thus easily oxidised. Thus, oxidation of Cr^{2+} to Cr^{3+} is the easiest.

56. $Zn(s) + 2H^{+} \longrightarrow Zn^{2+}(aq) + H_2(g)$

Reaction quotient, $Q = \dfrac{[Zn^{2+}]}{[H^{+}]^{2}}$

Corresponding cell is

$$\underset{\text{anode}}{\overset{-}{Zn}} \mid Zn^{2+}(C_1) \parallel H^{+}(aq) \mid \underset{\text{cathode}}{\overset{+}{Pt(H_2)}}$$

and $E_{cell} = E^{\circ}_{cell} - \dfrac{0.0591}{2}\log K$

$$= E^{\circ}_{cell} - \frac{0.0591}{2}\log\frac{[Zn^{2+}]}{[H^{+}]^{2}}$$

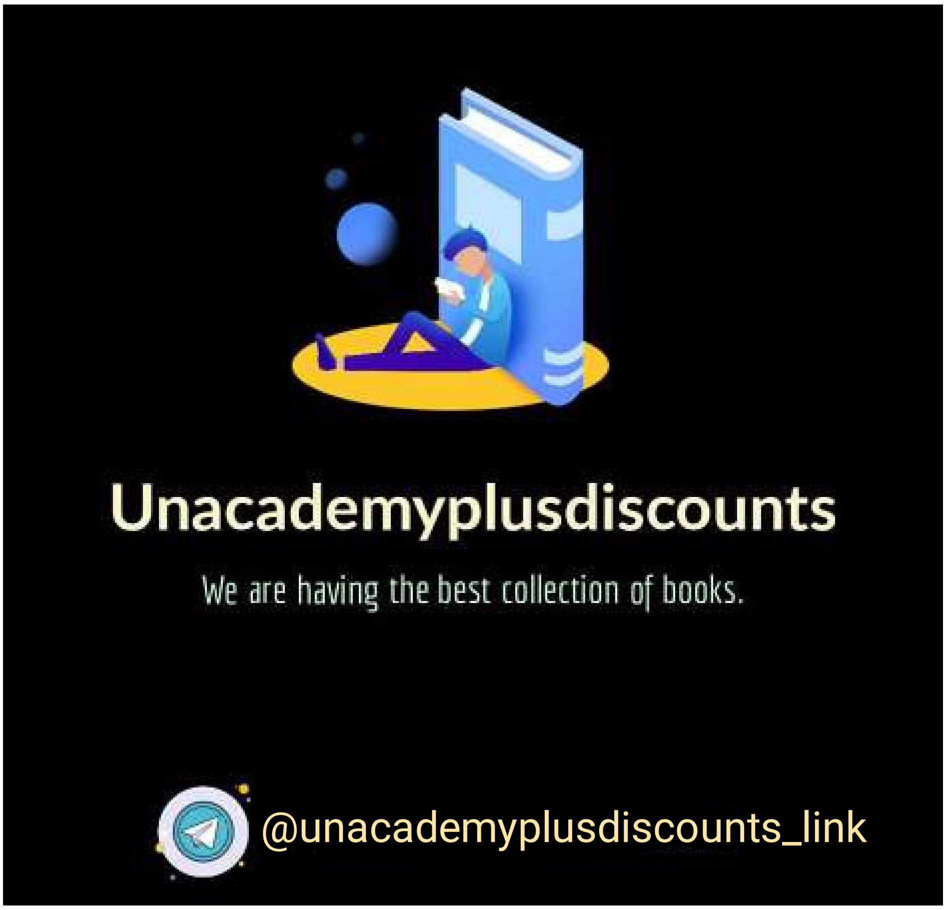
$$= E^{\circ}_{cell} + \frac{0.0591}{2}\log\frac{[H^{+}]^{2}}{[Zn^{2+}]}$$

If H_2SO_4 is added to cathodic compartment, (towards reactant side), then Q decrease (due to increase in H^{+}).

Hence, equilibrium is displaced towards right and E_{cell} increases.

57. More negative value of E° means higher reducing power. Thus, the correct order is

$$B > C > A$$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4 Chemical Kinetics

JEE Main MILESTONE

- Chemical Reactions
- Elementary and Complex Reactions
- Rate of a Chemical Reaction
- Rate Law and Rate Constant
- Molecularity of Reaction
- Order of Reaction
- Differential and Integral Forms of Different Order Reactions
- Methods of Determination of Order of Reaction
- Effect of Temperature on Rate of Reaction
- Theories of Rate of Reaction

4.1 Chemical Reactions

When one or more substance(s) undergoes such a change which result in the formation of a new product that differ from the original one in composition and properties, the change is called chemical reactions.

Chemical reactions involve breaking and formation of bonds. Therefore, different bonds require different amount of energy for breaking and different amount of energy is evolved during bond formation. Thus, the rates of different reactions are different.

Chemical kinetics is that branch of science which deals with the speeds or the rate of chemical reactions, the factors affecting the rate of reactions and the mechanism by which reactions proceed.

Types of Chemical Reactions

Depending upon their rates or speeds, chemical reactions can be classified as

(a) Instantaneous or Fast Reactions

These are infact very fast reactions and it is practically impossible to measure the speed of such reactions. Typical examples of such reactions include

(i) ionic reactions

(ii) organic substitution reactions

(iii) explosive reactions of oxygen with hydrogen and hydrocarbons.

(b) Extremely Slow Reactions

Such reactions proceed at very slow speed and here the speed is so slow that again it is not possible to measure the speed of such reactions, *e.g.,* rusting of iron.

(c) Moderately Slow Reactions

Reactions belonging to third category, *i.e.,* **with moderate speed** are utilised in the study of chemical kinetics. Inversion of cane sugar and hydrolysis of starch are common examples of this type of reactions.

4.2 Elementary and Complex Reactions

Elementary or Simple Reactions

The reactions taking place in one step are called elementary reactions.

Complex Reactions

The reactions which do not take place in one step are called complex reactions. These are the reactions in which all the atoms, ions, or molecules as represented in the balanced chemical reaction may not come together to collide simultaneously. *e.g.*,

$$5Br^{\ominus}(aq) + BrO_3^{\ominus}(aq) + 6H^+(aq) \longrightarrow 3Br_2(aq) + 3H_2O(l)$$

It is impossible for all the 12 ions of the reactant to come together simultaneously to collide. Such reactions are called complex reactions. Such reactions take place in a sequence of a number of steps. Each of these step reactions is called an elementary reaction. Molecularity is defined only for an elementary reaction, not for the complex reactions.

Caution Point *Different steps of complex reaction are also elementary reactions.*

4.3 Rate of a Chemical Reaction

The rate or speed or velocity of a reaction is the rate of change of concentration of reactants or products in unit time. When a reaction occurs, the concentration of reactants starts decreasing while the concentration of products starts increasing.

Therefore,

Rate of a reaction

$$= \frac{\text{decrease in the concentration of reactants}}{\text{time interval}}$$

or Rate of reaction

$$= \frac{\text{increase in the concentration of product}}{\text{time interval}}$$

e.g., in the reaction

$$A + B \longrightarrow C + D$$

$$\text{Rate of reaction} = -\frac{\Delta[A]}{\Delta t} \text{ or } -\frac{\Delta[B]}{\Delta t}$$
$$= +\frac{\Delta[C]}{\Delta t} \text{ or } +\frac{\Delta[D]}{\Delta t}$$

In general for a reaction,

$$n_1A + n_2B \longrightarrow m_1C + m_2D$$

The rate expression may be expressed as

$$\text{Rate of reaction} = -\frac{1}{n_1}\frac{\Delta[A]}{\Delta t} = -\frac{1}{n_2}\frac{\Delta[B]}{\Delta t}$$
$$= +\frac{1}{m_1}\frac{\Delta[C]}{\Delta t} = +\frac{1}{m_2}\frac{\Delta[D]}{\Delta t}$$

Caution Point *The negative sign indicates that the concentration of reactants decreases with time whereas the positive sign indicates that the concentration of products increases with time.*

Types of Rate of Reactions

The rate of a reaction can be categorised into

(a) Average Rate of Reaction

Average rate of a reaction is defined as the rate of change of concentration per unit time. It is calculated by dividing the total change in concentration of any one of the reactant or product by the total time taken to do so. For the reaction,

$$PCl_5 \longrightarrow Cl_2 + PCl_3$$

$$\text{Average rate} = \frac{\text{decrease in conc. of } PCl_5}{\text{time taken}}$$

It can also be expressed in terms of increase in concentration of PCl_3 and Cl_2 as

$$\text{Rate} = -\frac{\Delta[PCl_5]}{\Delta t} = +\frac{\Delta[Cl_2]}{\Delta t} = +\frac{\Delta[PCl_3]}{\Delta t}$$

Sample **Problem 1** *For the reaction, $R \longrightarrow P$, the concentration of a reactant changes from 0.03 M to 0.02 M in 25 min. Calculate the average rate of reaction using units of time in seconds.* **[NCERT]**

(a) 6.66×10^{-5} (b) 6.6×10^{-6}

(c) 5.67×10^{-5} (d) 7.26×10^{-6}

Interpret (*b*) For the reaction $R \longrightarrow P$

Average rate of reaction

$$= \frac{\text{change in concentration of reactant/product}}{\text{time taken}}$$
$$= \frac{-\Delta[R]}{\Delta t} = -\frac{[R_2]-[R_1]}{t_2 - t_1} = -\frac{(0.02 - 0.03)\text{ M}}{(25 \times 60)\text{ s}}$$
$$= -\frac{(-0.01)\text{ M}}{(1500)\text{ s}} = 6.66 \times 10^{-6}\text{ Ms}^{-1}$$
$$= 6.66 \times 10^{-6}\text{ mol L}^{-1}\text{ s}^{-1}$$

(b) Instantaneous Rate of Reaction

The rate of reaction at any particular instant of time is known as **instantaneous rate** of reaction. It is equal to the small change in concentration (dx) in small interval of time (dt).

$$\text{Rate} = \frac{dx}{dt}$$

In general, for a reaction,

$$n_1A + n_2B \longrightarrow m_1C + m_2D$$

The rate expression may be expressed as

$$-\frac{1}{n_1}\frac{\Delta[A]}{\Delta t} = -\frac{1}{n_2}\frac{\Delta[B]}{\Delta t}$$

$$= \frac{1}{m_1}\frac{\Delta[C]}{\Delta t} = \frac{1}{m_2}\frac{\Delta[D]}{\Delta t}$$

Thus, for the reaction,

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

stoichiometric coefficient of NO, O_2, and NO_2 are 2, 1, and 2, respectively, and hence, the rate is given by

$$\text{Rate} = \frac{-d[NO]}{2\,dt} = \frac{-d[O_2]}{dt} = \frac{-d[NO_2]}{2\,dt}$$

Caution Point *In aqueous solution, the rate of reaction is not expressed in terms of change of concentration of water because there is a negligible change, e.g., from* 55.5 *M to* 55.49 *M.*

Sample **Problem 2** *The decomposition of* NH_3 *on platinum surface is zero order reaction. What are the rates of production of* N_2 *and* H_2 *if* $k = 2.5 \times 10^{-4}$ mol^{-1} L s^{-1}? **[NCERT]**

(a) 3.75×10^{-4} *and* 1.25×10^{-4} *respectively*

(b) 1.25×10^{-4} *and* 3.75×10^{-4} *respectively*

(c) 3.75×10^{-3} *and* 2.45×10^{-3} *respectively*

(d) 1.25×10^{-3} *and* 3.25×10^{-3} *respectively*

Interpret (*b*) $2NH_3 \longrightarrow N_2 + 3H_2$

By dividing the equation by 2

$$NH_3 \longrightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2$$

$$\text{Rate} = -\frac{d[NH_3]}{dt} = +\frac{2d[N_2]}{dt} = \frac{2}{3}\frac{d[H_2]}{dt}$$

For zero order reaction, rate $= k$

So, $$\frac{-d[NH_3]}{dt} = \frac{2d[N_2]}{dt} = \frac{2}{3}\frac{d[H_2]}{dt}$$

$$= 2.5 \times 10^{-4}\ \text{mol L}^{-1}\text{s}^{-1}$$

$\therefore$ Rate of production of $N_2 = \frac{d[N_2]}{dt}$

$$= \frac{(2.5 \times 10^{-4}\ \text{mol L}^{-1}\text{s}^{-1})}{2}$$

$$= 1.25 \times 10^{-4}\text{mol L}^{-1}\text{s}^{-1}$$

$\therefore$ Rate of production of

$$H_2 = \frac{d[H_2]}{dt} = \frac{3}{2} \times (2.5 \times 10^{-4}\ \text{mol L}^{-1}\text{s}^{-1})$$

$$= 3.75 \times 10^{-4}\ \text{mol L}^{-1}\text{s}^{-1}$$

Note For zero order reaction rate $= k$. You will read about this in further chapter.

Calculation of Rates by Graphical Method

To calculate rate, a graph is plotted between the concentration and time.

Then, rate is calculated as

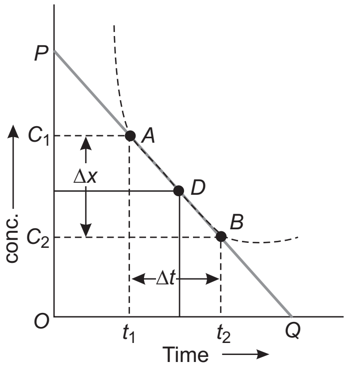


Fig. 4.1 Graph of concentration *vs* time

$$\text{Average rate} = \frac{\Delta x}{\Delta t} = \frac{C_2 - C_1}{t_2 - t_1}$$

$$\text{Instantaneous rate} = \frac{OP}{OQ}$$

Units of Rate of Reaction

Rate of reaction has the units of concentration or molarity divided by time. Therefore, the units of rate of reaction may be expressed as mol L^{-1} s^{-1} or mol L^{-1} min^{-1} etc.

In case of gaseous reactions, pressure is used in place of molar concentration and as pressure is expressed in atmosphere, therefore, the units of rate of reaction becomes atmosphere/sec or atmosphere/min etc.

Factors Affecting Rate of Reaction

The factors which affect the rate of reaction are as follows

(a) Concentration of Reactants

An increase in concentration of reactants increases the reaction rate.

(b) Nature of Reactants

The nature of bonds in a molecule influences the rate of reaction at which it changes into products.

(c) Temperature

Reaction rates are normally favoured by increase of temperature. The temperature effect is expressed in terms of temperature coefficient which is the ratio of the velocity constant of a reaction at two temperature differing by 10°C.

$$\text{Temperature coefficient} = \frac{k_{(t+10)°\text{C}}}{k_{t°\text{C}}}$$

For most of the reactions, the rate is doubled for every 10°C *rise in temperature.*

Sample **Problem 3** *The velocity constant of a reaction at 290 K was found to be* 3.2×10^{-3}. *At 300 K, it will be*

(a) 9.6×10^{-3}
(b) 3.2×10^{-4}
(c) 6.4×10^{-3}
(d) 1.25×10^{-2}

Interpret (c) As we know that the velocity constant become double by increasing the temperature by 10°C. So at 290 K, velocity constant $= 3.2 \times 10^{-3}$ then at 300 K,

velocity constant $= 2(k_{290}) = 2 \times 3.2 \times 10^{-3} = 6.4 \times 10^{-3}$

(d) Presence of Catalyst

A catalyst is a substance which alters the reaction rate but itself remains unchanged in amount and chemical composition at the end of the reaction. Actually the reactants in a reaction have to cross an energy barrier to form the product. The higher the energy barrier, the slower is the reaction rate.

A catalyst provides a new reaction path with a lower energy barrier. So that more and more reactant molecules can form the product. The same can be seen through the graph given below.

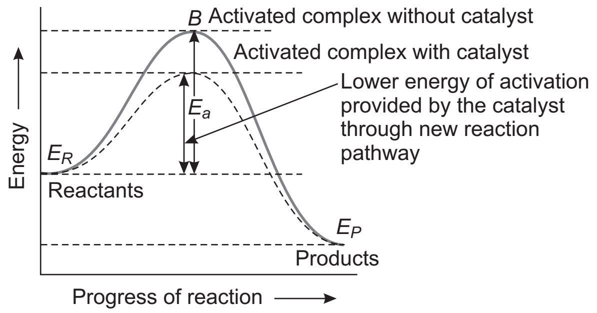


Fig. 4.2 Energy profile diagram in the absence and presence of catalyst

(e) Surface Area of Reactants

The rate of reaction increases as the surface area of the reactant increases.

(f) Presence of Light

Reaction rate normally becomes faster in the presence of light. Light gives the necessary activation energy for starting the reaction.

Check Point 1

1. What is the significance of writing negative and positive signs before the expression for rate of reaction?
2. Why is the use of instantaneous rate of reaction preferred over average rate of reaction?
3. Explain, why powdered sugar dissolves faster than crystalline sugar?
4. The rate of reaction, on increasing the temperature of the reaction system by 10°C becomes almost double. Explain it.

4.4 Rate Law and Rate Constant

The mathematical relation between the rate of reaction and the concentration of the reactants is termed as the Rate Equation or Rate Law Expression.

The rate law for a given reaction has to be established by experimental study of the rate over a wide range of concentration of the reactants. The rate law thus established is also called **differential rate equation** or **rate expression.**

If we consider the reaction,

$$A + B \longrightarrow \text{products}$$

Now if $[A]^\alpha$ and $[B]^\beta$ are the molar concentrations of A and B respectively then

$$\text{Rate} \propto [A]^\alpha [B]^\beta \quad \text{or} \quad \text{Rate} = k[A]^\alpha [B]^\beta$$

here, $k =$ velocity constant or rate constant

Now, if all concentrations are taken as unity, *i.e.,*

$$[A] = [B] = 1 \text{ mol/L}$$

then $\text{Rate} = k$

Thus, *rate constant is defined as the rate of the reaction when the concentration of each reactant is taken as unity.* It is also known as *specific reaction rate.*

Different Characteristics of rate constant are given below

1. It is the measure of the rate of reaction. Greater is the value of rate constant, faster is the reaction.
2. Each reaction has a particular value of rate constant at a particular temperature.
3. The value of rate constant for the same reaction changes with temperature.
4. The value of rate constant for a reaction does not depend upon the concentration of the reactants.

Unit of Rate Constant

Since the dimensions of rate are concentration/time and the SI units for concentration are mol m^{-3}, mol dm^{-3}, or mol L^{-1} and second for time but other units are used depending on how fast or slow is the reaction. For very slow reactions, time may be chosen in years and for very fast reactions it may be chosen in nano (10^{-9}) or pico (10^{-12}) second.

For the nth order of a reaction.

$$nA \longrightarrow \text{Product}$$

$$\text{Rate} = k[A]^n.$$

$$\therefore \qquad k = \frac{\text{Rate}}{[A]^n}$$

Thus, the dimensions of k are equal to

$$\frac{\text{Concentration / Time}}{[\text{Concentration}]^n} = [\text{Concentration}]^{1-n}[\text{Time}]^{-1}$$

$$= (\text{mol})^{1-n}\ \text{L}^{n-1}\ \text{s}^{-1}$$

where, n = order of reaction.

Units of Rate Constants for Gaseous Reactions

In case of gaseous reactions, concentrations are expressed in terms of pressure in the units of atmosphere. Thus, the rate has the units of atm per second. New the unit of different rate constants would be listed in the following table.

Table 4.1 **Units of Rate Constant**

	Reaction	Order	Unit of rate constant	Units of k for gaseous reactions
(a)	Zero order reaction	0	$\frac{(\text{mol L}^{-1})}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^0}$ $= \text{mol L}^{-1}\text{s}^{-1}$	atm s^{-1}
(b)	First order reaction	1	$\frac{(\text{mol L}^{-1})}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})} = \text{s}^{-1}$	s^{-1}
(c)	Second order reaction	2	$\frac{(\text{mol L}^{-1})}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^2}$ $= \text{mol}^{-1}\text{ L s}^{-1}$	atm^{-1} s^{-1}
(d)	nth order reaction	n	$\frac{(\text{mol L}^{-1})}{s} \times \frac{1}{(\text{mol L}^{-1})^n}$ $= (\text{mol/L})^{1-n}\text{s}^{-1}$ $= \text{mol}^{1-n}\ \text{L}^{n-1}\text{s}^{-1}$	atm^{1-n} s^{-1}

Sample **Problem 4** *The decomposition of dimethyl ether leads to the formation of* CH_4, H_2 *and* CO *and the reaction rate is given by :*

Rate $= k[CH_3OCH_3]^{3/2}$. *The rate of reaction is followed by increase in pressure in a closed vessel, so the rate can be expressed in terms of the partial pressure of dimethyl ether i.e,* Rate $= k\,(p_{CH_3OCH_3})^{3/2}$. *If the pressure is measured in bar and time in minutes, then the units of rate and rate constants are respectively?* **[NCERT]**

(a) *bar* min^{-1}, *bar* min^{-1}
(b) min^{-1} bar^{-1}, *bar* min^{-1}
(c) *bar* min^{-1}, $bar^{-1/2}$, min^{-1}
(d) *bar* min^{-1}, $bar^{-3/2}$ min^{-1}

Interpret (c) Unit of rate = bar min^{-1}

$$\text{Unit of } k = \frac{\text{Rate}}{[(p_{CH_3OCH_3}]^{3/2}}$$

$$= \frac{\text{bar min}^{-1}}{(\text{bar})^{3/2}} = \text{bar}^{-1/2}\ \text{min}^{-1}$$

4.5 Molecularity of Reaction

It can be defined as "*The number of atoms or molecules which collide together at the same time for the reaction to occur*". Reactions are classified in terms of molecularity as unimolecular, bimolecular, termolecular depending upon the number of molecules involved in the reaction. Example of these reactions are as follows

Unimolecular reaction

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Bimolecular reaction

$$CH_3COOC_2H_5 + NaOH \rightleftharpoons CH_3COONa + C_2H_5OH$$

Termolecular reaction

$$2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$$

Caution Point *Only a few termolecular reactions are known while no reaction having molecularities more than three is known because more than three molecules may not mutually collide with each other.*

Determination of Molecularity

In case of simple reactions (elementary reactions), the molecularity is simply the sum of the molecules of different reactants as represented by the balanced chemical equation, *e.g.*,

$$O_2F_2 \longrightarrow O_2 + F_2 \qquad \text{(Unimolecular)}$$

$$2HI \longrightarrow H_2 + I_2 \qquad \text{(Bimolecular)}$$

$$2NO + O_2 \longrightarrow 2NO_2 \qquad \text{(Termolecular)}$$

In case of complex reactions (multistep reactions) the atoms, molecules or ions participating in rate determining step decide the molecularity. Among many steps, the **slowest step is the rate determining step.** So atoms, molecules or ions participating in this rate determining step, determine the molecularity of the reaction.

e.g., consider the reaction

$$HBrO_3 + 6HI \longrightarrow HBr + 3H_2O + 3I_2$$

The reaction takes place through following steps

$$HBrO_3 + HI \xrightarrow{\text{Slow}} HBrO_2 + HIO$$

$$HBrO_2 + 4HI \xrightarrow{\text{Fast}} HBr + 2H_2O + 2I_2$$

$$HIO + HI \xrightarrow{\text{Fast}} H_2O + I_2$$

Here, 2 molecules participate in the slowest step, thus reaction is of bimolecular type.

Characteristics of Molecularity

1. Molecularity of a reaction is always a whole number. It can never be fractional or zero.
2. It does not provide any idea about the rate or mechanism of the reaction.

4.6 Order of Reaction

In chemical kinetics the reactions are generally classified in terms of their order. The order of a reaction is defined as "*The sum of the concentration terms on which the rate of a reaction actually depends as observed experimentally*".

OR

"*The order of reaction is given as the sum of the exponents (powers) to which the concentration terms in the rate law equation are raised to express the observed rate of the reaction.*"

In the reaction rate expression,

$$\text{Rate} = k[A]^{\alpha}\,[B]^{\beta}$$

the sum $\alpha + \beta =$ **order of reaction**

Order of reaction is purely experimental quantity. It may be whole number, zero or in fractions. Depending upon whether $\alpha + \beta$ is equal to zero, 1, 2 or 3, the reactions are said to be of zero order, first order, second order or third order respectively.

Caution Points

(*i*) *Order of a reaction can change with change in conditions such as temperature, pressure etc.*

(*ii*) *When one of the reactants is present in large excess, the second order rate expression becomes a first order rate expression because the value of change in concentration for other reactant is taken as negligible.*

Sample **Problem 5** *A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reaction is*

(*i*) *doubled*
(*ii*) *reduced to half?* **[NCERT]**

(*a*) *Becomes 4 times and $\frac{1}{4}$ times respectively*
(*b*) *Becomes $\frac{1}{4}$ times and $\frac{1}{2}$ times respectively*
(*c*) *Becomes 2 times and 4 times respectively*
(*d*) *Becomes 4 times and 2 times respectively*

Interpret (*a*) (For II order reaction), rate $= k[A]^2$. Find the rate expression when concentration is doubled or reduced to half and compare it with the normal rate. e.g.,

For a reaction, $A \longrightarrow$ Products

$$\text{Rate} = k[A]^2 = ka^2$$

(i) When concentration of A is doubled

i.e., $[A] = 2a$

$$\text{Rate} = k(2a)^2 = 4ka^2$$

Rate of reaction becomes 4 times

(ii) When concentration of A is reduced to $\frac{1}{2}$

i.e., $[A] = \frac{1}{2}a$

$$\text{Rate} = k\left(\frac{a}{2}\right)^2 = \frac{1}{4}ka^2$$

Rate of reaction becomes $\frac{1}{4}$ times *i.e.,* reduced to one fourth.

The main differences between molecularity and order of reaction are tabulated below.

Table 4.2 **Difference between Order and Molecularity**

S.N.	Molecularity	Order of reaction
1.	It is the total number of reacting species (molecules, atoms or ions) which bring the chemical change.	It is the sum of powers of molar concentrations of the reacting species in the rate equation of the reaction.
2.	It is a theoretical concept.	It is experimentally determined.
3.	It is always a whole number.	It may be a whole number, zero, fractional, positive or negative.
4.	It is meaningful only for simple reactions or individual steps of a complex reaction.	It is meant for the reaction and not for its individual steps.

4.7 Differential and Integral Forms of Different Order Reactions

For a general reaction :

$$aA + bB \longrightarrow cC + dD$$

$$\text{Rate} = \frac{-d[R]}{dt} = k[A]^{\alpha}[B]^{\beta}$$

This form of the equation is called differential rate equation. It relates the rate of change of concentration with time or instantaneous rate. It is not always convenient to determine the instantaneous rate as it is measured by the determination of the slope of the tangent at point *t* in the concentration *versus* time curve. This makes it difficult to determine the rate law and hence, the determination of the order of the reaction. In order to avoid this difficulty, we can integrate the rate equation and obtain integrated rate equation that gives a relation between directly measured experimental quantities, *i.e.,* concentrations at different times. The integrated rate equations are different for reactions of different orders.

Zero Order Reactions

Reactions in which the concentration of reactants do not change with time and the concentration rates remain constant throughout are said to be zero order reactions.

For the reaction,

$$A \longrightarrow \text{products to be zero order,}$$

$$\text{Rate} = \frac{-d[A]}{dt} = k[A]^0 = k$$

or $$d[A] = -k\,dt$$

Integrating both sides, we get

$$[A] = -kt + I \qquad \text{...(i),}$$

where, *I* is a constant of integration

At $t = 0$, $[A] = [A]_0$

$\therefore$ $[A]_0 = I$

Substituting this value of *I* in Eq. (i), we get

$$[A] = -kt + [A]_0 \qquad \text{...(ii)}$$

or $$kt = [A]_0 - [A]$$

or $$k = \frac{1}{t}\{[A]_0 - [A]\} \qquad \text{...(iii)}$$

This is the expression for the rate constant for reactions of zero order.

Characteristics of Zero Order Reactions

1. Any reaction of zero order must obey Eq. (ii)

$$[A] = [A]_0 - kt$$

This shows that the plot of concentration of reactants against time will be a straight line passing through the origin.

2. Also, as the rate is independent of concentration, the plot of rate *versus* concentration will be a straight line parallel to the concentration axis.

Caution Point *The rate of reaction remains constant throughout the course of the reaction.*

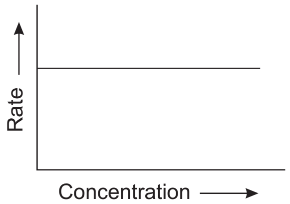


Fig 4.3 Plot of rate *versus* concentrations for the reaction of zero order

3. The units of rate constant for zero order reaction is mol L^{-1} time^{-1}.
4. The time required to reduce the initial concentration of the reactant to half of its initial value is called **half life time** or **half life period** and is denoted by $t_{1/2}$. When $[A] = [A]_0/2$, $t = t_{1/2}$, substituting these values in Eq. (iii), we get

$$t_{1/2} = \frac{1}{k}\{[A]_0 - [A]/2\} = \frac{[A]_0}{2k}$$

i.e., $$t_{1/2} = \frac{[A]_0}{2k}$$

or $$t_{1/2} \propto [A]_0.$$

Thus, the half-life period of zero order reaction is directly proportional to initial concentration, *i.e.,* $t_{1/2} \propto [A]_0$.

Caution Point *In zero order reaction, it is the amount of reactant that changes and not the concentration.*

Some Examples of Zero Order Reactions

(i) Photochemical synthesis of HCl, *i.e.,*

$$H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl$$

(ii) Decomposition of ammonia in the presence of a catalyst, *i.e.,*

$$2NH_3 \xrightarrow{\text{Mo or W}} N_2 + 3H_2$$

Hot Spot 1

FIRST ORDER Reactions

It is an important topic for JEE Main examination. The nature of question is generally numerical type. The level of question very from moderate to typical.

The **first order reaction** is defined as "The reaction in which the reaction rate is determined by the change of one concentration term of the reactant only", *e.g.,* In the reaction

$$\begin{array}{cccl} A & \longrightarrow & B + C & \\ a & & 0 \quad 0 & \text{(concentration initially)} \\ (a-x) & & x \quad x & \text{(concentration after time } t\text{)} \end{array}$$

The rate of reaction after time t is given by the expression.

$$\frac{dx}{dt} = k(a-x) \qquad \text{...(i)}$$

or $$\frac{dx}{(a-x)} = k\,dt$$

Upon integration of above equation,

$$\int \frac{dx}{(a-x)} = k \int dt$$

or $$-\log(a-x) = kt + c \qquad \text{...(ii)}$$

where c is the integration constant.

When $t = 0, x = 0$

$$c = -\log a$$

Putting the value of c in Eq. (ii), we get

$$-\log(a-x) = kt - \log a$$

or $$\log a - \log(a-x) = kt$$

or $$\log \frac{a}{(a-x)} = kt$$

or $$k = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

or $$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]} \qquad \text{...(iii)}$$

This is known as the **kinetic equation for a reaction of the first order.**

Eq. (iii) can be written in the exponential form as

$$\frac{[A]_0}{[A]} = e^{kt}$$

or $$\frac{[A]}{[A]_0} = e^{-kt}$$

or $$[A] = [A]_0 e^{-kt} \qquad \text{...(iv)}$$

Characteristics of First Order Reactions

1. Any reaction of the first order must obey Eq. (iii) which can also be written as

$$\log[A] = \frac{-kt}{2.303} + \log[A]_0 \qquad \text{...(v)}$$

This is the equation of a straight line ($y = mx + c$)

Thus, if log $[A]$ or log $(a-x)$ values are plotted against time t, the graph obtained should be a straight line. The intercept on y-axis would be log $[A]_0$ and the slope of the line would be equal to $\left(\frac{-k}{2.303}\right)$, *i.e.,* slope $= \frac{-k}{2.303}$

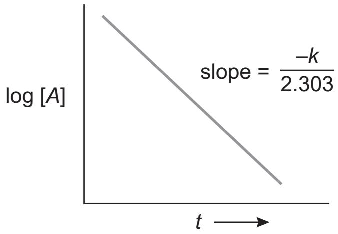


Fig. 4.4 Plot of log $[A]$ *vs* time (t)

Thus, if we plot log $\frac{[A]_0}{[A]}$ *versus t,* a staight line graph will be obtained with slope $= \frac{k}{2.303}$ as shown belown

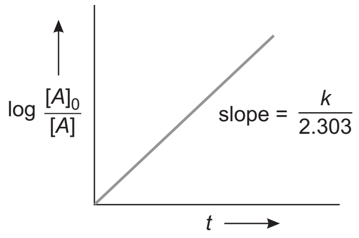


Fig. 4.5 Plot of log ($[A_0]/[A]$) *vs* time (t)

2. The time taken for the completion of same fraction of change *i.e.,* half life is independent of initial concentration. *e.g.*, for half change,

$$x = 0.5a \text{ and } t = t_{1/2}$$

so, $$k = \frac{2.303}{t_{1/2}} \log \frac{a}{0.5a} = \frac{2.303}{t_{1/2}} \log 2 = \frac{0.693}{t_{1/2}}$$

or $$t_{1/2} = \frac{0.693}{k}$$

Thus, $t_{1/2}$ is independent of initial concentration a.

3. Since the rate is independent of concentration and depends inversely on the time, the unit of k will be time^{-1}, *i.e.,* s^{-1} or h^{-1}.

4. Average life $(\lambda) = \frac{1}{k} = \frac{t_{1/2}}{0.693} = 1.443\,t_{1/2}$

5. Relation between $t_{1/2}$ and $t_{x\%}$ (amount decomposed):

$$t_{x\%\,\text{decomposes}} = \frac{2.3}{k}\log\left(\frac{100}{100-x}\right) \quad \text{...(vi)}$$

$$t_{1/2} = \frac{0.69}{k} = \frac{0.3 \times 2.3}{k} \quad \text{...(vii)}$$

Divide Eq. (vii) by (vi)

$$\frac{t_{1/2}}{t_{x\%}} = \frac{0.3}{\log\left(\dfrac{100}{100-x}\right)}$$

Sample Problem 6 *The half-life for radioactive decay of ^{14}C is 5730 yr. An archaeological artifact containing wood had only 80% of the ^{14}C found in a living tree. Estimate the age of the sample.* **[NCERT]**

(a) 1400 *yr* (b) 1500 *yr*
(c) 1850 *yr* (d) 1100 *yr*

Interpret (c) Decay constant $(k) = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730}\text{ yr}^{-1}$

All radioactive decay follow first order kinetics

$$t = \frac{2.303}{k}\log\frac{[A]_0}{[A]}$$

Given, $[A] = 80\%$ It means that $[A]_0 = 100\%$

$$t = \frac{2.303 \times 5730}{0.693}\text{yr} \times \log\frac{100}{80}$$

$$= \frac{2.303 \times 5730 \times 0.0969}{0.693}$$

$$= 1845 \text{ yr}$$

Estimated age = 1845 yr

Sample Problem 7 *For a first order reaction, show how time required for 99% completion is related to the time required for the completion of 90% of reaction.* **[NCERT]**

(a) $t_{90\%} = 2 \times t_{99\%}$ (b) $t_{90\%} = 4 \times t_{99\%}$
(c) $t_{99\%} = \frac{1}{2} \times t_{90\%}$ (d) $t_{99\%} = 2 \times t_{90\%}$

Interpret (d) To solve out such problem follow the following steps.

Step I If $a = 100$; $(a - x) = (100 - 99) = 1$

For 99% completion of the reaction

$$t_{99\%} = \frac{2.303}{k}\log\frac{100}{1} = \frac{2.303}{k}\log 10^2$$

$$= \frac{2.303 \times 2}{k}$$

$$t_{99\%} = \frac{4.606}{k} \quad \text{...(i)}$$

Step II If $a = 100$; $(a - x) = (100 - 90) = 10$

For 90% completion of the reaction

$$t_{90\%} = \frac{2.303}{k}\log\frac{100}{10}$$

$$= \frac{2.303}{k}\log 10 = \frac{2.303}{k} \quad \text{...(ii)}$$

Step III On dividing Eq. (i) by Eq. (ii), we get

$$\frac{t_{99\%}}{t_{90\%}} = \frac{4.603}{k} \times \frac{k}{2.303} = 2$$

It means that time required for 99% completion of the reaction is twice the time required to complete 90% of the reaction.

Sample Problem 8 *The experimental data for decomposition of N_2O_5 $[2\,N_2O_5 \longrightarrow 4NO_2 + O_2]$ in gas phase at 318 K are given below :*

t/s	0	400	800	1200	1600	2000	2400	2800	3200
$10^{-2} \times [N_2O_5]$/ mol L^{-1}	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35

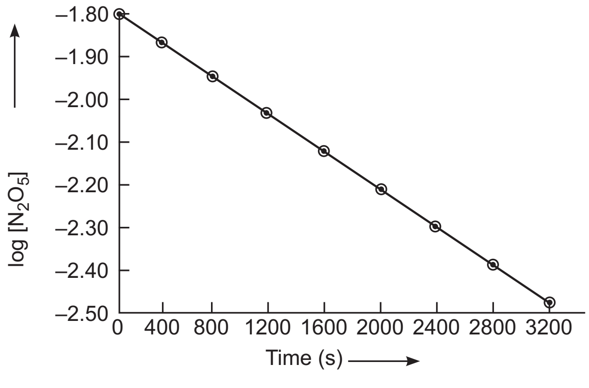
Calculate the rate constant and the half-life period. **[NCERT]**

(a) $4.8 \times 10^{-4}\ s^{-1}$, 1400 *s* (b) $3.92 \times 10^{-4}\ s^{-1}$, 1445 *s*
(c) $2.72 \times 10^{-4}\ s^{-1}$, 1200 *s* (d) $8.29 \times 10^{-4}\ s^{-1}$, 1575 *s*

Interpret (a) In order to solve such problem first we have to plot a graph between log $[A]$ and t and then obtain k from the slope and $t_{1/2}$ from K.

For graph between log $[N_2O_5]$ and time, we first find the values of log$[N_2O_5]$.

Time (s)	0	400	800	1200	1600	2000	2400	2800	3200
$[N_2O_5] \times 10^{-2}$ mol L^{-1}	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35
log $[N_2O_5]$	–1.79	–1.87	–1.94	–2.03	–2.11	–2.19	–2.28	–2.37	–2.46



Since, the graph between log$[N_2O_5]$ and time is a straight line, the reaction is of first order.

The rate law : Rate = $k\,[N_2O_5]$

$$\text{Slope of the line} = -\frac{k}{2.303} = \frac{-2.46-(-1.79)}{3200-0} = \frac{-0.67}{3200}$$

$$\frac{-k}{2.303} = \frac{-0.67}{3200}$$

$$k = \frac{0.67 \times 2.303}{3200}$$

or $$k = 4.82 \times 10^{-4}\ \text{s}^{-1}$$

$$\text{Half-life period } (t_{1/2}) = \frac{0.693}{k}$$
$$= \frac{0.693}{4.82 \times 10^{-4}\ \text{s}^{-1}}$$
$$= 1438\ \text{s}$$

Typical First Order Gas Phase Reactions

Consider a typical first order gas phase reaction:

$$A(g) \longrightarrow B(g) + C(g)$$

Let p_0 be the initial pressure of A and p_t is the total pressure at time t. The integrated rate equation for such a reaction can be derived as :

Total pressure $(p_t) = p_A + p_B + p_C$ (pressure units), where p_A, p_B, and p_C are the partial pressures of A, B and C, respectively.

If x atmosphere be the decrease in the pressure of A at time t and one mole each of B and C is being formed, then increase in the pressure of B and C will also be x atm each.

	$A(g)$	$\longrightarrow$	$B(g)$	+	$C(g)$
At $t = 0$	p_0 atm		0 atm		0 atm
At time t	$(p_0 - x)$ atm		x atm		x atm

where p_0 is the initial pressure at time $t = 0$.

$$p_t = (p_0 - x) + x + x = p_0 + x$$
$$x = (p_t - p_0)$$

where, $$p_A = p_0 - x = p_0 - (p_t - p_0)$$
$$= 2p_0 - p_t$$
$$k = \left(\frac{2.303}{t}\right)\left(\log \frac{p_0}{p_A}\right)$$
$$= \frac{2.303}{t} \log \frac{p_0}{(2p_0 - p_t)} \qquad \text{...(i)}$$

Sample **Problem 9** *The following data were obtained during the first order thermal decomposition of* $N_2O_5(g)$ *at constant volume.*

$$2N_2O_5(g) \longrightarrow 2N_2O_4(g) + O_2(g)$$

S.N.	Time (s)	Total pressure (atm)
(i)	0	0.5
(ii)	100	0.512

Calculate the rate constant. **[NCERT Exemplar]**

(a) $3.39 \times 10^{-4}\ s^{-1}$

(b) $1.39 \times 10^{-5}\ s^{-1}$

(c) $5.45 \times 10^{-4}\ s^{-1}$

(d) $4.98 \times 10^{-4}\ s^{-1}$

Interpret (*d*) Let the pressure of $N_2O_5(g)$ decreases by $2x$ atm. As 2 moles of N_2O_5 decompose to give 2 moles of $N_2O_4(g)$ and 1 mole of $O_2(g)$, the pressure of $N_2O_4(g)$ increases by $2x$ atm and that of $O_2(g)$ increases by x atm.

	$2N_2O_5(g)$	$\longrightarrow$	$2N_2O_4(g)$	+	$O_2(g)$
When $t = 0$	0.5 atm		0 atm		0 atm
At time t	$(0.5 - 2x)$ atm		$2x$ atm		x atm

$$\text{Total pressure } (p_t) = p_{(N_2O_5)} + p_{(N_2O_4)} + p_{(O_2)}$$
$$= (0.5 - 2x) + 2x + x$$
$$= 0.5 + x$$
$$\therefore \qquad x = p_t - 0.5$$
$$p_{N_2O_5} = 0.5 - 2x$$
$$= 0.5 - 2(p_t - 0.5)$$
$$= 1.5 - 2p_t$$

At $t = 100$ s; $p_t = 0.512$ atm

$$p_{(N_2O_5)} = 1.5 - 2 \times 0.512 = 0.476\ \text{atm}$$
$$\therefore \qquad k = \frac{2.303}{t} \log \left(\frac{p_0\ (N_2O_5)}{p_A\ (N_2O_5)}\right)$$
$$= \frac{2.303}{100\ \text{s}} \log \left(\frac{0.5\ \text{atm}}{0.476\ \text{atm}}\right)$$
$$= \frac{2.303}{100\ \text{s}} \times 0.02136$$
$$= 4.92 \times 10^{-4}\ \text{s}^{-1}$$

Direct or Indirect Estimation of Reactants

Sometimes volumes of reagents are given in volumetric analysis (when one of the reactant is estimated directly or indirectly, *i.e.*, when V_∞ is not given). Let us take an example of decomposition of hydrogen peroxide (H_2O_2).

$$2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$$

The rate of this first order reaction is measured by titrating a fixed volume of H_2O_2 (undecomposed) against a standard solution of $KMnO_4$. Here $KMnO_4$ acts as oxidizing agent and H_2O_2. acts as reducing agent. The volumes of $KMnO_4$ used for H_2O_2 after regular intervals of time are as follows.

Time instants	$t = 0$	t_1	t_2	t_3	t_4	t_5
Volume of $KMnO_4$	V_0	V_1	V_2	V_3	V_4	V_5

Volume of $KMnO_4$ at $t = 0$ corresponds to volume of H_2O_2 initially present.

$$\Rightarrow \qquad c_0 \propto V_0$$

Volume of $KMnO_4$ at time instant $t_1, t_2, t_3, \ldots$ corresponds to volume of H_2O_2 remaining after $t_1, t_2, t_3, \ldots$

$$\Rightarrow \qquad c_1 \propto V_t$$

Now, it being a first order reaction, follows first order kinetics, so

$$k = \frac{2.303}{t} \log \frac{V_0}{V_t}$$

Now, using the above expression, if we calculate the values of k for different intervals $t_1, t_2, \ldots$ (for actual numerical data), the values of k should be same if the reaction follows first order kinetics.

Sample **Problem 10** *In the dehydration of oxalic acid by conc.* H_2SO_4

$$(COOH)_2 \longrightarrow CO + CO_2 + H_2O$$

2 mL of the solution was withdrawn at different times and titrated against 0.1 *N* $KMnO_4$ *solution. Find the order of reaction.*

Time (mins)	0	300	450	600
Vol of $KMnO_4$ used (mL)	22.0	17.0	15.0	13.4

(*a*) 0 (*b*) 1 (*c*) 2 (*d*) 3

Interpret (*b*) $(COOH)_2 \longrightarrow CO + CO_2 + H_2O$

$$k = \frac{2.303}{t}\log\frac{V_0}{V_t}$$

(i) $$k = \frac{2.303}{300}\log\frac{22}{17} = \frac{2.303 \times 0.119}{300} = 0.00085\ \text{min}^{-1}$$

(ii) $$k = \frac{2.303}{450}\log\frac{22}{15} = 0.00085\ \text{min}^{-1}$$

(iii) $$k = \frac{2.303}{600}\log\frac{22}{13.4} = 0.00085\ \text{min}^{-1}$$

The value of k is constant. Hence, the reaction is of first order.

Direct or Indirect Estimation of Products

Consider a condition when one of the product is estimated directly or indirectly, *i.e.,* when V_0 is not given. *e.g.,* in the decomposition of NH_4NO_2, the volume of N_2 is directly measured at different intervals of time.

The volume of nitrogen (N_2) collected after a regular interval of times are as follows

Time instants	$t = 0$	t_1	t_2	t_3	t_4	t_∞
Volume of N_2	V_0	V_1	V_2	V_3	V_4	V_∞

At $t = 0$, clearly the volume of $N_2 = 0$.

Time instant $t = \infty$ means the end of a reaction, *i.e.,* when whole of NH_4NO_2 is decomposed.

At $t = \infty, V_\infty$ corresponds to the initial volume of NH_4NO_2.

Always keep in mind that the ratio of stoichiometric coefficient for both $N_2 : NH_4NO_2$ is 1 : 1

$$c_0 \propto V_t$$

At $t = t_1, t_2, t_3, \ldots$ the volume of N_2 corresponds to the concentration of product formed, *i.e.,* equal to x.

$$x \propto V_t$$
$$c_0 - x \propto V_\infty - V_t$$

Hence, from first order kinetic,

$$k = \frac{2.303}{t}\log\frac{V_\infty}{V_\infty - V_t}$$

Sample **Problem 11** *The following data were reported for the decomposition of* N_2O_5 *in* CCl_4 *at 303 K*

Time (min)	120	160	200	240	∞
Volume of O_2 (mL)	37.70	45.85	52.67	58.34	84.35

Calculate the rate constant.

(*a*) 0.089 min^{-1} (*b*) 0.0049 min^{-1}
(*c*) 0.0025 min^{-1} (*d*) 0.0035 min^{-1}

Interpret (*b*) $2N_2O_5 \longrightarrow 4NO_2 + O_2$

$$k = \frac{2.303}{t}\log\frac{V_\infty}{V_\infty - V_t}$$

(i) $$k = \frac{2.303}{120}\log\frac{84.35}{84.35 - 37.70} = \frac{2.303}{120}\log\frac{84.35}{46.65}$$

$$= \frac{2.303}{120} \times 0.2572 = 0.0049\ \text{min}^{-1}$$

(ii) $$k = \frac{2.303}{160}\log\frac{84.35}{84.35 - 45.85} = 0.0049\ \text{min}^{-1}$$

(iii) $$k = \frac{2.303}{200}\log\frac{84.35}{84.35 - 52.67} = 0.0049\ \text{min}^{-1}$$

(iv) $$k = \frac{2.303}{240}\log\frac{84.35}{84.35 - 58.34} = 0.0049\ \text{min}^{-1}$$

Since, the value of k is constant, the reaction is of first order. (Remember, here it is necessary to find out the value of k from all the values as if they are not same, the reaction is not of first order and does not follow this equation.)

Hydrolysis of Ester (CH_3COOR') in Acidic Medium

$$CH_3COOR'\ (\text{Ester}) + H_2O + HCl(H^{\oplus}) \longrightarrow CH_3COOH + R'OH$$

The reaction rate is measured by titrating the acid (CH_3COOH) produced against a standard alkali solution. Note that when a test sample is prepared from the reacting mixture, there are two acids : one is mineral acid $H^{\oplus}$ (HCl or any other) and second is CH_3COOH produced. So the volume of alkali used gives the titration value for both acids. The data is collected in the following manner.

Time instants	$t = 0$	t_1	t_2	t_3	t_4	t_∞
Volume of NaOH	V_0	V_1	V_2	V_3	V_4	V_∞

(i) When V_0 is given

At $t = 0, V_0$ is the volume NaOH used to neutralize the mineral acid present ($H^{\oplus}$) being used as catalyst (At $t = 0$, no CH_3COOH is yet produced)

At $t = \infty$ (*i.e.,* at the end of hydrolysis), V_∞ is the volume of NaOH used to neutralize whole of CH_3COOH plus the volume of HCl present. At $t = \infty$, the volume of CH_3COOH corresponds to the volume of ester taken initially.

$\Rightarrow$ $c_0 \propto V_\infty - V_0$ (as $V_0 \equiv$ volume of HCl)

At $t = t_1, t_2, t_3, \ldots, V_1, V_2, V_3, \ldots$ correspond to the volume of HCl plus the volume of CH_3COOH being produced.

$$\Rightarrow \quad x \propto V_t - V_0$$
$$\Rightarrow \quad c_0 - x \propto (V_\infty - V_0) - (V_t - V_0)$$
$$\Rightarrow \quad c_0 - x \propto V_\infty - V_t$$

Hence, from the first order kinetics, it follows :

$$k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$

(ii) When V_0 is not given

Let $[V_\infty - V_0 = c_0$ and $V_\infty - V_t = c_t]$

When $t = t_1$, then

$$k = \frac{2.303}{t_1} \log \frac{c_0}{c_{t_1}} \qquad \text{...(i)}$$

Similarly, when $t = t_2$

$$k = \frac{2.303}{t_2} \log \frac{c_0}{c_{t_2}} \qquad \text{...(ii)}$$

Operating Eq. (i) – Eq. (ii), we get

$$k(t_1 - t_2) = 2.303 \log \frac{c_{t_2}}{c_{t_1}}$$

or
$$k = \frac{2.303}{(t_1 - t_2)} \log \frac{c_{t_2}}{c_{t_1}} \qquad \text{...(iii)}$$

Similarly, when $t = t_3$ and so on, we get

$$k = \frac{2.303}{(t_1 - t_3)} \log \frac{c_{t_3}}{c_{t_1}} \qquad \text{...(iv)}$$

Sample **Problem 12** *Methyl acetate is hydrolysed with* 0.1 *N* HCl *at* 25°*C. 5 mL of the reacting mixture is withdrawn at various time intervals and is quickly titrated with* 1.0 *N* NaOH. *The volumes of* NaOH *consumed are as follows :*

Time (s)	339	1242	2745	4546	∞
Volume of NaOH (mL)	26.34	27.80	29.70	31.81	39.81

Find the average rate constant (*k*).

(*a*) $4.29 \times 10^{-4}\ s^{-1}$ (*b*) $3.29 \times 10^{-4}\ s^{-1}$

(*c*) $8.68 \times 10^{-4}\ s^{-1}$ (*d*) $1.23 \times 10^{-4}\ s^{-1}$

Interpret (*d*) For ester hydrolysis, equation

$$k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$

Since, V_0 is not given

or
$$k = \frac{2.303}{(t_1 - t_2)} \log \frac{c_{t_2}}{c_{t_1}} \qquad \text{...(iii)}$$

Now, find c_t.

t	339 s	1242 s	2745 s	4546 s
$c_t = V_\infty - V_t$	39.81 – 26.34 = 13.47 mL	39.81 – 27.80 ≈ 12.0 mL	39.81 – 29.70 = 10.11 mL	39.81 – 31.81 = 8.0 mL

and
$$t_1 - t_2 = 339 - 1242 = -903 \text{ s}$$
$$t_1 - t_3 = 339 - 2745 = -2406 \text{ s}$$
$$t_1 - t_4 = 339 - 4546 = -4207 \text{ s}$$

Using relation given in Eq. (iii),

$$\therefore \quad k_1 = \frac{2.303}{-903} \log \frac{12.0}{13.47} = -0.0025 \times \log (0.89)$$
$$= -0.0025 \times -0.0506 = 1.27 \times 10^{-4} \text{ s}^{-1}$$
$$k_2 = \frac{2.303}{-2406} \log \frac{10.11}{13.47} = -0.0095 \times \log (0.75)$$
$$= -0.00095 \times -0.1249 = 1.19 \times 10^{-4} \text{ s}^{-1}$$
$$k_3 = \frac{2.303}{-4207} \log \frac{8.0}{13.47} = -0.00054 \times \log (0.59)$$
$$= -0.00054 \times -0.2291 = 1.23 \times 10^{-4} \text{ s}^{-1}$$
$$k_{\text{average}} = 1.23 \times 10^{-4} \text{ s}^{-1}$$

Examples of First Order Reactions

(i) Decomposition of H_2O_2,

$$H_2O_2 \longrightarrow H_2O + \frac{1}{2} O_2$$

(ii) Dissociation of N_2O_5,

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

(iii) Decomposition of ammonium nitrite,

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

(iv) Decomposition of SO_2Cl_2,

$$SO_2Cl_2 \longrightarrow SO_2 + Cl_2$$

(v) Inversion of cane sugar,

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} \xrightarrow{H_2O/H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

(vi) Hydrolysis of methyl acetate,

$$CH_3COOCH_3 + H_2O \rightleftharpoons CH_3COOH + CH_3OH$$

Second Order Reactions

The reaction is said to be of **second order** if its reaction rate is determined by the variation of two concentration terms of reactants. It can be represented as

$$-\frac{\Delta R}{\Delta t} \text{ or } \frac{\Delta p}{\Delta t} = k[A]^2 \qquad (\text{For } 2A \longrightarrow \text{ product})$$

or
$$-\frac{\Delta R}{\Delta t} \text{ or } \frac{\Delta p}{\Delta t} = k[A][B] \quad (\text{For } A + B \longrightarrow \text{ product})$$

e.g., In the reactions where the concentrations of both the reactants are equal.

$$\begin{array}{cccccl} A & + & B & \longrightarrow & \text{Product} & \\ a & & a & & 0 & \text{(initially)} \\ (a-x) & & (a-x) & & x & \text{(after time t)} \end{array}$$

The rate constant, k for the reaction is given by

$$k = \frac{1}{t} \times \frac{x}{a(a-x)}$$

In cases where the concentration of reactants are not equal

$$\begin{array}{cccccl} A & + & B & \longrightarrow & \text{Product} & \\ a & & b & & 0 & \text{(initially)} \\ (a-x) & & (b-x) & & x & \text{(after time } t\text{)} \end{array}$$

The rate constant, k for the reaction is given by

$$k = \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}$$

The units of k are given as L mol^{-1} time^{-1}. The time required to complete a certain fraction of the reaction is inversely proportional to the initial concentration of reactants in the case of second order reactions.

Some examples of second order reactions are

(i) Dissociation of HI,

$$2HI \longrightarrow H_2 + I_2$$

(ii) Saponification of ethyl acetate,

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COO^-Na^+ + C_2H_5OH$$

(iii) Reaction between NO and O_3,

$$NO + O_3 \longrightarrow NO_2 + O_2$$

(iv) Reaction between potassium persulphate and potassium iodide,

$$K_2S_2O_8 + 2KI \longrightarrow 2K_2SO_4 + I_2$$

Third Order Reactions

A reaction is said to be of third order if its rate is determined by the variation of three concentration terms.

$$-\frac{\Delta R}{\Delta t} \text{ or } \frac{\Delta P}{\Delta t} = k[A]^3 \qquad \text{(For } 3P \rightarrow \text{product)}$$

or $$-\frac{\Delta R}{\Delta t} \text{ or } \frac{\Delta P}{\Delta t} = k[A][B][C] \qquad \text{(For } A + B + C \rightarrow \text{product)}$$

When the concentration of all the three reactants is same or three molecules of the same reactant are involved, the rate expression is given as

$$\begin{array}{cccccccl} A & + & B & + & C & \longrightarrow & \text{Product} & \\ a & & a & & a & & 0 & \text{(initially)} \\ (a-x) & & (a-x) & & (a-x) & & x & \text{(after time } t\text{)} \end{array}$$

The rate constant, k for the reaction is given by

$$k = \frac{1}{t} \cdot \frac{x(2a-x)}{2a^2(a-x)^2}$$

The units of rate constant for third order reaction are L^2 mol^{-2} time^{-1}

Reactions of **third** and **higher orders** are rare, but some examples of 3rd order reactions are definitely seen. This is due to the fact that the chances of three molecules of coming to a single point simultaneously, *i.e.*, probability of trimolecular collisions is much less as compared to unimolecular or bimolecular collisions.

Examples of third order reactions are

(i) $2NO + O_2 \longrightarrow 2NO_2$

(ii) $2NO + Cl_2 \longrightarrow 2NOCl$

(iii) $2NO + Br_2 \longrightarrow 2NOBr$

(iv) Reaction between silver acetate and sodium formate *i.e.*,

$$2CH_3COOAg + HCOONa \longrightarrow 2Ag + CO_2 + CH_3COOH + CH_3COO^-Na^+$$

Reactions Involving Order in Fraction

There are some reactions, rate of which is expressed by fractions of concentration terms. For example

(i) $$CO + Cl_2 \longrightarrow COCl_2$$
$$\text{Rate} = k[CO]^2[Cl_2]^{1/2}$$
Order = 2.5

(ii) $$COCl_2 \longrightarrow Cl_2 + CO$$
$$\text{Rate} = k[COCl_2]^{3/2}$$
Order = 1.5

(iii) $$CH_3CHO \longrightarrow CH_4 + CO$$
$$\text{Rate} = [CH_4CHO]^{3/2}$$
Order = 1.5

(iv) $$H_2 + Br_2 \longrightarrow 2HBr$$
$$\text{Rate} = k[H_2][Br_2]^{1/2}$$
Order = 1.5

(v) Reaction between H_2 and D_2
$$\text{Rate} = k_pH_2\,(p_{D_2})^{1/2}$$

The conversion of parahydrogen to orthohydrogen at high temperature; Rate = $k(p_{H_2})^{1.5}$.

The non-integer values are generally due to complex nature of reaction which involves more than one elementary step. The overall rate law is obtained by combining rates of individual elementary steps.

Negative Order Reactions

Sometimes the rate of reaction decreases as the concentration of one of the constituent is increased, *e.g.*, transformation of ozone into oxygen, *i.e.*, $2O_3 \longrightarrow 3O_2$

$$\text{rate} = -\frac{1}{2}\frac{d}{dt}[O_3] = K\frac{[O_3]^2}{[O_2]} = K[O_3]^2[O_2]^{-1}$$

Because the reaction involves two steps as

$$O_2 + O \xrightarrow{\text{Fast}} O_3 \qquad \text{...(i)}$$

$$O_3 + O \xrightarrow{\text{Slow}} 2O_2 \qquad \text{...(ii)}$$

Reaction (ii) gives the rate law as it is the slow step.

$$\text{Rate} = k[O_3][O] \qquad \text{...(iii)}$$

Since [O] is an intermediate species and takes part in the fast reaction, so

$$K' = \frac{[O_3]}{[O_2][O]} \text{ or } [O] = \frac{O_3}{K'[O_2]}$$

On putting the value of [O] in rate law, we get,

$$\text{Rate} = \frac{k[O_3][O_3]}{k'[O_2]} = k_1[O_3]^2[O_2]^{-1} \qquad [\text{where, } k_1 = k \cdot K']$$

Consecutive or Sequential Reactions

A reactant (A) decomposes to (B), which in turn decomposes to (C), *i.e.,*

$$A \xrightarrow[\text{Step 1}]{k_1} B \xrightarrow[\text{Step 2}]{k_2} C$$

$$\therefore \qquad \frac{-d[A]}{dt} = k_1[A], \ \frac{-d[B]}{dt} = k_1[A] - k_2[B],$$

$$\frac{-d[C]}{dt} = k_2[B]$$

If $t = 0$, $[B] = 0$, and $k_1 < k_2$, then at $t = t$.

$$[B]_t = \frac{k_1[A]_0}{k_2 - k_1}[e^{-k_1 t} - e^{-k_2 t}]$$

(where, $[A]_0$ = initial concentration of (A))

Also maximum concentration of $[B]$ at time t is given by

$$t_{\max} = \frac{2.303}{k_2 - k_1} \log\left[\frac{k_2}{k_1}\right]$$

Side or Parallel or Concurrent Elementary Reactions

A single reactant gives two products B and C simultaneously with different decay constants. For first order reaction:

$$A \begin{cases} \xrightarrow{k_1} B \ (90\%) \ (\text{Main reaction}) \\ \xrightarrow{k_2} C \ (10\%) \ (\text{Side reaction}) \end{cases}$$

$$\text{Rate} = -\frac{d[A]}{dt} = k_1[A] + k_2[A] = (k_1 + k_2)[A] = k_{av}[A]$$

If after a time interval say $x\,M$ of B are formed and $y\,M$ of C are formed, then if reaction is carried out with A, when $t = 0$, $[B] = [C] = 0$.

$$\therefore \qquad \frac{x}{y} = \frac{k_1}{k_2}$$

$$\text{Also} \qquad \frac{\frac{d[B]}{dt}}{\frac{d[C]}{dt}} = \frac{k_1}{k_2}$$

$$k_1 = (\% \text{ yield of } B) \times k_{av}$$

$$\Rightarrow \qquad \% \text{ yield of } B = \frac{k_1}{k_{av}} = \frac{k_1}{k_1 + k_2}$$

$$k_2 = (\% \text{ yield of } C) \times k_{av}$$

$$\Rightarrow \qquad \% \text{ yield of } C = \frac{k_2}{k_{av}} = \frac{k_2}{k_1 + k_2}$$

Some examples

(i) Phenol $\xrightarrow[\text{Nitration}]{}$ o-nitrophenol + p-nitrophenol

(ii) $$C_2H_5Br + KOH \begin{cases} \longrightarrow H_2C{=}CH_2 + KBr + H_2O \\ \longrightarrow C_2H_5OH + KBr \end{cases}$$

Opposed or Reversible Elementary Reactions

(i) $$H_2 + I_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2HI$$

$$\text{Rate} = \frac{1}{2}\frac{d[HI]}{dt} = k_1[H_2][I_2] - k_2[HI]^2$$

(ii) $$2NO_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2O_4$$

$$-\frac{d[NO_2]}{dt} = 2k_1[NO_2]^2 - 2k_2[N_2O_4]$$

Case I First order-opposed by first order

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

$$\begin{array}{lcc} [t = 0] & a & 0 \\ [t = t] & a - x & x \end{array}$$

$$t = \frac{2.303}{(k_1 + k_2)} \log \frac{X_{eq}}{X_{eq} - x}$$

($X_{eq} = [B]$ formed at equilibrium)

Case II First order-opposed by first order

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B.$$

$$\begin{array}{lcc} [t = 0] & a & b \\ [t = t] & a - x & b + x \end{array}$$

$$t = \frac{2.303}{(k_1 + k_2)} \log \frac{X_{eq}}{X_{eq} - x}$$

($X_{eq} = [B]$ formed a equilibrium)

Pseudomolecular Reactions

There are several reactions which are considered as unimolecular, although in reality they are bi-or tri-molecular, *e.g.,* consider the hydrolysis of methyl acetate in the presence of acid

$$CH_3COOCH_3 + H_2O \xrightarrow{\text{acid}} CH_3COOH + CH_3OH$$

According to the law of mass action, this reaction seems to follow bimolecular process with the rate dependent on concentration of both ester and water. However, it is found that the rate is independent of water, it depends only on concentration of ester. Hence, reactions showing such a behaviour are called **pseudounimolecular reactions.**

The pseudounimolecular nature of above written reaction can be explained on the basis of the fact that here water is present in such excess that its concentration remains practically constant during the course of reaction. The pseudounimolecular reactions are also called **pseudo first order reactions.**

4.8 Methods of Determination of Order of Reaction

Several methods are used to determine order of a reaction, like initial rate method, integration method, half-life method, Ostwald isolation method, etc.

1. Integration Method

The **integration method** is also called **hit and trial method.** In this method a, x and t are determined and substituted in kinetic equations of various orders. The equation which gives the most constant value of rate constant for a series of time intervals is the one to which the order of reaction corresponds.

In this method the kinetic equation used for same molar concentration are

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x} \text{ for first order reactions}$$

$$k = \frac{1}{t}\left[\frac{1}{a-x} - \frac{1}{a}\right] \text{ for second order reactions}$$

$$k = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right] \text{ for third order reactions}$$

In general for the reactions of n order, given as below,

$$nA \longrightarrow \text{Products}$$

the rate equation of the form given below is obtained.

$$k_n = \frac{1}{t(n-1)}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right]$$

This equation is applicable for all orders except first order.

2. Half-life Method

The half-life method is also called **fractional change method.** The half-life period (time required to reduce the initial concentration to half of its value) depends differently on the initial concentrations of reactants for different orders of reactions, *i.e.,*

For zero order reaction

$$t_{1/2} \propto [A]_i$$

For first order reaction, $t_{1/2}$ is independent of initial concentration. For first order reaction half-life period depends upon the rate constant as

$$t_{1/2} = \frac{0.693}{k}$$

For n order reaction

$$t_{1/2} \propto \frac{1}{[A]_i^{n-1}}$$

Now suppose initial concentration of A is a, then

$$t_{1/2} \propto \frac{1}{a^{(n-1)}}$$

Starting with two independent reactions having initial concentrations a_1 and a_2 at corresponding half-lives $(t_{1/2})_1$ and $(t_{1/2})_2$ we have

$$(t_{1/2})_1 \propto \frac{1}{a_1^{(n-1)}}$$

$$(t_{1/2})_2 \propto \frac{1}{a_2^{(n-1)}}$$

or

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

Taking log on both the sides we obtain

$$\log \frac{(t_{1/2})_1}{(t_{1/2})_2} = (n-1) \log \left(\frac{a_2}{a_1}\right)$$

$$n = 1 + \frac{\log [(t_{1/2})_1/(t_{1/2})_2]}{\log (a_2/a_1)}$$

Hence, from this equation, n, the order of reaction is calculated.

For gaseous equations, the initial pressure (p) is taken instead of initial concentration a, thus, for them the above formula is changed to

$$n = 1 + \frac{\log [(t_{1/2})_1/(t_{1/2})_2]}{\log (p_2/p_1)}$$

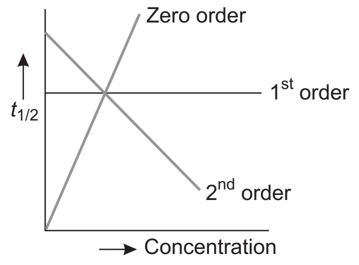


Fig. 4.6 Plots between half-life period and concentration

Average life is reciprocal of the rate constant

$$t_{av} = \frac{1}{k}$$

and for first order reaction,

$$t_{av} = 1.44 t_{1/2}$$

3. Ostwald Isolation Method

This method is employed in determining the order of complicated reactions by isolating one of the reactants so far as its influence on the reaction rate is concerned. Suppose the reaction under consideration is

$$n_1A + n_2B + n_3C \longrightarrow \text{products}$$

In this reaction for the determination of any of the reactants say A, rest of the reactants *i.e.*, B and C are taken in large excess, so that there is no change practically in their concentrations.

The order of the reaction for A is then determined by using any of the methods written before. The procedure is likewise for B and C also. *e.g.*, It is observed as follows

(i) Keeping the concentrations of B and C constant, if concentration of A is doubled, the rate of reaction becomes 4 times. This means that

$$\text{Rate} \propto [A]^2$$

i.e., order of reaction with respect to A is 2.

(ii) Keeping the concentrations of A and C constant, if concentration of B is doubled, the rate of reaction becomes 2 times. This means that

$$\text{Rate} \propto [B]$$

i.e., order of reaction with respect to B is 1.

(iii) Keeping the concentrations of A and B constant, if the concentration of C is doubled, the rate of the reaction remains unaffected. This means that rate is independent of concentration of C, *i.e.*, order of reaction with respect to C is zero.

Hence, the overall rate law expression will be

$$\text{Rate} = k\,[A]^2\,[B]\,[C]^0$$

Thus, order of reaction = 2 + 1 + 0 = 3

Hot Spot 2

INITIAL Rate Method

It is also an important topic of the chapter for JEE Main examination. The questions are generally numerical type and level of question is average generally.

In this method, the order of a reaction is determined by varying the concentration of one of the reactants while others are kept constant (The initial rate, r_1 is determined either numerically or from the slope of the curve of concentration *versus* time at time, $t = 0$)

Thus, for the reaction

$$aA + bB + cC \longrightarrow \text{product}$$
$$r_i = k\,[A_i]^a[B_i]^b[C_i]^c$$

Now if $[B]$ and $[C]$ remain constant,

$$r_i = k_i[A_i]^a \quad \text{where,} \quad k_i = k[B_i]^b[C_i]^c$$

Here the value of a can be determined by inspecting the rate at different values of $[A]$ as

If we know the initial rates at different concentration of A we have

$$[r_i]_1 = k_i[A_i]_1^a,\ [r_i]_2 = k_i[A_i]_2^a$$

where, $[r_i]_1$ and $[r_i]_2$ are the initial rates of reaction and $[A_i]_1$, and $[A_i]_2$ are initial concentrations of A. On dividing both the equations, we get

$$\frac{[r_i]_1}{[r_i]_2} = \left[\frac{[A_i]_1}{[A_i]_2}\right]^a$$

Taking log on both the sides, we obtain

$$\log\frac{[r_i]_1}{[r_i]_2} = a\log\frac{[A_i]_1}{[A_i]_2},$$

$$a = \frac{\log\,[(r_i)_1/(r_i)_2]}{\log\,[(A_i)_1/(A_i)_2]}$$

In this way, the order of reaction with respect to a is determined. Similarly, it can also be determined for other reactants also, The overall order of reaction is the sum of all such orders, *i.e.*,

$$n = a + b + c\ \ldots$$

Sample Problem 13 *In a reaction between A and B the initial rate of reaction (r_0) was measured for different initial concentrations of A and B as given below.*

A / mol L^{-1}	0.20	0.20	0.40
B / mol L^{-1}	0.30	0.10	0.05
r_0 / mol L^{-1}s^{-1}	5.07×10^{-5}	5.07×10^{-5}	1.43×10^{-5}

What is the rate law? **[NCERT]**

(a) $r = k[A]^2[B]$
(b) $r = k[A]^{1.5}[B]$
(c) $r = k[A][B]^2$
(d) $r = k[A]^{1.5}$

Interpret (*d*) Let the order of reaction with respect to A and B are respectively x and y, so rate law can be written as

$$\text{Rate} = k\,[A]^x\,[B]^y$$

On putting values,

$$(\text{Rate})_1 = k\,[0.20]^x\,[0.30]^y = 5.07 \times 10^{-5} \quad \ldots\text{(i)}$$
$$(\text{Rate})_2 = k\,[0.20]^x\,[0.10]^y = 5.07 \times 10^{-5} \quad \ldots\text{(ii)}$$
$$(\text{Rate})_3 = k\,[0.40]^x\,[0.05]^y = 1.43 \times 10^{-4} \quad \ldots\text{(iii)}$$

Dividing Eq. (i) by Eq. (ii)

$$\frac{(\text{Rate})_1}{(\text{Rate})_2}=\frac{k\,[0.20]^x\,[0.30]^y}{k\,[0.20]^x\,[0.10]^y}=\frac{5.07\times10^{-5}}{5.07\times10^{-5}}=1$$

$$[3]^y=[3]^0=1;\ y=0$$

Now dividing Eq. (ii) by Eq. (iii)

$$\frac{(\text{Rate})_2}{(\text{Rate})_3}=\frac{k\,[0.20]^x\,[0.10]^0}{k\,[0.40]^x\,[0.05]^0}=\frac{5.07\times10^{-5}}{1.43\times10^{-4}}$$

$$\left[\frac{1}{2}\right]^x=\frac{1}{2.82}$$

$$2^x=2.82$$

$$x\log 2=\log 2.82$$

$$\therefore\quad x=1.4957\simeq 1.5$$

Order with respect to $A=1.5$

Order with respect to $B=0$

$$r=k[A]^{1.5}[B]^0$$

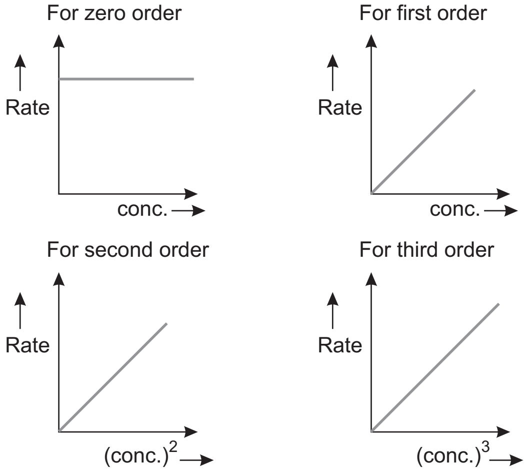
---

4. Graphical Method

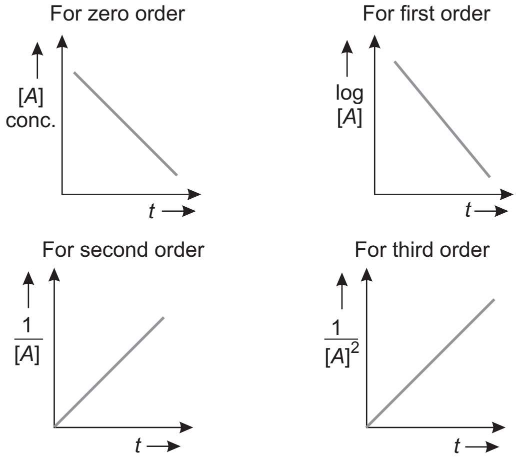
In this method, the values of $\Delta x/\Delta t$ at different intervals of time is determined by plotting a curve between x (the amount of substance decomposed) and time t. The value of $\Delta x/\Delta t$ at a particular time corresponding to a particular value of $(a-x)$ is given by the slope of the curve at that curve.

Linear Plots for Different Order Reactions are as

(a) Plots of Rate *vs* Concentration



(b) Plots From Integrated Rate Equations



Hence, in graphical method

1. If the plot of $\log(a-x)$ *versus* t is a straight line, the reaction follows first order.
2. If the plot of $\frac{1}{(a-x)}$ *versus* t is a straight line, the reaction follows second order.
3. If the plot of $\frac{1}{(a-x)^2}$ *versus* t is a straight line, the reaction follows third order.
4. If graphs are plotted between $\log\left(\frac{dx}{dt}\right)$ and $\log(a-x)$, the slope of the line gives the order of reaction.

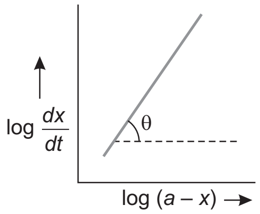


Fig. 4.7 Plot of $\log\left(\frac{dx}{dt}\right)$ *vs* $\log(a-x)$

$$\because\quad \frac{dx}{dt}=k(a-x)^n$$

$$\therefore\quad \log\left(\frac{dx}{dt}\right)=\log k+n\log(a-x)$$

Thus, slope $n=\tan\theta$

4.9 Effect of Temperature on Rate of Reaction

Rate constants and, therefore rate of a chemical reaction depends strongly on temperature. Typically rates of all reactions increase with increase in temperature. A rough rule, valid for many reactions in solution, is that near room temperature, rate constant (k) doubles or triples for each 10°C rise in temperature.

Arrhenius Equation

In year 1889, Arrhenius noted that $k(T)$ data for many reactions fit the equation.

$$k = Ae^{-E_a/RT}$$

here, A = a constant called frequency factor (because it gives the frequency of binary collisions of the reacting molecules per second per litre). It is also called **collision number** or **pre-exponential factor**

R = gas constant, T = absolute temperature

E_a = energy of activation

The factor $e^{-E_a/RT}$ is referred as Boltzmann factor and gives the fraction of molecules having energy equal to or greater than activation energy.

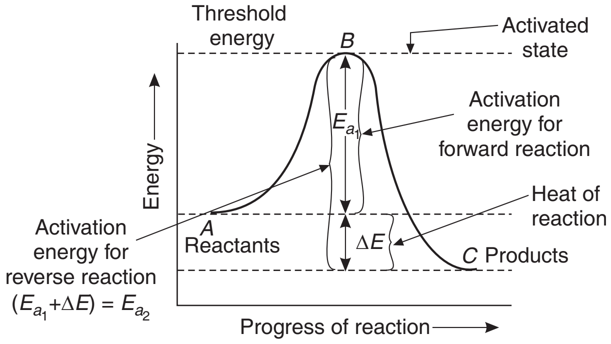
Hot Spot 3

ACTIVATION Energy

It is an another topic of the chapter from which questions have frequently seen in JEE Main examination. The question is generally numerical type and its level is easy to moderate.

The activation energy can also be defined as "The energy that activates passive or non-active molecules after its adsorption or minimum energy in excess to normal energy of molecules, which molecules must possess in order to form product on collision.

The concept of activation energy gives us an idea whether a given reaction is slow or fast at a given temperature. A reaction which has lower activation energy proceed at a faster rate at a given temperature or *vice-versa*. The differences in activation energy are mainly responsible for observed difference in rates of reactions. The concept of activation energy as applied to chemical reaction can be explained by plotting energy against the progress of reaction as shown in the figure below.



$$E_a = E_{th} - E_R$$

where, E_{th} = threshold energy (the minimum energy required over and above the energy possessed by the reactants in order to cross the energy barrier).

E_R = energy possessed by the reactant.

Calculation of Activation Energy

Activation energy can be calculated by knowing the rate constants at two different temperatures, assuming that E_a and A remains constant.

Taking log of both the sides in Arrhenius equation, we get

$$\ln k = \ln A - \frac{E_a}{RT}$$

Now, if the values of rate constant at temperatures T_1 and T_2 are k_1 and k_2 respectively then

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \qquad \text{...(i)}$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2} \qquad \text{...(ii)}$$

Subtracting the Eq. (i) from (ii), we get

$$\ln k_2 - \ln k_1 = -\frac{E_a}{RT_2} - \left(-\frac{E_a}{RT_1}\right)$$

$$= \frac{E_a}{RT_1} - \frac{E_a}{RT_2}$$

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$= \frac{E_a}{R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right) \qquad \text{[Here, } T_2 > T_1\text{]}$$

This relation is used when rate constants at two different temperatures are given.

This reaction is also written as

$$\frac{d \log k}{dT} = \frac{E}{RT^2}$$

Arrhenius equation is purely an empirical equation that gives a reasonably good representation of temperature dependence of the rate constant.

When $\log k$ is plotted against $1/T$, we get a straight line which is represented by Arrhenius equation as

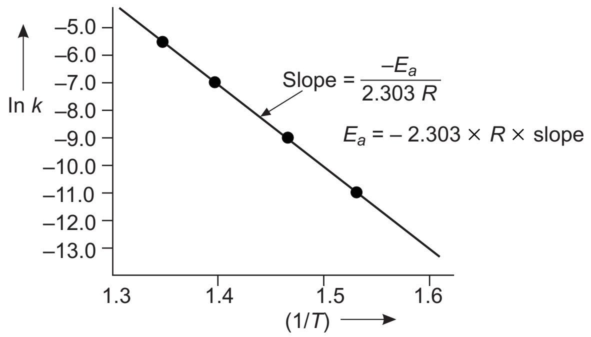
$$k = Ae^{-E_a/RT}$$

$$\ln k = \ln A - E_a/RT$$

$$\log k = \log A - \frac{E_a}{2.303\,RT}$$

The intercept of this line is equal to $\log A$ and slope is equal to $-\frac{E_a}{2.303\,R}$.

Therefore, $E_a = -2.303\,R \times \text{slope}$



Caution Points

(*i*) *Different reactions have different rates because their activation energies are different. Lesser the activation energy, faster is the reaction rate.*

(*ii*) *Activation energy can never be zero. If $E_a = 0$, then according to Arrhenius equation, $k = A$, i.e., every collision between molecules leads to a chemical reaction. This can never be true.*

Sample **Problem 14** *The rate constant for the first order decomposition of H_2O_2 is given by the following equation, $\log k = 14.34 - 1.25 \times 10^4\ \text{K}/\text{T}$. Calculate E_a for this reaction and at what temperature will its half-life period be 256 min?* **[NCERT]**

(a) 239.3 *kJ and* 669 *K*

(*b*) 846 *kJ and* 700 *K*

(c) 134.2 *kJ and* 492 *K*

(*d*) 239.3 *kJ and* 339 *K*

Interpret (*a*) **Calculation of activation energy E_a**

According to Arrhenius equation; $k = Ae^{-E_a/RT}$

$$\log k = \log A - \frac{E_a}{2.303\ RT} \quad \text{...(i)}$$

$$\log k = 14.34 - \frac{1.25 \times 10^4\ \text{K}}{T} \quad \text{...(ii)}$$

On comparing both equations.

$$\frac{E_a}{2.303RT} = \frac{1.25 \times 10^4\ \text{K}}{T}$$

$$E_a = 1.25 \times 10^4\ \text{K} \times 2.303 \times 8.314\ (\text{JK}^{-1}\ \text{mol}^{-1})$$

$$= 23.93 \times 10^4\ \text{J mol}^{-1}$$

$$= 239.3\ \text{kJ mol}^{-1}$$

Calculation of required temperature If $t_{1/2} = 256$ min.

For first order reaction ;

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{(256\ \text{min})} = \frac{0.693}{256 \times 60\ \text{s}}$$

$$= 4.51 \times 10^{-5}\ \text{s}^{-1}$$

According to Arrhenius theory,

$$\log k = 14.34 - \frac{1.25 \times 10^4\ \text{K}}{T}$$

$$\log (4.51 \times 10^{-5}) = 14.34 - \frac{1.25 \times 10^4\ \text{K}}{T}$$

$$-4.35 = 14.34 - \frac{1.25 \times 10^4\ \text{K}}{T}$$

$$\frac{1.25 \times 10^4}{T} = 14.34 + 4.35 = 18.69$$

$$T = \frac{1.25 \times 10^4}{18.69} = 669\ \text{K}$$

Sample **Problem 15** *The first order rate constant for the decomposition of C_2H_5I by the reaction,*

$$C_2H_5I(g) \longrightarrow C_2H_4(g) + HI(g)$$

at 600 K is $1.60 \times 10^{-5}\ s^{-1}$. Its energy of activation is 209 kJ mol^{-1}. Calculate the rate constant at 700 K. **[NCERT Exemplar]**

(a) $4.87 \times 10^{-4}\ s^{-1}$

(*b*) $6.36 \times 10^{-3}\ s^{-1}$

(c) $1.98 \times 10^{-4}\ s^{-1}$

(*d*) $2.68 \times 10^{-3}\ s^{-1}$

Interpret (*b*) We know that

$$\log k_2 - \log k_1 = \frac{E_a}{2.303\ R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\log k_2 = \log k_1 + \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$= \log (1.60 \times 10^{-5}) + \frac{209 \times 10^3\ \text{J mol}^{-1}}{2.303 \times 8.314\ \text{J mol}^{-1}\ \text{K}^{-1}} \times \left[\frac{10}{600 \times 700}\right]\text{K}$$

$$\log k_2 = -4.796 + 2.599 = 2.197$$

$$k_2 = \text{Antilog}\ (-2.197)$$

$$= \text{Antilog}\ (\bar{3}.803)$$

$$= 6.36 \times 10^{-3}\ \text{s}^{-1}$$

Sample **Problem 16** *How faster would a reaction proceed at 25°C than at 0°C if the activation energy is 65 kJ?*

(a) 11 *times* (b) 9 *times*
(c) 6 *times* (d) 2 *times*

Interpret (a) $2.303 \log \frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$

$$\therefore \qquad 2.303 \log \frac{k_2}{k_1} = \frac{65 \times 10^3}{8.314}\left[\frac{25}{298 \times 273}\right]$$

$$\therefore \qquad k_2/k_1 = 11.05$$

Sample **Problem 17** *Milk turns sour at 40°C three times faster as at 0°C. The energy of activation for souring of milk is*

(a) 5.683 *kcal* (b) 2.532 *kcal*
(c) 4.693 *kcal* (d) 4.246 *kcal*

Interpret (c) $2.303 \log \frac{k_2}{k_1} = \frac{E_a}{R} \frac{[T_2 - T_1]}{T_1 T_2}$

$$\therefore \qquad 2.303 \log 3 = \frac{E_a}{2} \frac{[313 - 273]}{313 \times 273}$$

$$E_a = 4.693 \text{ kcal}$$

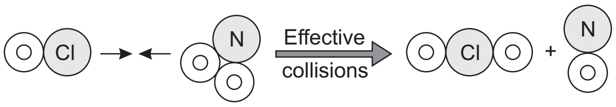
4.10 Theories of Rate of Reaction

Following theories are given to explain the rate of a reaction.

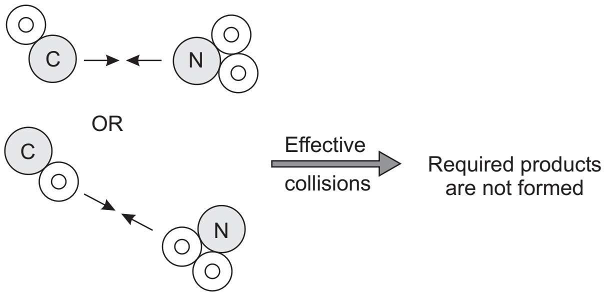
Collision Theory of Bimolecular Reactions

The collision theory states that

1. If two molecules are to react together, they must collide with each other.
2. The collision between all molecules do not lead to chemical reaction.
3. The collisions in which the molecules acquire energy greater than the activation energy, results in chemical reaction.



Properly oriented collisions to form products



Collisions are not properly oriented

Fig. 4.8 Orientation of reactants

4. The colloiding molecules must posses certain minimum energy (**threshold energy**) to make the collision effective.
5. The additional energy required by the molecule to attain threshold energy is called **activation energy.** During the collisions, this energy is acquired by the molecules as a result of interchange of energies. Thus,

Activation energy = threshold energy − energy of colliding molecules

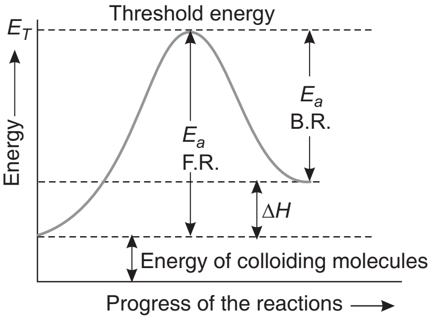


Fig. 4.9 Energy profile diagram

If we assume that the rate of reaction is equal to the rate of collisions per unit volume per unit time multiplied by the fraction of collisions (that have sufficient relative kinetic energy to overcome the energy barrier E^*) then the rate constant is given by the expression

$$k = Z_{AB} \cdot e^{-E^*/KT} \qquad \text{...(i)}$$

here, Z_{AB} = **collision frequency factor,** *i.e.*, the number of collisions between reactant molecules A and B per unit volume per unit time divided by N_A and N_B, the number of molecules per unit volume of A and B respectively.

It can be shown by kinetic theory of gases that

$$Z_{AB} = (8KT/\pi\mu)^{1/2}\pi d^2$$

here, $\mu = \frac{m_A \times m_B}{m_A + m_B}$ *i.e.*, reduced mass of colliding reactant molecules

$d = r_A + r_B$ *i.e.*, the sum of radii of two reactant molecules. Now, putting the value of Z_{AB} in Eq. (i), we get

$$k = \left(\frac{8KT}{\pi\mu}\right)^{1/2} \times \pi d^2 \times e^{-E^*/KT}$$

If we assume that energy required for Avogadro number of effective collisions, $E_a = N_A E^*$ then

$$k = \left(\frac{8KT}{\pi \mu}\right)^{1/2} \times \pi d^2 \times e^{-E_a/RT}$$

$$k = Z_{AB} \times e^{-E_a/RT}$$

For a successful collision, however it is also important that the molecules must be oriented properly in space alongwith their energy requirements. Thus, if P is the **orientation factor** (also called steric factor) then above rate equation can be changed as

$$K = PZ_{AB}\, e^{-E_a/RT}$$

Now, if we compare above equation, with Arrhenius equation we get

$$A = PZ_{AB}$$

where, $A =$ Arrhenius collision factor

Transition State Theory

This theory is also known as **absolute reaction rate theory** or **activated complex theory.** This theory is based on the idea that bond breaking and bond making involved in a chemical reaction must occur continuously or simultaneously. According to this theory

1. The reactant molecules must come together to form an activated complex, whose energy is higher than the reactant molecules.
2. The activated complex is supposed to be in equilibrium with the reactant molecules and has all the attributes of normal molecule except that one of the vibrational degree of freedom is converted into translational degree of freedom.
3. This complex though unstable, has a transient existence and its potential energy is maximum. Finally it decomposes into products.
4. The energy of activation according to this theory is the additional energy which the reacting molecules must acquire to form the activated complex.

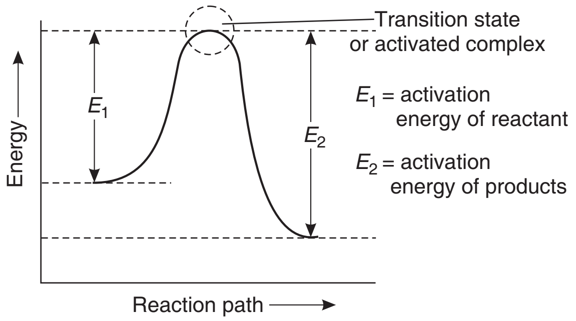


Fig. 4.10 Energy profile diagram of an exothermic reaction

Mathematical Expression of Transition State Theory

Consider the following reaction

$$A + B \longrightarrow X^* \longrightarrow \text{products}$$

The equilibrium constant, K^* for the activated complex is,

$$K^* = \frac{[X^*]}{[A][B]}$$

or $$[X^*] = K^*[A][B] \qquad \text{...(i)}$$

Now, according to transition state theory, the rate of reaction is the number of activated complexes which pass over the potential barrier per unit time, which in turn is equal to the concentration of activated complexes multiplied by the frequency at which the complex would decompose into products. Mathematically

$$\text{Rate of reaction} = \frac{d\,[\text{product}]}{dt}$$

$$\frac{\Delta x}{\Delta t} = [X^*] \times \text{ rate of dissociation of activated complex}$$

Now, putting the value of $[X^*]$ from the above Eq. (i) we get

$$\frac{\Delta x}{\Delta t} = K^*[A][B] \times \text{rate of dissociation of activated complex} \qquad \text{... (ii)}$$

The activated complex would decompose only if the enough vibrational energy is supplied to the system *i.e.,* vibration degree of freedom will be converted into translational degree of freedom. Due to this vibrational energy, the atoms vibrate with certain critical frequency leading to the bond rupture. This frequency of bond rupture is equal to the frequency with which the activated complex decomposes into products.

Therefore,

frequency for the dissociation of activated complex $= E_{\text{vib}}/h$

where, $E_{\text{vib}} =$ average vibrational energy at temperature T

Vibrational energy is also equal to kT or $\frac{RT}{N}$.

where R = universal gas constant
N = Avogadro number.
and $h =$ Planck's constant
Thus, frequency $= RT/Nh$

Now putting this value into Eq. (ii), we get

$$\frac{\Delta x}{\Delta t} = K^*[A][B] \times \frac{RT}{Nh} \qquad \text{...(iii)}$$

We also know that for a bimolecular conversion of reactants into products,

$$\frac{\Delta x}{\Delta t} = k\,[A][B] \qquad \text{...(iv)}$$

Putting this value into Eq. (iii) we get

$$k[A][B] = k^*[A][B] \times \frac{RT}{Nh}$$

$$\therefore \qquad k = k^* \times \frac{RT}{Nh} \qquad \text{... (v)}$$

This is called mathematical statement of transition state theory.

Relation Between K^* and ΔG^*

K^* can be correlated with ΔG^* as

$$\Delta G^* = -RT \ln K^*$$

where $\Delta G^* =$ [free energy of activated complex – free energy of reactants] and called **standard free energy change.**

So $\qquad \Delta G^* = \Delta H^* - T\Delta S^*$

or $\qquad -RT \ln k^* = \Delta H^* - T\Delta S^*$

or $\qquad \ln k^* = \dfrac{-(\Delta H^* - T\Delta S^*)}{RT}$

or $\qquad k^* = e^{-(\Delta H^* - T\Delta S^*)/RT} \qquad$ ...(vi)

Putting this value into the mathematical statement of transition state theory, we get

$$k = e^{-(\Delta H^* - T\Delta S^*)/RT} \times \frac{RT}{Nh}$$

also $\qquad k = \dfrac{RT}{Nh} \times e^{-\Delta H^*/RT} \cdot e^{\Delta S^*/R}$

here, $\Delta H^* =$ standard enthalpy change, *i.e.,* standard heat of activation

$\Delta S^* =$ standard entropy change, *i.e.,* standard entropy of activation

The activation energy for the forward reaction (E_a^f) and the activation energy for the reverse reaction (E_a^r) are related to the enthalpy (ΔH) of the reaction by the equation

$$\Delta H = E_a^f - E_a^r$$

For endothermic reaction,

$$\Delta H > 0 \Rightarrow E_a^r < E_a^f$$

For exothermic reaction,

$$\Delta H < 0 \Rightarrow E_a^r > E_a^f$$

Check Point 3

1. Molecularity of reaction is not found more than three. Why?
2. Can a reaction has zero activation energy?
3. Explain, why hydrogen and oxygen do not react at room temperature?
4. Differentiate between the chemical reactions having high and low activation energy.

WORKED OUT
Examples

Example 1 *The rate law for a reaction between the substances A and B is given by rate $= k[A]^a [B]^b$. On doubling the concentration of A and halving the concentration of B, the ratio of the new rate to the earlier rate of the reaction will be as*

(a) $2^{\frac{1}{a+b}}$ (b) $a+b$ (c) $a-b$ (d) $2^{(a-b)}$

Solution (d)

$$r_1 = k[A]^a [B]^b$$

$$r_2 = k[2A]^a \left[\frac{B}{2}\right]^b = k[A]^a [B]^b \, 2^{(a-b)}$$

$$\therefore \quad \frac{r_2}{r_1} = 2^{(a-b)}$$

Example 2 *The rate constant k, for the reaction*

$N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$ *is* $2.3 \times 10^{-2} s^{-1}$. *Which equation given below describe the change of* $[N_2O_5]$ *with time?* $[N_2O_5]_0$ *and* $[N_2O_5]_t$ *correspond to concentration of* N_2O_5 *initially and at time* t.

(a) $[N_2O_5]_t = [N_2O_5]_0 + kt$

(b) $[N_2O_5]_t = [N_2O_5]_0 \, e^{kt}$

(c) $\ln \frac{[N_2O_5]_0}{[N_2O_5]_t} = kt$

(d) $\log_{10}[N_2O_5]_t = \log_{10}[N_2O_5]_0 - kt$

Solution (c) $N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$

$$\text{Rate constant} = 2.3 \times 10^{-2} \text{ s}^{-1}$$

The unit of rate constant (*i.e.*, s^{-1}), shows that reaction is of first order.

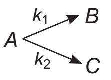
For first order reaction,

$$k = \frac{1}{t}\ln\frac{a}{a-x} \quad \Rightarrow \quad k = \frac{1}{t}\ln\frac{[N_2O_5]_0}{[N_2O_5]_t}$$

or

$$\ln\frac{[N_2O_5]_0}{[N_2O_5]_t} = kt$$

Example 3 *A substance undergoes first order decomposition. The decomposition follows the parallel first order reactions as*



$k_1 = 1.26 \times 10^{-4} \text{ s}^{-1}$

$k_2 = 3.8 \times 10^{-5} \text{ s}^{-1}$

The percentage distribution of B and C are

(a) 76.83, 23.17 (b) 24.9, 75.1

(c) 60, 40 (d) 50, 50

Solution (a) % distribution of $B = \frac{k_1}{k_1 + k_2} \times 100$

$$= \frac{1.26 \times 10^{-4}}{1.26 \times 10^{-4} + 3.8 \times 10^{-5}} \times 100$$

$$= 76.83\%$$

and, % distribution of $C = \frac{k_2}{k_1 + k_2} \times 100$

$$= \frac{3.8 \times 10^{-5}}{1.26 \times 10^{-4} + 3.8 \times 10^{-5}} \times 100$$

$$= 23.17\%$$

Example 4 *For a chemical reaction,* $A \to B$, *the rate of reaction increases by a factor of 1.837 when the concentration of A is increased by 1.5 times. The order of reaction with respect to A is*

(a) 0 (b) 1 (c) 1.5 (d) 2

Solution (c)

$$r_1 = k[A]^n$$

$$r_2 = 1.837\, r_1 = k[1.5 \text{ A}]^n$$

$$\therefore \quad \frac{r_2}{r_1} = 1.837 = (1.5)^n$$

$\Rightarrow \quad n = \frac{3}{2} = 1.5$ (On solving by logarithmic method)

Example 5 *For a reaction* $A + B \longrightarrow C + D$, *if the concentration of A is doubled without altering the concentration of B, the rate gets doubled. If the concentration of B is increased by nine times without altering the concentration of A, the rate gets tripled. The order of the reaction is*

(a) 1 (b) 1.5 (c) 2 (d) –1

Solution (b) For reaction, $A + B \longrightarrow C + D$

$$r_1 = k[A]^a [B]^b \qquad \text{...(i)}$$

$$r_2 = 2r_1 = k[2A]^a [B]^b \qquad \text{...(ii)}$$

and

$$r_3 = 3r_1 = k[A]^a [9B]^b \qquad \text{...(iii)}$$

From (i) and (ii) $a = 1$

Form (i) and (iii), $b = \frac{1}{2}$

$$\therefore \quad \text{Order} = a + b$$

$$= 1 + \frac{1}{2} = \frac{3}{2} = 1.5$$

Example 6 *The time of completion of 90% of the first order reaction is approximately*

(a) $4.4t_{1/2}$ (b) $3.3t_{1/2}$ (c) $2.2t_{1/2}$ (d) $1.1t_{1/2}$

Solution (b) For first order reaction

$$k = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}$$

or

$$t = \frac{2.303}{k}\log_{10}\frac{100}{(100-90)}$$

$$= \frac{2.303 \times t_{1/2}}{0.693} \times \log 10 \qquad \left[\because k = \frac{t_{1/2}}{0.693}\right]$$

$$= 3.3 \times t_{1/2}$$

Example 7 *The half-time of a first order decomposition of nitramide is* 2.1 *h at* 15°*C.*

$$NH_2NO_2(aq) \longrightarrow N_2O(g) + H_2O(l)$$

If 6.2 *g of nitramide is allowed to decompose then time taken for it to decompose* 99% *will be*

(a) 2.1 *h* (b) 12 *h* (c) 13.96 *h* (d) 33 *h*

Solution (c) For first order reaction,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.1} = 0.33\ \text{h}^{-1}$$

and

$$k = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}$$

or

$$t = \frac{2.303}{k}\log_{10}\frac{100}{(100-99)}$$

$$= \frac{2.303}{0.33} \times \log_{10} 100$$

$$= \frac{2.303}{0.33} \times 2 = 13.96\ \text{h}$$

Example 8 *The chemical reaction between mercuric chloride and potassium oxalate proceeds as under :*

$$2HgCl_2 + K_2C_2O_4 \longrightarrow 2KCl + 2CO_2 + Hg_2Cl_2$$

The mass of Hg_2Cl_2 *precipitated from different solutions in a given time, at* 100°*C was as follows*

Exp. no.	**$HgCl_2$** (mol L^{-1})	**$K_2C_2O_4$** (mol L^{-1})	**Time** (min)	**Hg_2Cl_2 precipitated** (mol)
(i)	0.0836	0.404	65	0.0068
(ii)	0.0836	0.202	120	0.0031
(iii)	0.0418	0.404	60	0.0032

The order of reaction will be

(a) 1 (b) 2 (c) 3 (d) 0

Solution (c) rate $= k[HgCl_2]^{\alpha}\,[K_2Cr_2O_4]^{\beta}$

$$\frac{0.0068}{65} = k(0.0836)^{\alpha}\,(0.404)^{\beta} \qquad \text{...(i)}$$

$$\frac{0.0031}{120} = k(0.0836)^{\alpha}\,(0.202)^{\beta} \qquad \text{...(ii)}$$

$$\frac{0.0032}{60} = k(0.0418)^{\alpha}\,(0.404)^{\beta} \qquad \text{...(iii)}$$

From (i) and (ii), $4 = 2^{\beta} \Rightarrow \beta = 2$

From (i) and (iii), $2 = 2^{\alpha} \Rightarrow \alpha = 1$

$\therefore$ Order of reaction $= \alpha + \beta = 1 + 2 = 3$

Example 9 *A first order reaction is* 50% *completed in* 30 *min at* 27°*C and in* 10 *min at* 47°*C. Calculate the activation energy of the reaction.*

(a) 43.8 *kJ* mol^{-1} (b) 4.38 *kJ* mol^{-1}

(c) 0.438 *kJ* mol^{-1} (d) 438 *kJ* mol^{-1}

Solution (a) At 27°C, $t_{1/2} = 30$ min

$$k_1 = \frac{0.693}{30} = 0.0231$$

and at 47°C, $t_{1/2} = 10$ min

$$k_2 = \frac{0.693}{10} = 0.0693$$

From,

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$\Rightarrow$

$$\log\frac{0.0693}{0.0231} = \frac{E_a}{2.303 \times 8.314}\left[\frac{1}{300} - \frac{1}{320}\right]$$

or

$$\log 3 = \frac{E_a}{2.303 \times 8.314}\left[\frac{20}{300 \times 320}\right]$$

or

$$0.4771 = \frac{E_a \times 20}{2.303 \times 8.314 \times 300 \times 320}$$

or

$$E_a = 43848\ \text{J mol}^{-1} = 43.8\ \text{kJ mol}^{-1}$$

Example 10 *The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at* 25°*C are* $3.0 \times 10^{-4}\ s^{-1}$, 104.4 *kJ* mol^{-1} *and* $6.0 \times 10^{14}\ s^{-1}$ *respectively. The value of the rate constant at* $T \to \infty$ *is*

(a) $2.0 \times 10^{18}\ s^{-1}$ (b) $6.0 \times 10^{14}\ s^{-1}$

(c) $3.6 \times 10^{30}\ s^{-1}$ (d) *infinity*

Solution (b) Given, $T_1 = 25°\text{C} = 298$ K, $T_2 = T$ (say)

$$E_a = 104.4\ \text{kJ mol}^{-1} = 104.4 \times 10^3\ \text{J mol}^{-1}$$

$$k_1 = 3 \times 10^{-4}\ \text{s}^{-1}, k_2 = ?$$

From,

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log\frac{k_2}{3 \times 10^{-4}} = \frac{104.4 \times 10^3}{2.303 \times 8.314}\left[\frac{1}{298} - \frac{1}{T}\right]$$

or

$$\log\frac{k_2}{3 \times 10^{-4}} = \frac{104.4 \times 10^3}{2.303 \times 8.314} \times \frac{1}{298} \quad \left[\text{as } T \to \infty, \frac{1}{T} \to 0\right]$$

or

$$\log\frac{k_2}{3 \times 10^{-4}} = 18.297$$

or

$$\frac{k_2}{3 \times 10^{-4}} = 1.98 \times 10^{18}$$

or

$$k_2 = 1.98 \times 10^{18} \times 3 \times 10^{-4}$$

$$= 5.94 \times 10^{14} \approx 6 \times 10^{14}\ \text{s}^{-1}$$

Start **Practice** *for* JEE Main

Round I (Topically Divided Problems)

Rate of Reaction and Factors Affecting it

1. Which of the following statements is correct? **[NCERT Exemplar]**

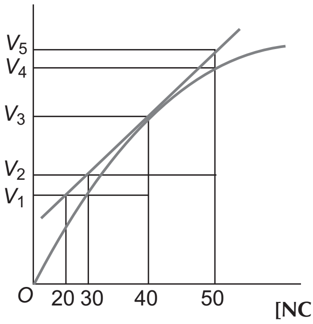
(a) The rate of a reaction decreases with passage of time as the concentration of reactants decreases

(b) The rate of a reaction is same at any time during the reaction

(c) The rate of a reaction is independent of temperature change

(d) The rate of a reaction decreases with increase in concentration of reactant(s)

2. A graph of volume of hydrogen released *vs* time for the reaction between zinc and dil.HCl is given in figure. On the basis of this mark the correct option.



[NCERT Exemplar]

(a) Average rate upto 40s is $\frac{V_3 - V_2}{40}$

(b) Average rate upto 40 seconds is $\frac{V_3 - V_2}{40 - 30}$

(c) Average rate upto 40 seconds is $\frac{V_3}{40}$

(d) Average rate upto 40 seconds is $\frac{V_3 - V_1}{40 - 20}$

3. Consider the graph given in Q. 2. Which of the following options does not show instantaneous rate of reaction at 40th second? **[NCERT Exemplar]**

(a) $\frac{V_5 - V_2}{50 - 30}$ (b) $\frac{V_4 - V_2}{50 - 30}$

(c) $\frac{V_3 - V_2}{40 - 30}$ (d) $\frac{V_3 - V_1}{40 - 20}$

4. In a reaction, $2A \longrightarrow$ products, the concentration of A decreases from 0.5 mol L^{-1} to 0.4 mol L^{-1} in 10 min. The rate during this interval is **[NCERT]**

(a) 0.05 mol L^{-1} min^{-1} (b) 0.42 mol L^{-1} min^{-1}

(c) 0.005 mol L^{-1} min^{-1} (d) 0.5 mol L^{-1} min^{-1}

5. Which of the following expression is correct for the rate of reaction given below? **[NCERT Exemplar]**

$$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(aq) + 3H_2O(l)$$

(a) $\frac{\Delta[Br^-]}{\Delta t} = 5\frac{\Delta[H^+]}{\Delta t}$ (b) $\frac{\Delta[Br^-]}{\Delta t} = \frac{6}{5}\frac{\Delta[H^+]}{\Delta t}$

(c) $\frac{\Delta[Br^-]}{\Delta t} = \frac{5}{6}\frac{\Delta[H^+]}{\Delta t}$ (d) $\frac{\Delta[Br^-]}{\Delta t} = 6\frac{\Delta[H^+]}{\Delta t}$

6. For a gaseous reaction, the units of rate of reaction are

(a) L atm s^{-1} (b) atm s^{-1}

(c) atm mol^{-1} s^{-1} (d) mol s^{-1}

7. Pieces of wood burn faster than a log of wood of the same mass because

(a) surface area of log of wood is larger and needs more time to burn

(b) pieces of wood have large surface area

(c) all pieces of wood catch fire at the same time

(d) block of wood has higher density than pieces of the same wood

8. The rate constant for the reaction,

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

is 3.0×10^{-5} s^{-1}. If the rate is 2.40×10^{-5} then the concentration of N_2O_5 (in mol/L) is

(a) 1.4 (b) 1.2 (c) 0.04 (d) 0.8

9. For a chemical reaction $2X + Y \longrightarrow Z$, the rate of appearance of Z is 0.05 mol L^{-1} min^{-1}. The rate of disappearance of X will be

(a) 0.05 mol L^{-1} h^{-1} (b) 0.05 mol L^{-1} min^{-1}

(c) 0.1 mol L^{-1} min^{-1} (d) 0.25 mol L^{-1} min^{-1}

10. In the reversible reaction

$$2NO_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2O_4$$

the rate of disappearance of NO_2 is equal to

(a) $\frac{2k_1}{k_2}[NO_2]^2$ (b) $2k_1[NO_2]^2 - 2k_2[N_2O_4]$

(c) $2k_2[NO_2]^2 - k_2[N_2O_4]$ (d) $(2k_1 - k_2)[NO_2]$

Molecularity and Rate Law Expression

11. For which type of reaction order and molecularity have the same value? **[NCERT** Exemplar**]**

(a) first order reaction

(b) bimolecular reaction

(c) termolecular reaction

(d) elementary reaction

12. For a single step reaction,

$A + 2B \longrightarrow$ Products, the molecularity is

(a) 0 (b) 1

(c) 2 (d) 3

13. Rate law for the reaction $A + 2B \longrightarrow C$ is found to be

$$\text{Rate} = k[A][B]$$

Concentration of reactant 'B' is doubled, keeping the concentration of 'A' constant, the value of rate constant will be **[NCERT** Exemplar**]**

(a) the same (b) doubled

(c) quadrupled (d) halved

14. The conversion of molecules x to y follows second order kinetics. If concentration of x is increased to three times, the rate of formation of y will **[NCERT]**

(a) increase by three times

(b) decrease by three times

(c) increase by nine times

(d) decrease by nine times

15. The rate of a gaseous reaction is equal to $k[A][B]$. The volume of the reaction vessel containing these gases is reduced by one-fourth of the initial volume. The rate of the reaction would be

(a) $\frac{1}{16}$ (b) $\frac{16}{1}$

(c) $\frac{1}{8}$ (d) $\frac{8}{1}$

16. The hydrolysis of ethyl acetate was carried out separately with 0.05 M HCl and 0.05 M H_2SO_4. The rate constants were found to be (k_1) and (k_2) respectively then

(a) $k_1 < k_2$ (b) $k_1 > k_2$

(c) $k_1 = k_2$ (d) $k_2 = 2k_1$

17. Units of rate constant of first and zero order reactions in terms of molarity M unit are respectively

(a) s^{-1}, M s^{-1} (b) s^{-1}, M

(c) M s^{-1}, s^{-1} (d) M, s^{-1}

18. In the sequence of reaction,

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D$$

$k_3 > k_2 > k_1$ then the rate determining step of the reaction is

(a) $A \longrightarrow B$ (b) $B \longrightarrow C$

(c) $C \longrightarrow D$ (d) $A \longrightarrow D$

19. Given the hypothetical reaction mechanism

$$A \xrightarrow{\text{I}} B \xrightarrow{\text{II}} C \xrightarrow{\text{III}} D \xrightarrow{\text{IV}} E$$

and the data as,

Species formed	Rate of its formation
B	0.002 mol/h, per mole of A
C	0.030 mol/h, per mole of B
D	0.011 mol/h, per mole of C
E	0.042 mol/h, per mole of D

The rate determining step is

(a) step I (b) step II

(c) step III (d) step IV

20. The rate of the reaction,

$$CCl_3CHO + NO \longrightarrow CHCl_3 + NO + CO$$

is equal to rate $k[CCl_3CHO][NO]$. If concentration is expressed in mol/L, the unit of k is

(a) L mol^{-1} s^{-1} (b) mol L^{-1} s^{-1}

(c) L^2 mol^{-2} s^{-1} (d) s^{-1}

Order of Reaction

21. For the reaction $A \longrightarrow B$, the rate expression is $r = k[A]^n$. When the concentration of A is doubled, the rate of reaction is quadrupled. The value of n is

(a) 1 (b) zero

(c) 3 (d) 2

22. Which of the following statements is not correct about order of a reaction? **[NCERT** Exemplar**]**

(a) The order of a reaction can be a fractional number.

(b) Order of a reaction is experimentally determined quantity.

(c) The order of a reaction is always equal to the sum of the stoichiometric coefficients of reactants in the balanced chemical equation for a reaction.
(d) The order of a reaction is the sum of the powers of molar concentration of the reactants in the rate law expression.

23. For a reaction, $A + B \longrightarrow$ product; the rate law is given by, $r = k[A]^{1/2}[B]^2$. What is the order of the reaction? **[NCERT]**
(a) $\frac{2}{3}$ (b) $\frac{5}{2}$
(c) $\frac{1}{2}$ (d) $\frac{3}{2}$

24. If a certain reaction is first order with respect to A, second order with respect to B and zero order with respect to C then what is the order of reaction?
(a) First (b) Second
(c) Third (d) Zero

25. The unit and value of rate constant and that of rate of reaction are same for
(a) zero order (b) first order
(c) second order (d) third order

26. In the reaction $A + B \longrightarrow$ products, if B is taken in excess, then it is an example of
(a) second order reaction
(b) zero order reaction
(c) pseudounimolecular reaction
(d) first order reaction

27. The rate constant for a chemical reaction has unit L mol^{-1} s^{-1}, order of the reaction will be
(a) 0 (b) 1
(c) 2 (d) 3

28. The rate constant of a zero order reaction is 0.2 mol dm^{-3} h^{-1}. If the concentration of the reactant after 30 min is 0.05 mol dm^{-3}, then its initial concentration would be
(a) 0.01 mol dm^{-3} (b) 0.15 mol dm^{-3}
(c) 0.25 mol dm^{-3} (d) 4.00 mol dm^{-3}

29. What is the two third life of a first order reaction having $k = 5.48 \times 10^{-14}$ s^{-1}?
(a) 2.01×10^{13} s (b) 2.01×10^{12} s
(c) 4.02×10^{13} s (d) 4.02×10^{26} s

30. Half-life of a reaction is found to be inversely proportional to the cube of initial concentration. The order of reaction is
(a) 4 (b) 3
(c) 5 (d) 2

31. Radioactive decay is a
(a) first order reaction
(b) zero order reaction
(c) second order reaction
(d) third order reaction

32. The inversion of cane sugar into glucose and fructose according to the equation

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

is an example of
(a) first order reaction (b) third order reaction
(c) second order reaction (d) zero order reaction

33. The reaction $L \longrightarrow M$ is started with 10.0 g of L. After 30 and 90 min, 5.0 g and 1.25 g of L respectively are left. The order of the reaction is
(a) 0 (b) 1
(c) 2 (d) 3

34. The rate law for the reaction

RCl + NaOH $\longrightarrow$ ROH + NaCl is given by

Rate = k [RCl]. The rate of this reaction
(a) is doubled by doubling the concentration of NaOH
(b) is halved by reducing the concentration of RCl by one half
(c) is increased by increasing the temperature of the reaction
(d) in unaffected by change in temperature

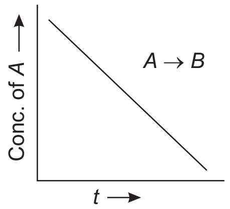
35. Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law, with $t_{1/2} = 3.00$ h. What fraction of sample of sucrose remains after 8 h? **[NCERT]**
(a) 1.023 M (b) 0.8725 M
(c) 0.023 M (d) 0.1576 M

36. The rate constant for a first order reaction is 60 s^{-1}. How much time will it take to reduce the initial concentration of the reactant to its 1/16th value? **[NCERT]**
(a) 0.046 s (b) 0.025 s
(c) 0.098 s (d) 0.060 s

37. The half-life of two samples are 0.1 and 0.8 s. Their respective concentration are 400 and 50 respectively. The order of the reaction is
(a) 0 (b) 2
(c) 1 (d) 4

38. In a second order reaction when the concentrations of both the reactants are equal, the reaction is completed in 500 s. How long will it take for the reaction to go to 60% completion?
(a) 1000 s (b) 300 s
(c) 3000 s (d) 2000 s

39. For a general reaction, $A \longrightarrow B$, plot of concentration of A *vs* time is given in figure.
What are the units of rate constant?



[NCERT Exemplar]

(a) mol L^{-1} s^{-1} (b) mol^{-1} L s^{-1}
(c) s^{-1} (d) mol^{-2} L^2 s^{-1}

40. 1 g of $_{79}Au^{198}$ ($t_{1/2} = 65$ h) gives stable mercury by β-emission. What amount of mercury will left after 260 h?
(a) 0.9375 g (b) 0.3758 g
(c) 0.7586 g (d) 0.9000 g

41. Compounds 'A' and 'B' react according to the following chemical equation.

$$A(g) + 2B(g) \longrightarrow 2C(g)$$

Concentration of either 'A' or 'B' were changed keeping the concentrations of one of the reactants constant and rates were measured as a function of initial concentration. Following results were obtained.

Experiment	Initial concentration of [A]/mol L^{-1}	Initial concentration of [B]/mol L^{-1}	Initial rate of formation of [C]/mol L^{-1} s^{-1}
1.	0.30	0.30	0.10
2.	0.30	0.60	0.40
3.	0.60	0.30	0.20

Choose the correct option for the rate equations for this reaction. **[NCERT Exemplar]**
(a) Rate = $k[A]^2[B]$ (b) Rate = $k[A][B]^2$
(c) Rate = $k[A][B]$ (d) Rate = $k[A]^2[B]^0$

42. A first order reaction is 50% completed in 1.26×10^{14} s. How much time would it take for 100% completion? **[NCERT Exemplar]**
(a) 1.26×10^{15} s (b) 2.52×10^{14} s
(c) 2.52×10^{28} s (d) Infinite

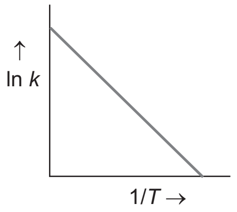
Effect of Temperature on Rate of Reaction

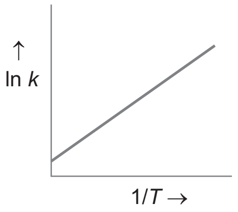
43. Consider the Arrhenius equation given below and mark the correct option. **[NCERT Exemplar]**

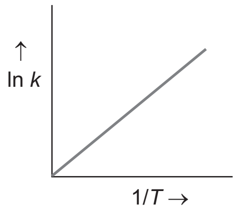
$$k = Ae^{-E_a/RT}$$

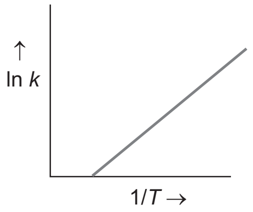
(a) Rate constant increases exponentially with increasing activation energy and decreasing temperature
(b) Rate constant decreases exponentially with increasing activation energy and decreasing temperature
(c) Rate constant increases exponentially with decreasing activation energy and decreasing temperature
(d) Rate constant increases exponentially with decreasing activation energy and increasing temperature

44. According to Arrhenius equation rate constant k is equal to $Ae^{-E_a/RT}$. Which of the following options represents the graph of ln k *vs* $\frac{1}{T}$? **[NCERT Exemplar]**

(a)


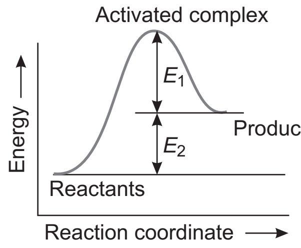
(b)


(c)


(d)


45. When a graph is plotted between ln k and $1/T$ for a first order reaction, a straight line is obtained. The slope of the line is equal to
(a) $-\frac{E_a}{2.303}$ (b) $-\frac{E_a}{2.303R}$
(c) $-\frac{2.303}{E_aR}$ (d) $-\frac{E_a}{R}$

46. Consider figure and mark the correct option.



[NCERT Exemplar]

(a) Activation energy of forward reaction is $E_1 + E_2$ and product is less stable than reactant.

(b) Activation energy of forward reaction is $E_1 + E_2$ and product is more stable than reactant

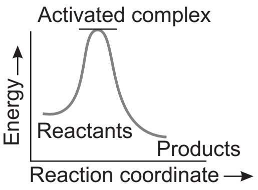
(c) Activation energy of both forward and backward reaction is $E_1 + E_2$ and reactant is more stable than product.

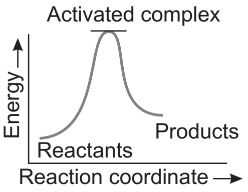
(d) Activation energy of backward reaction is E_1 and product is more stable than reactant

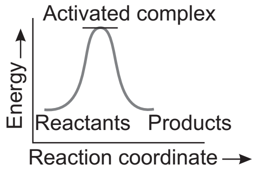
47. An endothermic reaction $A \longrightarrow B$ has an activation energy of 15 kcal/mol and the energy of reaction is 5 kcal/mol. The activation energy for the reaction $B \longrightarrow A$ is

(a) 20 kcal/mol (b) 15 kcal/mol
(c) 10 kcal/mol (d) zero

48. Which of the following graphs represents exothermic reaction?

(i)


(ii)


(iii)


(a) (i) only (b) (ii) only
(c) (iii) only (d) (i) and (ii)

49. Arrhenius equation may not be represented as

(a) $\ln \frac{A}{k} = \frac{E_a}{RT}$

(b) $\frac{d \ln k}{dT} = \frac{E}{RT^2}$

(c) $\log A = \log k + \frac{E_a}{2.303\, RT}$

(d) $\log \left[-\frac{E_a}{RT} \right] = \frac{k}{A}$

50. The rate constant (k') of one of the reaction is found to be double that of the rate constant (k'') of another reaction. Then the relationship between the corresponding activation energies of the two reactions $(E_a'$ and $E_a'')$ can be represented as

(a) $E_a' > E_a''$ (b) $E_a' = 4E''$
(c) $E_1' = E_a''$ (d) $E_a' < E_a''$

51. Which of the following statements is incorrect about the collision theory of chemical reaction?

[NCERT Exemplar]

(a) It considers reacting molecules or atoms to be hard spheres and ignores their structural features

(b) Number of effective collisions determines the rate of reaction

(c) Collision of atoms or molecules possessing sufficient threshold energy results into the product formation

(d) Molecules should collide with sufficient threshold energy and proper orientation for the collision to be effective

52. For the decomposition of N_2O_5 at a particular temperature, according to the equations

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$
$$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2} O_2$$

The activation energies are E_1 and E_2 respectively then

(a) $E_1 > E_2$ (b) $E_1 < E_2$
(c) $E_1 = 2E_2$ (d) $E_1 = E_2$

53. If the reaction rate at a given temperature becomes slower then

(a) the free energy of activation is higher

(b) the free energy of activation is lower

(c) the entropy changes

(d) the initial concentration of the reactants remains constant

54. In Arrhenius equation, $k = Ae^{-E_a/RT}$; A may be called the rate constant at

(a) very low temperature

(b) zero activation energy

(c) the boiling temperature of reaction mixture

(d) All of the above

55. The rate of a reaction quadruples when the temperature changes from 293 K to 313 K. Calculate the energy of activation of the reaction assuming that it does not change with temperature. **[NCERT]**

(a) 48.625 kJ mol^{-1} (b) 654.35 kJ mol^{-1}
(c) 354.20 kJ mol^{-1} (d) 52.863 kJ mol^{-1}

56. The decomposition of A into product has values of k as $4.5 \times 10^3\ s^{-1}$ at 10°C and energy of activation 60 kJ mol^{-1}. At what temperature would k be $1.5 \times 10^4\ s^{-1}$. **[NCERT]**

(a) 273.15 K (b) 24.19°C
(c) 280.39 K (d) 45.29°C

57. The rate constant of the chemical reaction doubled for an increase of 10 K in absolute temperature from 295 K. Calculate E_a. **[NCERT]**

(a) 51.8 kJ mol^{-1} (b) 82.1 kJ mol^{-1}
(c) 23.8 kJ mol^{-1} (d) 62.1 kJ mol^{-1}

58. The activation energy for the given reaction $2HI(g) \longrightarrow H_2(g) + I_2(g)$ is $209.5 \text{ kJ mol}^{-1}$ at 581 K. Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy. **[NCERT]**

(a) 1.82×10^{-18}

(b) 1.47×10^{-19}

(c) 2.67×10^{-16}

(d) 3.89×10^{-19}

59. The rate constant of a reaction increases by 5% when its temperature is raised from 27°C to 28°C. The activation energy of the reaction is

(a) 36.6 kJ/mol (b) 16.6 kJ/mol

(c) 46.6 kJ/mol (d) 26.6 kJ/mol

60. The activation energy of a reaction is 9 kcal/mol. The increase in the rate constant when its temperature is raised from 295 to 300 K is approximately

(a) 10% (b) 50%

(c) 100% (d) 28%

Round II (Mixed Bag)

Only One Correct Option

1. The rate of a reaction is expressed in different ways as follows

$$+\frac{1}{2}\frac{d[C]}{dt} = -\frac{1}{5}\frac{d[D]}{dt} = +\frac{1}{3}\frac{d[A]}{dt} = -\frac{d[B]}{dt}$$

The reaction is

(a) $4A + B \longrightarrow 2C + 3D$

(b) $B + 5D \longrightarrow 3A + 2C$

(c) $4A + 2B \longrightarrow 2C + 3D$

(d) $B + \frac{1}{2}D \longrightarrow 4A + 2C$

2. Which of the following statements are incorrect?

(a) Rate of the reaction involving conversion of *ortho* hydrogen to *para* hydrogen $= -\frac{d[H_2]}{dt} = k[H_2]^{3/2}$

(b) Rate of the reaction involving the thermal decomposition of acetaldehyde $= k[CH_3CHO]^{1/2}$

(c) In the formation of phosgene from CO and Cl_2, the rate of the reaction $= k[CO][Cl_2]^{1/2}$

(d) In the decomposition of H_2O_2, the rate of reaction $= k[H_2O_2]$

3. In a first order reaction the concentration of reactant decreases from 800 mol/dm^3 to 50 mol/dm^3 in 2×10^4 s. The rate constant of the reaction in s^{-1} is

(a) 2×10^4 (b) 3.45×10^{-5}

(c) 1.386×10^{-4} (d) 2×10^{-4}

4. The chemical reaction $2O_3 \longrightarrow 3O_2$ proceeds as follows

$$O_3 \rightleftharpoons O_2 + O \text{ (fast)}$$
$$O + O_3 \longrightarrow 2O_2 \text{ (slow)}$$

The rate law expression should be

(a) $r = k[O_3]^2$ (b) $r = k[O_3]^2[O_2]^{-1}$

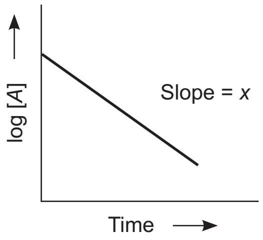
(c) $r = k[O_3][O_2]$ (d) unpredictable

5. The rate of a chemical reaction doubles for every 10°C rise in temperature. If the temperature is increased by 60°C, the rate of reaction increases by

(a) 20 times (d) 32 times

(c) 64 times (d) 128 times

6. For a first order reaction, the graph $\log[A]$ *vs* t is given below



x is equal to

(a) $\frac{0.693}{k}$ (b) $\frac{k}{2.303}$

(c) $-\frac{k}{2.303}$ (d) $\log[A]_0$

7. Two first order reactions have half-lives in the ratio 8 : 1. Calculate the ratio of time intervals $t_1 : t_2$. The time t_1 and t_2 are the time period for (1/4)th and (3/4)th completion.

(a) 1 : 0.602 (b) 2 : 301

(c) 0.256 : 0.603 (d) 0.2 : 0.301

8. The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308 K. If the value of A is $4 \times 10^{10} \text{ s}^{-1}$. Calculate k at 318 K. **[NCERT]**

(a) $2.89 \times 10^{-2} \text{ s}^{-1}$

(b) $3.26 \times 10^{-2} \text{ s}^{-1}$

(c) $1.03 \times 10^{-2} \text{ s}^{-1}$

(d) $0.03 \times 10^{-2} \text{ s}^{-1}$

9. The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume.

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

Experiment	Time/s^{-1}	Total pressure/atm
1	0	0.5
2	100	0.6

Calculate the rate of the reaction when total pressure is 0.65 atm. **[NCERT Exemplar]**

(a) 2.84×10^{-7} atm s^{-1} (b) 7.80×10^{-4} atm s^{-1}

(c) 4.42×10^{-7} atm s^{-1} (d) 5.62×10^{-4} atm s^{-1}

10. During nuclear explosion one of the products is ^{90}Sr with half-life of 28.1 yr. If 1 μ g of ^{90}Sr was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 60 yr if it is not lost metabolically? **[NCERT]**

(a) 0.184 μg (b) 0.025 μg

(c) 0.262 μg (d) 0.228 μg

11. For the decomposition of azoisopropane to hexane and nitrogen at 543 K, the following data are obtained. Calculate the rate constant. **[NCERT]**

t (s)	p (mm of Hg)
0	35.0
360	54.0
720	63.0

(a) 2.21×10^{-3} s^{-1} (b) 3.48×10^{-3} s^{-1}

(c) 1.26×10^{-3} s^{-1} (d) 8.46×10^{-3} s^{-1}

12. The rate constant of a reaction is given by $k = 2.1\times10^{10}\exp(-2700RT)$.

It means that

(a) $\log k$ *vs* $1/T$ will be a curved line with slope $= -\dfrac{2700}{2.303R}$

(b) $\log k$ vs $1/T$ will be a straight line with intercept on $\log k$ axis $= \log 2.1\times10^{10}$

(c) the number of effective collisions are 2.1×10^{10} cm^{-3} s^{-1}

(d) half-life of the reaction increases with increase of temperature

13. Which of the following statements are correct?

1. Order of a reaction can be known from experimental result and not from the stoichiometry of reaction.
2. Overall molecularity of a reaction may be determined in a manner similar to overall order of reaction.
3. Overall order of reaction,
   $A^m + B^n \longrightarrow AB_x$ is $(m+n)$
4. Molecularity of a reaction refers to
   (i) molecularity of each of the elementary steps (slow steps) in a multistep reaction.
   (ii) molecularity of that particular step in a single step reaction.

Select the correct answer by using the codes given below.

(a) 1, 3 and 4 (b) 1, 2 and 3

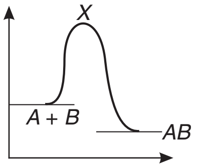
(c) 2, 3 and 4 (d) 1, 2 and 4

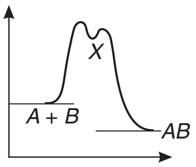
14. An exothermic chemical reaction occurs in two steps as follows

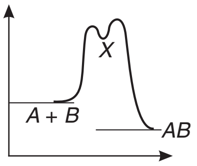
(I) $A + B \longrightarrow X$ (fast)

(II) $X \longrightarrow AB$ (slow)

The progress of the reaction can be best represented by

(a) 

(b) 

(c) 

(d) All are correct

15. The decomposition of hydrocarbon follows the equation $k = (4.5\times10^{11}\ s^{-1})\,e^{-28000}$ K/T. Calculate the activation energy E_a. **[NCERT]**

(a) 232.79 kJ mol^{-1} (b) 425.25 kJ mol^{-1}

(c) 300 kJ mol^{-1} (d) 885.2 kJ mol^{-1}

More than One Correct Option

16. In any unimolecular reaction **[NCERT Exemplar]**

(a) only one reacting species is involved in the rate determining step.

(b) the order and the molecularity of slowest step are equal to one.

(c) the molecularity of the reaction is one and order is zero.

(d) both molecularity and order of the reaction are one.

17. Rate law cannot be determined from balanced chemical equation if **[NCERT Exemplar]**

(a) reverse reaction is involved.

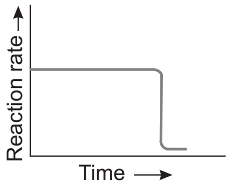
(b) it is an elementary reaction.

(c) it is a sequence of elementary reactions.

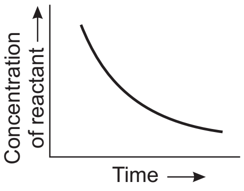
(d) any of the reactants is in excess.

18. Which of the following graphs is correct for a zero order reaction?

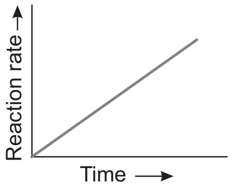
(a)



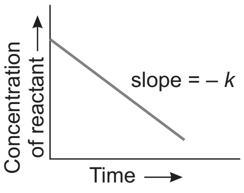
(b)



(c)



(d)



19. For a reaction $2A + B \longrightarrow C$ with the rate law $\frac{d[C]}{dt} = k[A][B]^{-1}$ and started with A and B in stoichiometric proportion which is/are true?

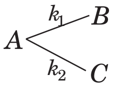
(a) $[C] = 2\,kt$

(b) $[C] = kt$

(c) unit of k is mol L^{-1} s^{-1}

(d) $[A][B]$ and $[C]$ all will be linear funtions of time

20. Consider the following case of completing first order reactions



After the start of the reaction at $t = 0$ with only A, the $[B]$ is equal to the $[C]$ at all times. The time in which all three concentrations will be equal is given by

(a) $t = \frac{1}{3k_1}\ln 2$ (b) $t = \frac{1}{2k_1}\ln 3$

(c) $t = \frac{1}{3k_2}\ln 2$ (d) $t = \frac{1}{2k_2}\ln 3$

Assertion and Reason

Directions (Q. Nos. 21 to 25) *Each of these questions contains two statements : Statement* I (*Assertion*) *and Statement* II (*Reason*). *Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes* (*a*), (*b*), (*c*), (*d*) *given below :*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I.

(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.

(c) Statement I is true; Statement II is false.

(d) Statement I is false; Statement II is true.

21. Statement I Order and molecularity are same.

Statement II Order is determined experimentally and molecularity is the sum of the stoichiometric coefficient of rate determining elementary step. **[NCERT Exemplar]**

22. Statement I Rate constants determined from Arrhenius equation are fairly accurate for simple as well as complex molecules.

Statement II Reactant molecules undergo chemical change irrespective of their orientation during collision. **[NCERT Exemplar]**

23. Statement I The numerical value of specific rate constant is independent of the concentration of any species present in the reaction mixture.

Statement II When a reaction is carried out in aqueous solution and some alcohol is added to the reaction mixture, the rate of reaction will not change.

24. Statement I In the reaction $I_2 + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I^-$, the two $S_2O_3^{2-}$ ions are used for every I_2.

Statement II The rate of disappearance of I_2 is one half the rate of disappearance of $S_2O_3^{2-}$.

25. Statement I Lower the activation energy, faster is the reaction.

Statement II If the activation energy of reaction is zero, temperature will have no effect on the rate constant.

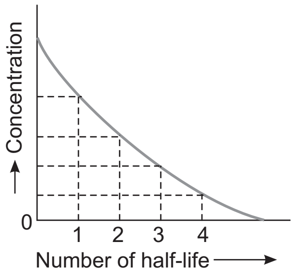
Comprehension Based Questions

Directions (Q. Nos. 26 to 28) $t_{1/2}$ of reaction is the time required for the concentration of reactant to decrease by half, *i.e.*,

$$[A]_t = \frac{1}{2}[A].$$

$$t_{1/2} = 0.693 / k$$

that is $t_{1/2}$ is independent of initial concentration. Figure shows that typical variation of concentration of reactant exhibiting first order kinetics. It may be noted that though the major portion of the first order kinetics may be over in a finite time, but the reaction will never cease as the concentration of reactant will be zero only at infinite time.



26. 75% of a reaction of the first order was completed in 32 min. When was it half completed?

(a) 8 min (b) 16 min
(c) 64 min (d) 48 min

27. The half-life period for a first order reaction is 693 s. The rate constant of this reaction would be

(a) $1 \times 10^{-2}\ s^{-1}$ (b) $1 \times 10^{-3}\ s^{-1}$
(c) $0.1\ s^{-1}$ (d) $-1 \times 10^{-4}\ s^{-1}$

28. The rate of a first order reaction is 1.5×10^{-2} mol L^{-1} min^{-1} at 0.5 M concentration of the reactant. The half-life of the reaction is

(a) 13.6 min (b) 42.5 min
(c) 23.1 min (d) 32.5 min

Directions (Q. Nos. 29 to 31) Note all chemical reactions proceed to a stage at which the concentrations of the reactants become vanishingly small. Here we consider the kinetics of such reactions. Let a reaction be represented in general terms by the scheme

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

where k_1 and k_2 represent the rate constants for the forwards and reverse reactions respectively. The equilibrium constant for this reaction may be written as

$$k = [B]_\infty / [A]_\infty = k_1 / k_2$$

The initial concentration of species A is $[A]_0$ and that of B is $[B]_0$. After a time t, let the concentration of species A be $[A]_t$ and that of B be $[B]_t$. The total rate of change of $[A]_t$ is given by

$$d[A]_{t/dt} = -k_1[A]_t + k_2[B]_t$$

$$d[A]_{t/dt} = -k_1[A]_t + k_2([A]_0 - [A]_t)$$

$$d[A]_{t/dt} = -(k_1 + k_2)\left([A]_t - \frac{k_2}{k_1 + k_2}[A]_0\right)$$

29. What is the k_c of the reaction $2C \rightleftharpoons 2A$ if $[C] = 0.4$ and $[A] = 0.6$?

(a) 9/4 (b) 2/3
(c) 4/3 (d) 5/2

30. At what time is the rate of change of concentration of A equal to rate of change of concentration of C in magnitude?

(a) $t = 10$ only (b) $t = 0$ only
(c) $t \geq t_{\text{equilibrium}}$ (d) All times

31. Which of the following relation is correct for k_f and k_b in an equilibrium process that contains equal moles of reactants and products?

(a) $k_f < k_b$ (b) $k_f > k_b$
(c) $k_f = k_b$ (d) Not predictable

Previous Years' Questions

32. The rate of a chemical reaction doubles for every 10°C rise of temperature. If the temperature is raised by 50°C, the rate of the reaction increases by about **[AIEEE 2011]**

(a) 10 times (b) 24 times
(c) 32 times (d) 64 times

33. A reactant (A) forms two products

$$A \xrightarrow{k_1} B, \text{Activation energy } E_{a_1}$$

$$A \xrightarrow{k_2} C, \text{ Activation energy } E_{a_2}$$

If $E_{a_2} = 2\,E_{a_1}$, then k_1 and k_2 are related as **[AIEEE 2011]**

(a) $k_1 = 2k_2e^{E_{a2}/RT}$ (b) $k_1 = k_2e^{E_{a1}/RT}$
(c) $k_2 = k_1e^{E_{a2}/RT}$ (d) $k_1 = A\,k_2e^{E_{a1}/RT}$

34. The time for half-life period of a certain reaction, $A \rightarrow$ products is 1 h. When the initial concentration of the reactant 'A' is 2.0 mol L^{-1}, how much time does it take for its concentration to come from 0.50 to 0.25 mol L^{-1}, if it is a zero order reaction? **[AIEEE 2010]**

(a) 4 h (b) 0.5 h
(c) 0.25 h (d) 1 h

35. Consider the reaction,

$$Cl_2(aq) + H_2S(aq) \longrightarrow S(s) + 2H^+(aq) + 2Cl^-(aq)$$

The rate equation for this reaction is,

$$\text{rate} = k[Cl_2][H_2S]$$

Which of these mechanisms is/are consistent with this rate equation? **[AIEEE 2010]**

(A) $Cl_2 + H_2S \longrightarrow H^+ + Cl^- + Cl^+ + HS^-$ (slow)
$Cl^+ + HS^- \longrightarrow H^+ + Cl^- + S$ (fast)
(B) $H_2S \rightleftharpoons H^+ + HS^-$ (fast equilibrium)
$Cl_2 + HS^- \longrightarrow 2\ Cl^- + H^+ + S$ (slow)

(a) (B) only (b) Both A and B
(c) Neither A nor B (d) A only

36. The half-life period of a first order chemical reaction is 6.93 min. The time required for the completion of 99% of the chemical reaction will be (log 2 = 0.301)

(a) 230.3 min (b) 23.03 min
(c) 46.06 min (d) 460.6 min

37. For a reaction $\frac{1}{2}A \longrightarrow 2B$, rate of disappearance of 'A' is related to the rate of appearance of 'B' by the expression **[AIEEE 2008]**

(a) $-\frac{d[A]}{dt}=\frac{1}{2}\frac{d[B]}{dt}$ (b) $-\frac{d[A]}{dt}=\frac{1}{4}\frac{d[B]}{dt}$

(c) $-\frac{d[A]}{dt}=\frac{d[B]}{dt}$ (d) $-\frac{d[A]}{dt}=4\frac{d[B]}{dt}$

38. Consider the reaction, $2A + B \rightarrow$ products. When concentration of B alone was doubled, the half-life did not change. When the concentration of A alone was doubled, the rate increased by two times. The unit of rate constant for this reaction is **[AIEEE 2007]**

(a) L mol^{-1} s^{-1} (b) no unit

(c) mol L^{-1} s^{-1} (d) s^{-1}

39. The energies of activation for forward and reverse reactions for $A_2 + B_2 \rightleftharpoons 2AB$ are 180 kJ mol^{-1} and 200 kJ mol^{-1} respectively. The presence of a catalyst lowers the activation energy of both (forward and reverse) reactions by 100 kJ mol^{-1}. The enthalpy change of the reaction $(A_2 + B_2 \rightarrow 2AB)$ in the presence of catalyst will be (in kJ mol^{-1}) **[AIEEE 2007]**

(a) 300 (b) 120

(c) 280 (d) 20

40. The following mechanism has been proposed for the reaction of NO with Br_2 to form NOBr

$$NO(g) + Br_2(g) \rightleftharpoons NOBr_2(g)$$
$$NOBr_2(g) + NO(g) \longrightarrow 2NOBr(g)$$

If the second step is the rate determining step, the order of the reaction with respect to NO (g) is **[AIEEE 2006]**

(a) 1 (b) 0

(c) 3 (d) 2

41. Rate of a reaction can be expressed by Arrhenius equation as

$$k = Ae^{-E/RT}$$

In this equation, E represents **[AIEEE 2006]**

(a) the energy above which all the colliding molecules will react

(b) the energy below which colliding molecules will not react

(c) the total energy of the reacting molecules at a temperature, T

(d) the fraction of molecules with energy greater than the activation energy of the reaction

42. A reaction involving two different reactants can never be **[AIEEE 2005]**

(a) bimolecular reaction

(b) second order reaction

(c) first order reaction

(d) unimolecular reaction

43. Consider an endothermic reaction $X \rightarrow Y$ with the activation energies E_b and E_f for the backward and forward reactions respectively. In general **[AIEEE 2005]**

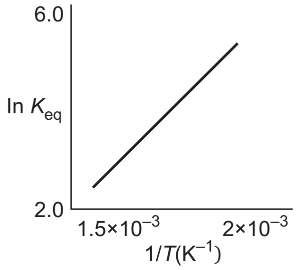
(a) there is no definite relation between E_b and E_f

(b) $E_b = E_f$

(c) $E_b > E_f$

(d) $E_b < E_f$

44. A schematic plot of $\ln K_{eq}$ *versus* inverse of temperature for a reaction is shown below



The reaction must be **[AIEEE 2005]**

(a) highly spontaneous at ordinary temperature

(b) one with negligible enthalpy change

(c) endothermic

(d) exothermic

45. The rate equation for the reaction $2A + B \rightarrow C$ is found to be rate $= k[A][B]$

The correct statement in relation to this reaction is that the **[AIEEE 2004]**

(a) unit of k must be s^{-1}

(b) $t_{1/2}$ is a constant

(c) rate of formation of C is twice the rate of disappearance of A

(d) value of k is independent of the initial concentrations of A and B

46. In a first order reaction, the concentration of the reactant, decreases from 0.8 M to 0.4 M in 15 min. The time taken for the concentration to change from 0.1 M to 0.025 M is **[AIEEE 2004]**

(a) 30 min (b) 15 min

(c) 7.5 min (d) 60 min

47. For the reaction system :

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

volume is suddenly reduced to half its value by increasing the pressure on it. If the reaction is of first order with respect to O_2 and second order with respect to NO; the rate of reaction will **[AIEEE 2003]**

(a) diminish to one-fourth of its initial value

(b) diminish to one-eight of its initial value

(c) increase to eight times of its initial value

(d) increase to four times of its initial value

48. For the reaction : $H_2 + I_2 \longrightarrow 2HI$, the differential rate law is **[AIEEE 2002]**

(a) $-\frac{d[H_2]}{dt} = -\frac{d[I_2]}{dt} = 2\frac{d[HI]}{dt}$

(b) $-2\frac{d[H_2]}{dt} = -2\frac{d[I_2]}{dt} = \frac{d[HI]}{dt}$

(c) $-\frac{d[H_2]}{dt} = -\frac{d[I_2]}{dt} = \frac{d[HI]}{dt}$

(d) $-\frac{d[H_2]}{2dt} = -\frac{d[I_2]}{2dt} = \frac{d[HI]}{dt}$

49. Rate constant, k of the first order reaction when initial concentration (C_0) and concentration at time t, (C_t) is given by the equation

$$kt = \log C_0 - \log C_t$$

Graph is a straight line if we plot **[AIEEE 2002]**

(a) t *vs* $\log C_0$

(b) t *vs* $\log C_t$

(c) t^{-1} *vs* $\log C_t$

(d) $\log C_0$ *vs* $\log C_t$

Answers

Round I

1. (a)	**2.** (c)	**3.** (b)	**4.** (c)	**5.** (c)	**6.** (b)	**7.** (b)	**8.** (d)	**9.** (c)	**10.** (b)
11. (d)	**12.** (d)	**13.** (a)	**14.** (c)	**15.** (b)	**16.** (a)	**17.** (a)	**18.** (a)	**19.** (a)	**20.** (a)
21. (d)	**22.** (c)	**23.** (b)	**24.** (c)	**25.** (a)	**26.** (c)	**27.** (c)	**28.** (b)	**29.** (a)	**30.** (a)
31. (a)	**32.** (a)	**33.** (b)	**34.** (b)	**35.** (d)	**36.** (a)	**37.** (b)	**38.** (c)	**39.** (a)	**40.** (a)
41. (b)	**42.** (d)	**43.** (d)	**44.** (a)	**45.** (d)	**46.** (a)	**47.** (c)	**48.** (a)	**49.** (d)	**50.** (d)
51. (c)	**52.** (d)	**53.** (a)	**54.** (b)	**55.** (d)	**56.** (b)	**57.** (a)	**58.** (b)	**59.** (a)	**60.** (d)

Round II

1. (b)	**2.** (b)	**3.** (c)	**4.** (b)	**5.** (c)	**6.** (c)	**7.** (a)	**8.** (c)	**9.** (b)	**10.** (d)
11. (a)	**12.** (b)	**13.** (d)	**14.** (c)	**15.** (a)	**16.** (a,b)	**17.** (a,c,d)	**18.** (a,d)	**19.** (a,c,d)	**20.** (b,d)
21. (d)	**22.** (c)	**23.** (c)	**24.** (b)	**25.** (b)	**26.** (b)	**27.** (b)	**28.** (c)	**29.** (a)	**30.** (d)
31. (d)	**32.** (c)	**33.** (b)	**34.** (c)	**35.** (d)	**36.** (c)	**37.** (b)	**38.** (a)	**39.** (d)	**40.** (d)
41. (b)	**42.** (d)	**43.** (d)	**44.** (d)	**45.** (d)	**46.** (a)	**47.** (c)	**48.** (b)	**49.** (b)	

the Guidance

Round I

1. Rate of reaction $= \frac{-\Delta[R]}{\Delta t}$

Where negative sign shows that rate of reaction decreases as concentration of reactants decreases.

2. Average rate $= \frac{\Delta R}{\Delta t} = \frac{V_3}{40}$

3. Instantaneous speed $= \frac{x_2 - x_1}{t_2 - t_1}$

$\therefore$ Instantaneous speed $= \frac{V_5 - V_2}{50 - 30}$

$$= \frac{V_3 - V_2}{40 - 30}$$

$$= \frac{V_3 - V_1}{40 - 20}$$

$$= \frac{V_4 - V_2}{45 - 30}$$

4. Rate of reaction = Rate of disappearance of A

$$= -\frac{1}{2}\frac{\Delta[A]}{\Delta t} = -\frac{1}{2}\frac{(0.4 - 0.5)\ \text{mol L}^{-1}}{10\ \text{min}}$$

$$= 0.005\ \text{mol L}^{-1}\ \text{min}^{-1}$$

5.
$$\text{Rate} = -\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = -\frac{1}{6}\frac{\Delta[H^+]}{\Delta t}$$

or
$$\frac{\Delta[Br^-]}{\Delta t} = +\frac{5}{6}\frac{\Delta[H^+]}{\Delta t}$$

8. For a first order reaction,

$$\text{rate} = k[\text{reactant}]$$

$$[\text{reactant}] = \frac{\text{rate}}{k}$$

$$= \frac{2.40 \times 10^{-5}}{3.0 \times 10^{-5}} = 0.8$$

9. For the reaction,

$$2X + Y \longrightarrow Z$$

$$\text{Rate} = -\frac{1}{2}\frac{d[X]}{dt} = \frac{d[Z]}{dt}$$

$$= 0.05 \text{ mol L}^{-1} \text{ min}^{-1}$$

$$-\frac{1}{2}\frac{d[X]}{dt} = 0.05$$

$$-\frac{d[X]}{dt} = 2 \times 0.05$$

$$= 0.1 \text{ mol L}^{-1} \text{ min}^{-1}$$

10.

$$2NO_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2O_4$$

$$\text{Rate} = -\frac{1}{2}\frac{d[NO_2]}{dt}$$

$$= k_1[NO_2]^2 - k_2[N_2O_4]$$

$\therefore$ Rate of disappearance of NO_2

i.e., $$-\frac{d[NO_2]}{dt} = 2k_1[NO_2]^2 - 2k_2[N_2O_4]$$

11. If the reaction is an elementary reaction,

order = molecularity.

13. Value of rate constant remains unaffected from change in concentration.

14. For second order kinetics, rate $= k\,[\text{reactant}]^2$, So make two equation first by taking initial rate and concentration, second by taking tripled concentration and unknown rate (r'). Compare them to find a relation between r and r'.

For the reaction $x \longrightarrow y$

$$\text{Reaction rate } (r) = k\,[x]^2 \qquad \ldots\text{(i)}$$

If the concentration of x is increased three times, then

$$\text{Reaction rate } (r') = k[3x]^2 = k \times [9x^2] \qquad \ldots\text{(ii)}$$

Dividing Eq. (ii) by Eq. (i);

$$\frac{r'}{r} = \frac{k \times [9x^2]}{k \times [x^2]} = 9$$

It means that the rate of formation of y will increase by **nine times**.

15. Rate $(r) = k[A][B] = kab$

When volume is reduced by one fourth then concentration becomes 4 times.

Hence, $$r' = k(4a)(4b)$$

$$= 16kab$$

$\therefore$ $$r' = 16r$$

16. In the presence of acid, hydrolysis of ethyl acetate is a pseudo-unimolecular reaction but the actual value of k depends upon the concentration of H^+ ion. As H_2SO_4 is stronger acid than HCl and moreover H^+ ions produced from 0.05 M H_2SO_4 is double than 0.05 M HCl therefore, $k_1 < k_2$.

17. For nth order reaction

$$k = (\text{mol L}^{-1})^{1-n} \text{ s}^{-1}$$

For first order reaction

Unit of $k = \text{s}^{-1}$

For zero order reaction

Unit of $k = \text{mol L}^{-1} \text{ s}^{-1} = \text{M s}^{-1}$

18. $A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D$

$\because$ $$k_3 > k_2 > k_1$$

As k_1 is slowest hence $A \longrightarrow B$ is the rate determining step of the reaction.

19. The slowest step is the rate determining step. Formation of B (*i.e.,* step I) is the slowest step, therefore, step I is the rate determining step.

20. For the reaction:,

$$CCl_3CHO + NO \longrightarrow CHCl_3 + NO + CO$$

$$\text{Rate} = \frac{dx}{dt} = k[CCl_3CHO][NO]$$

$$k = \frac{dx}{dt \times [CCl_3CHO][NO]}$$

$$= \frac{\text{mol / L}}{\text{s} \times \text{mol / L} \times \text{mol / L}}$$

$$k = \text{L mol}^{-1} \text{ s}^{-1}$$

21. Let $$r = k[A]^n \qquad \ldots\text{(i)}$$

When concentration is doubled then

$$4r = k(2A)^n \qquad \ldots\text{(ii)}$$

Divide Eq. (ii) by (i)

$$4 = 2^n$$

$\therefore$ $$n = 2$$

22. Order of reaction may or may not equal to the sum of stoichiometric coefficient of reactants in a balanced chemical equation.

23. Order = Sum of powers of the concentration of reactants.

$$\text{Order of reaction} = \frac{1}{2} + 2 = \frac{5}{2}$$

$$\text{Order} = \frac{5}{2}$$

24. Rate law $\frac{dx}{dt} = k[A]^1[B]^2[C]^0 = k[A]^1[B]^2$

Hence, order of reaction $= 1 + 2 = 3$

25. For zero order reaction, for example,

$$A \longrightarrow B$$

$$\frac{-d\,[A]}{dt} = k[A]^0$$

$$\frac{-d\,[A]}{dt} = k$$

27. Unit of rate constant $= \dfrac{\text{time}^{-1}}{\text{concentration}^{(n-1)}}$

where, n = order of reaction

Given, unit of rate constant $=$ L mol^{-1}s^{-1}

$$\therefore \quad \text{L mol}^{-1}\text{s}^{-1} = \frac{(\text{s})^{-1}}{(\text{L mol}^{-1})^{n-1}} = \frac{(\text{s})^{-1}}{(\text{L mol}^{-1})^{1-n}}$$

$$= \text{s}^{-1}(\text{L mol}^{-1})^{n-1}$$

$$\text{or} \qquad 1 = n - 1 \quad \text{or} \quad n = 2$$

$\therefore$ Order of reaction $= 2$

28. For zero order reaction,

$$x = kt$$

$$= 0.2 \text{ mol dm}^{-3}\text{ h}^{-1} \times \frac{30}{60}\text{ h}$$

$$= 0.1 \text{ mol dm}^{-3}$$

Now, concentration $=$ 0.05 mol dm^{-3}

Hence, initial concentration $=$ 0.1 $+$ 0.05 $=$ 0.15 mol dm^{-3}

29. For 2/3 of a reaction

$$[A]_0 = a, \qquad [A] = a - \frac{2}{3}a = \frac{a}{3}$$

$$\because \qquad t_{2/3} = \frac{2.303}{k}\log\frac{[A]_0}{[A]}$$

$$= \frac{2.303}{5.48 \times 10^{-14}}\log\frac{a}{a/3}$$

$$= \frac{2.303}{5.48 \times 10^{-14}}\log 3$$

$$t_{2/3} = 2.01 \times 10^{13}\text{ s}$$

30.
$$t_{1/2} \propto \frac{1}{a^{n-1}}$$

When $\qquad n = 4$

$$t_{1/2} \propto \frac{1}{a^3}$$

Hence, order of reaction $= 4$

34. $R\text{Cl} + \text{NaOH} \longrightarrow R\text{OH} + \text{NaCl}$

$$\text{Rate} = k[R\text{Cl}]$$

For this reaction, rate of reaction depends upon the concentration of RCl.

It means, the rate of reaction is halved by reducing the concentration of RCl by one half.

35. For first order reactions,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{(3.0\text{ h})}$$

$$t = \frac{2.303}{k}\log\frac{[A]_0}{[A]}$$

$$\text{or} \qquad \log\frac{[A]_0}{[A]} = \frac{k \times t}{2.303}$$

$$\log\frac{[A]_0}{[A]} = \frac{0.693}{3\text{ h}} \times \frac{(8\text{ h})}{2.303} = 0.8024$$

$$\frac{[A]_0}{[A]} = \text{Antilog}\, 0.8024 = 6.345$$

$$[A]_0 = 1\text{M};\ [A] = \frac{[A]_0}{6.345} = \frac{1\text{M}}{6.345}$$

$$= 0.1576\text{ M}$$

After 8 h sucrose left $=$ 0.1576 M

36. For first order reaction

$$t = \frac{2.303}{k}\log\frac{a}{(a-x)} \qquad \text{...(i)}$$

Given, $(a - x) = \dfrac{a}{16}$; $k = 60\text{ s}^{-1}$

Placing the values in Eq. (i)

$$t = \frac{2.303}{60\text{ s}^{-1}}\log\frac{a \times 16}{a} = \frac{2.303}{60\text{ s}^{-1}}\log 16 = \frac{2.303}{60\text{ s}^{-1}}\log 2^4$$

$$= \frac{2.303}{60\text{ s}^{-1}} \times 4\log 2 = \frac{2.303}{60\text{ s}^{-1}} \times 4 \times 0.3010$$

$$= 4.62 \times 10^{-2}\text{ s}$$

$$\text{Time} = 4.62 \times 10^{-2}\text{ s}$$

37. We know that

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left[\frac{a_2}{a_1}\right]^{n-1}$$

where, n = order of the reaction

Given, $(t_{1/2}) = 0.1\text{ s}$, $a_1 = 400$

$(t_{1/2})_2 = 0.8\text{ s}$, $a_2 = 50$

On substituting the values,

$$\frac{0.1}{0.8} = \left[\frac{50}{400}\right]^{n-1}$$

On taking log both sides

$$\log\frac{0.1}{0.8} = (n-1)\log\frac{50}{400}$$

$$\log\frac{1}{8} = (n-1)\log\frac{1}{8}$$

$$0.90 = (n-1)\,0.90$$

$$n - 1 = 1$$

$$n = 2$$

38.
$$k = \frac{1}{t}\left[\frac{x}{a(a-x)}\right]$$

$$k = \frac{1}{500}\left[\frac{0.2a}{a(a-0.2a)}\right]$$

$$k = \frac{1}{2000\,a}$$

$$\frac{1}{2000\,a} = \frac{1}{t}\left[\frac{0.6a}{a(a-0.6a)}\right]$$

$$t = 3000\text{ s.}$$

39. From the graph it is clear that the reaction is of zero order and hence, the units of rate constant = mol L^{-1} s^{-1}

40.
$$ {}_{79}Au^{198} \xrightarrow{-\beta} {}_{80}Hg^{198} $$
$$ k = \frac{0.693}{t_{1/2}} = \frac{0.693}{65} $$

After 260 hr,
$$ k = \frac{2.303}{260} \log \frac{a}{a-x} $$
$$ \frac{0.693}{65} = \frac{2.303}{260} \log \frac{a}{a-x} $$
$$ \frac{a}{a-x} = 16 $$
$$ \frac{1}{1-x} = 16 $$
$$ x = \frac{15}{16}\text{ g} = 0.9375\text{ g} $$

41. Let the order of reaction with respect to A is x and B is y.

$\therefore$ rate law, $r = k[A]^x[B]^y$ ...(iv)

On putting values, we get
$$ 0.10 = k[0.30]^x[0.30]^y \quad \text{...(i)} $$
$$ 0.40 = k[0.30]^x[0.60]^y \quad \text{...(ii)} $$
$$ 0.20 = k[0.60]^x[0.30]^y \quad \text{...(iii)} $$

From Eq. (i) and (ii) we get
$$ \frac{0.1}{0.4} = \left(\frac{0.30}{0.30}\right)^x \left(\frac{0.30}{0.60}\right)^y $$
$$ \frac{1}{4} = \left(\frac{1}{2}\right)^y $$

or $$ 4 = 2^y $$
$$ (2)^2 = 2^y \quad \text{or} \quad y = 2 $$

From Eq. (ii) and (iii), we get
$$ \frac{0.40}{0.20} = \left(\frac{0.30}{0.60}\right)^x \left(\frac{0.60}{0.30}\right)^y $$
$$ 2 = \left(\frac{1}{2}\right)^x (2)^y $$

On putting the values of y, we get
$$ 2 = \left(\frac{1}{2}\right)^x (2)^2 $$
$$ \frac{2}{4} = \left(\frac{1}{2}\right)^x $$
$$ \left(\frac{1}{2}\right)^1 = \left(\frac{1}{2}\right)^x $$

or $$ x = 1 $$

On putting the values of x and y in Eq. (iv), we get
$$ r = k[A]^1[B]^2 = k[A][B]^2 $$

42. Since the reaction is 50% completed in 1.26×10^{14} s.
$$ \therefore \quad t_{1/2} = 1.26 \times 10^{14}\text{ s} $$
$$ k = \frac{0.693}{t_{12}} = \frac{0.693}{1.26 \times 10^{14}} $$

For 100% completion,
$$ t = \frac{2.303}{k} \log \frac{a}{a-x} $$
$$ t = \frac{2.303 \times 1.26 \times 10^{14}}{0.693} \log \frac{100}{0} = \infty $$

43. The given equation clearly shown that the rate constant k increases exponentially with decreasing activation energy and increasing temperature.

44. $k = Ae^{-E_a/RT}$

On taking log, we get
$$ \log k = \log A - \frac{E_a}{2.203RT} $$

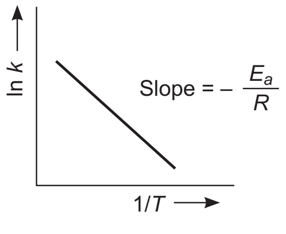
or $$ \ln k = \ln A - \frac{E_a}{RT} $$

$\therefore$ A graph between $\ln k$ *vs* $1/T$ is a straight line (according to equation of straight line *viz.* $y = mx + c$) with $-\frac{E_a}{k}$ slope (negative slope) and $\ln A$ intercept.

$\therefore$ Correct graph is graph (a).

In all other graphs slope is positive.

45. Arrhenius equation is
$$ k = Ae^{-E_a/RT} $$
$$ \ln k = \ln A - \frac{E_a}{RT} $$
$$ \ln k = \ln A - \frac{E_a}{RT} $$
$$ \text{Slope} = -\frac{E_a}{R} $$



46. Activation energy of backward reaction $= E_1$

$\therefore$ Activation energy of forward reaction $= E_1 + E_2$

Since the energy of product > energy of reactants

and $$ \text{energy} \propto \frac{1}{\text{stability}} $$

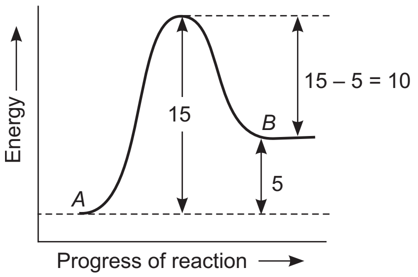
$\therefore$ Products are less stable than reactants.

47. For endothermic reaction $A \longrightarrow B$

Activation energy = 15 kcal/mol

Energy of reaction = 5 kcal/mol

Hence, activation energy for the reaction $B \longrightarrow A$ is $15 - 5 = 10$ kcal/mol



48. For exothermic reaction,
Energy of reactants > energy of product, which is the case given in (i).

50. $\because$ Rate constant (k') > rate constant (k'')
Greater the rate constant lesser will be the activation energy.

$$\therefore \qquad E_a' < E_a''$$

51. According to collision theory, the two main conditions for the formation of products are sufficient threshold energy and proper orientation.

52. Activation energy of a reaction is constant at constant temperature hence, $E_1 = E_2$.

53. Slow reaction rate indicates higher free energy of activation.

55. According to Arrhenius equation

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right];$$

$$[\because T_1 = 293\,\text{K}; T_2 = 313\,\text{K}; T_2 - T_1 = 20\,\text{K}]$$

$$\log \frac{4}{1} = \frac{E_a}{2.303 \times (8.314\ \text{J mol}^{-1}\ \text{K}^{-1})} \times \frac{20}{293 \times 313}$$

$$0.6021 = \frac{E_a}{2.303 \times (8.314\ \text{J mol}^{-1})} \times \frac{20}{293 \times 313}$$

$$E_a = \frac{0.6021 \times 2.303 \times 8.314 \times 293 \times 313}{20}\ \text{J mol}^{-1}$$

$$= 52863\ \text{J mol}^{-1}$$

$$E_a = 52.863\ \text{kJ mol}^{-1}$$

56. According to Arrhenius equation

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R} \times \frac{T_2 - T_1}{T_1\,T_2}$$

$$k_1 = 4.5 \times 10^3\,\text{s}^{-1}; k_2 = 1.5 \times 10^4\,\text{s}^{-1}\ ;\ T_1 = 10°\text{C} = 283\ \text{K}$$

$$\log \frac{1.5 \times 10^4}{4.5 \times 10^3} = \frac{(60000\ \text{J mol}^{-1})}{2.303 \times (8.314\ \text{J mol}^{-1})}\left(\frac{T_2 - 283}{283\,T_2}\right)$$

$$\log 3.333 = 3133.62\left(\frac{T_2 - 283}{283\,T_2}\right)$$

$$\frac{0.5228}{3133.62} = \frac{T_2 - 283}{283 T_2}$$

$$\frac{0.5288 \times 283}{3133.62} = \frac{T_2 - 283}{T_2}$$

$$1 - \frac{283}{T_2} = 0.04776$$

or $$T_2 = \frac{283}{1 - 0.04776} = \frac{283}{0.95224}$$

$$T_2 = 297.19\ \text{K}$$

$$= (297.19 - 273.0) = 24.19°\,\text{C}$$

Temperature = 24.19° C

57. According to Arrhenius equation.

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\frac{k_2}{k_1} = 2;\ T_1 = 295\ \text{K};\ T_2 = 305\ \text{K};\ R = 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}$$

$$\therefore \qquad \log 2 = \frac{E_a}{2.303 \times (8.314\ \text{JK}^{-1}\ \text{mol}^{-1})}\left[\frac{1}{295\,\text{K}} - \frac{1}{305\,\text{K}}\right]$$

or $$0.3010 = \frac{E_a}{2.303 \times (8.314\ \text{J mol}^{-1})} \times \frac{(10)}{295 \times 305}$$

$$E_a = \frac{0.3010 \times 2.303 \times 8.314 \times 295 \times 305}{10}\ (\text{J mol}^{-1})$$

$$= 51855\ \text{J mol}^{-1}$$

or $$= 51.855\ \text{kJ mol}^{-1}$$

Activation energy for the reaction = 51.855 kJ mol^{-1}

58. Fraction of molecules (x) having energy equal to or more than activation energy may be calculated as follows

$$x = n/N = e^{-E_a/RT}$$

$$\ln x = \frac{-E_a}{RT} \quad \text{or} \quad \log x = -\frac{E_a}{2.303\,RT}$$

or $$\log x = -\frac{209.5 \times 10^3\ \text{J mol}^{-1}}{2.303 \times (8.314\ \text{JK}^{-1}\ \text{mol}^{-1}) \times 581\ \text{K}}$$

$$= -\ 18.8323$$

$$x = \text{Antilog}\,(-\ 18.8324) = \text{Antilog}\,\overline{19}.1677$$

$$= 1.471 \times 10^{-19}$$

$$\text{Fraction of molecules} = 1.471 \times 10^{-19}$$

59. $$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\ R} \times \frac{T_2 - T_1}{T_1 \cdot T_2}$$

$$\log \frac{105}{100} = \frac{E_a}{2.303 \times 8.314} \times \frac{1}{300 \times 301}$$

$$E_a = 36.65\ \text{kJ}$$

60. $$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\log \frac{k_2}{k_1} = \frac{9000}{2.303 \times 2}\left(\frac{5}{295 \times 300}\right)$$

$$\log \frac{k_2}{k_1} = 0.1103$$

$$\frac{k_2}{k_1} = 1.288, \quad k_2 = 1.288\,k$$

i.e., increase by 28.8%

Round II

1. $B + 5D \longrightarrow 3A + 2C$

$$-\frac{d[B]}{dt} = -\frac{1}{5}\frac{d[D]}{dt} = +\frac{1}{3}\frac{d[A]}{dt} = +\frac{1}{2}\frac{d[C]}{dt}$$

2. Thermal decomposition,

$$CH_3CHO \xrightarrow{\Delta} CH_4 + CO$$

$$\frac{dx}{dt} = k[CH_3CHO]^{3/2}$$

3. $$C_n = \frac{C_0}{2^n}$$

or $$50 = \frac{800}{2^n}$$

$$2^n = \frac{800}{50} = 16 = 2^4$$

$\therefore$ $$n = 4$$

$$T = n \times t_{1/2}$$

$$t_{1/2} = \frac{2 \times 10^4}{4} = 0.5 \times 10^4 \text{ s}$$

$$k = \frac{0.693}{0.5 \times 10^4} = 1.386 \times 10^{-4}$$

4. Rate depends upon the slowest step. Hence, from equation

$$O + O_3 \longrightarrow 2O_2$$

$$r = k[O_3][O]$$

and from equation $O_3 \rightleftharpoons O_2 + O$

$$K_{eq} = \frac{[O_2][O]}{[O_3]}$$

$$[O] = \frac{K_{eq}[O_3]}{[O_2]}$$

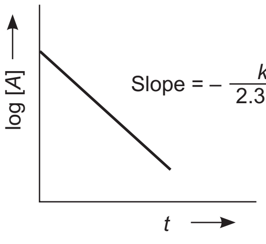
$\therefore$ $$r = k[O_3]\frac{K_{eq}[O_3]}{[O_2]}$$

$$= k'[O_3]^2[O_2]^{-1}$$

5. If the temperature is increased by 60°C then 10° increase has been made 6 times and therefore, rate will increase by $2^6 = 64$ times.

6. For first order reaction

$$\log[A] = -\frac{kt}{2.303} + \log[A]_0$$



7. $$t_1 = \frac{2.303\,(t_{1/2})_1}{0.693}\log\left(\frac{1}{1-(1/4)}\right)$$

and $$t_2 = \frac{2.303\,(t_{1/2})_2}{0.693}\log\left(\frac{1}{1-(3/4)}\right)$$

$$\frac{t_1}{t_2} = \frac{8}{1} \times \frac{\log(4/3)}{\log 4}$$

$$= \frac{8 \times 0.125}{0.602} = 1 : 0.602$$

8. For first order reaction : $k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$

At 298 K; $$k_1 = \frac{2.303}{t}\log\frac{100}{90} \quad \text{...(i)}$$

At 308 K; $$k_2 = \frac{2.303}{t}\log\frac{100}{75} \quad \text{...(ii)}$$

Dividing eq. (ii) by (i);

$$\frac{k_2}{k_1} = \frac{\log\frac{100}{75}}{\log\frac{100}{90}} = \frac{0.1249}{0.0458} = 2.73$$

According to Arrhenius theory;

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R} \times \frac{T_2 - T_1}{T_1 T_2}$$

$$\log 2.73 = \frac{E_a}{2.303\,R}\left[\frac{308 - 298}{298 \times 308}\right]$$

$$E_a = \frac{0.4361 \times 2.303 \times (8.314 \text{ J mol}^{-1}) \times 298 \times 308}{10}$$

$$E_a = 76640 \text{ Jmol}^{-1} = 76.640 \text{ kJ mol}^{-1}$$

Now, according to Arrhenius equation

$$\log k = \log A \frac{-E_a}{2.303\,RT}$$

$$\log k = \log(4 \times 10^{10}) - \frac{76640 \text{ J mol}^{-1}}{2.303 \times (8.314 \text{ J mol}^{-1}\text{K}^{-1}) \times (318 \text{ K})}$$

$$\log k = 10.6021 - 12.5870 = -1.9849$$

$$k = \text{Antilog}(-1.9849)$$

$$= \text{Antilog}(\bar{2}.0151) = 1.035 \times 10^{-2} \text{ s}^{-1}$$

9. $$\begin{array}{lccc} & SO_2Cl_2(g) & \longrightarrow SO_2(g) & + \; Cl_2(g) \\ \text{Initially} & p_i & 0 & 0 \\ \text{After time } t & p_i - p & p & p \end{array}$$

Total pressure after time t *i.e.,*

$$p_t = p_i - p + p + p = p_i + p$$

So, $$a = p_i$$

$$a - x = p_i - (p_t - p_i)$$

$$= p_i - p_t + p_i = 2p_i - p_t$$

Substitutions of the value of *a* and (*a* − *x*) gives

$$k = \frac{2.303}{t}\log\frac{p_i}{(2p_i - p_t)}$$

(a) Calculation of rate constant *k*

Given, $p_i = 0.5$ atm ; $p_t = 0.6$ atm,

$$k = \frac{2.303}{t}\log\frac{p_i}{(2p_i - p_t)}$$

$$= \frac{2.303}{(100\text{ s})}\log\frac{0.5\text{ atm}}{0.4\text{ atm}}$$

$$= \frac{2.303}{(100\text{ s})}\log 1.25 = \frac{2.303}{(100\text{ s})}\times 0.0969$$

$$= 2.23\times10^{-3}\text{ s}^{-1}$$

(b) Calculation of reaction rate when total pressure is 0.65 atm

$$p_{SO_2Cl_2} = 0.5 - (0.65 - 0.50)$$

$$= (1 - 0.65) = 0.35\text{ atm}$$

$$k = 2.23\times10^{-3}\text{ s}^{-1}$$

$$\text{Rate} = k\times p_{SO_2Cl_2} = (2.23\times10^{-3}\text{ s}^{-1})\times(0.35\text{ atm})$$

$$\text{Rate} = 7.8\times10^{-4}\text{ atm s}^{-1}$$

10. $t_{1/2} = 28.1\text{ yr}\ ;\ k = \frac{0.693}{t_{1/2}} = \frac{0.693}{28.1}\text{ yr}^{-1}$

For first order reaction

$$t = \frac{2.303}{k}\log\frac{a}{(a-x)}$$

$$a = 1\mu,\ t = 60\text{ yr}\ ;\ k = \frac{0.693}{28.1}\text{ yr}^{-1}$$

$$60\text{ yr} = \frac{2.303}{0.693/28.1}\times\log\frac{a}{(a-x)}$$

$$\log\frac{a}{(a-x)} = \frac{(60\text{ yr})\times 0.693/28.1\text{ yr}^{-1})}{2.303} = 0.642$$

$$\frac{a}{(a-x)} = \text{Antilog}\,0.642 = 4.385$$

$$(a-x) = \frac{a}{4.385} = \frac{(1\ \mu\text{g})}{4.385} = 0.2280\ \mu\text{g}$$

Amount left after 60 yr = 0.2280 μg

11. $(CH_3)_2CHN{=}NCH\,(CH_3)_2(g) \longrightarrow N_2(g) + C_6H_{14}\,(g)$

	$(CH_3)_2CHN{=}NCH(CH_3)_2$	N_2	C_6H_{14}
Initial pressure	p_i	0	0
After time *t*	$p_i - p$	p	p

Total pressure after time *t*,

i.e., $(p_t) = (p_i - p) + p + p = p_i + p$

or $p = p_t - p_i$

$a = p_i$; $(a - x) = p_i - p$ on substituting the values of p ;

$(a - x) = p_i - (p_t - p_i)$, *i.e.*, $(a - x) = 2p_i - p_t$

The decomposition reaction is of gaseous nature and the rate constant *k* can be calculated as

$$k = \frac{2.303}{t}\log\frac{a}{a-x}$$

Substitution of value of *a* and (*a* − *x*) gives

$$k = \frac{2.303}{t}\log\left(\frac{p_i}{2p_i - p_t}\right)$$

(i) Rate constant after 360 s = k_1

$$k_1 = \frac{2.303}{(360\text{ s})}\log\frac{(35\text{ atm})}{(70 - 54)\text{ atm}}$$

$$= \frac{2.303}{(360\text{ s})}\log\frac{35}{16} = \frac{2.303}{(360\text{ s})}\log 2.1875$$

$$= \frac{2.303\times 0.33995}{(360\text{ s})} = 2.17\times10^{-3}\text{ s}^{-1}$$

(ii) Rate constant after 720 s = k_2

$$k_2 = \frac{2.303}{(720\text{ s})}\log\frac{(35\text{ atm})}{(70 - 63)\text{ atm}}$$

$$= \frac{2.303}{(720\text{ s})}\log 5 = \frac{2.303\times 0.6990}{(720\text{ s})}$$

$$= 2.24\times10^{-3}\text{ s}^{-1}$$

$$\text{Average rate constant } k = \frac{(2.17 + 2.24)\times10^{-3}\text{ s}^{-1}}{2}$$

$$k = 2.21\times10^{-3}\text{ s}^{-1}$$

12. $k = 2.1\times10^{10}\exp(-2700/RT)$

i.e., $\log k$ *vs* $1/T$ will be straight line

intercept of $\log k$ axis = $\log 2.1\times10^{10}$

13. $A^m + B^n \longrightarrow ABx$

In this case,

overall order of reaction may or may not be = $m + n$

Hence, code 3 is wrong.

14. The reaction occurring in two steps has two activation energy peaks. The first step, being fast needs less activation energy. The second step being slow, needs more activation energy. Therefore, second peak will be higher than the first.

15. According to Arrhenius equation

$$k = Ae^{-E_a/RT} \qquad \text{...(i)}$$

According to the available data

$$k = (4.5\times10^{11}\text{s}^{-1})\,e^{-28000}\text{ K/T} \qquad \text{...(ii)}$$

On comparing both equations;

$$-\frac{E_a}{RT} = \frac{-28000\text{ K}}{T}$$

$$E_a = (28000\text{ K})\times R = (28000\text{ K})\times(8.314\ \text{K}^{-1}\text{J mol}^{-1})$$

$$= 232792\text{ kJ mol}^{-1}$$

$$E_a = 232.792\text{ kJ mol}^{-1}$$

16. Slowest step of a reaction is called the rate determining step. If in this step only one reactant is involved, the reaction is called unimolecular. For such reactions, the order and molecularity of slowest step are equal to one.

17. Only in case of elementary reaction, rate law is determined from the balanced chemical equation.

18. For zero order reaction,

$$\text{rate} = -\frac{d[A]}{dt} = k \quad \text{or} \quad \frac{d[A]}{dt} = -k$$

On integrating, we get

$$\int \frac{d[A]}{dt} = -\int k\,dt$$

$$[A] = -kt + c \qquad \ldots\text{(i)}$$

When, $t = 0$ $\quad [A] = [A]_0$

$\therefore$ $\quad C = [A]_0$

On putting the value of c in Eq. (i)

$$[A] = -kt + [A]_0$$

$\therefore$ A graph of $[A]$ *vs* t is a straight line with slope $= -k$. Here, $[A] =$ concentration of reactant.

Thus, graph (a) and (d) are correct.

19. Reaction is zero order so rate of formation of product or rate of decomposition of reactant is constant so concentration will be linear function.

For zero order reaction, $k = \frac{a}{2t_{1/2}}$

So unit of k is mol L^{-1} s^{-1}

$$\frac{dx}{dt} = k(2a-2x)\times(a-x)^{-1} = 2\text{K}$$

$$x = [C] = 2kt$$

20. $k_1 = k_2 = \frac{2}{3}$rd of A has reacted for $[A] = [B] = [C]$

$$\therefore \quad k_1 + k_2 = \frac{1}{t}\ln\frac{[A]_0}{\frac{1}{3}[A]_0}$$

or $$t = \frac{1}{k_1+k_2}\ln 3 = \frac{1}{2k_1}\ln 3 = \frac{1}{2k_2}\ln 3$$

21. Order and molecularity of a reaction may or may not be same. *e.g.,* pseudounimolecular reactions where molecularity is 2 and order is 1.

Order is determined experimentally whereas molecularity is the sum of stoichiometric coefficients of reactants in elementary step.

22. Only those reactant molecules undergo chemical change which have proper orientation and sufficient kinetic energy for the formation of products.

Rate constants determined from Arrhenius equation are fairly accurate for simple as well as complex molecules.

23. For reactions carried out in solution, changing the solvent will generally change the rate of a reaction. The rate of reaction will change, when some alcohol is added.

24. The change in the concentrations of all the reactants and products can be expressed as

$$\frac{-d[I_2]}{dt} = -\frac{1}{2}\frac{d[S_2O_3^{2-}]}{dt}$$

$$= \frac{d[S_4O_6^{2-}]}{dt} = \frac{1}{2}\frac{d[I^-]}{dt}$$

25. According to Arrhenius equation

$$k = Ae^{-E_a/RT}$$

when $E_a = 0, k = A$

26. $$k = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}$$

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{t}\log\frac{100}{100-75}$$

$\therefore$ $\quad t_{1/2} = 16$ min

27. $$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{693}\ s^{-1}$$

$$= 1\times10^{-3}\ s^{-1}$$

28. For a first order reaction

$$\text{Rate} = k\,(\text{concentration})$$

$$\therefore \quad k = \frac{\text{Rate}}{\text{concentration}} = \frac{1.5\times10^{-2}\ \text{mol L}^{-1}\ \text{min}^{-1}}{0.5\ \text{mol L}^{-1}}$$

$$= 3\times10^{-2}\,\text{min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{3\times10^{-2}}\text{min}$$

$$= \frac{69.3}{3}\text{min or } 23.1 \text{ min}$$

29. $$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} C$$

$$k_c = \frac{k_f}{k_b} = \frac{[C]}{[A]} = \frac{0.4}{0.6} = \frac{2}{3}$$

For $\quad 2C \rightleftharpoons 2A$

$$k_c = \left(\frac{1}{k_c}\right)^2 = \left(\frac{1}{2/3}\right)^2 = \frac{9}{4}$$

30. $$-\frac{dA}{dt} = k_f[A] - k_b[C]$$

and $d[C]/dt = k_f[A] - k_b[C]$ at any time

and slope between conc. and time is known as rate and they are always equal at any time.

31. $k_c = k_f/k_b$

$$= \frac{\text{Conc. of products as per rate law}}{\text{Conc. of reactants as per rate law}}$$

Stoichiometry of reaction is required.

32. For every 10°C rise of temperature, rate is doubled. Thus, temperature coefficient of the reaction = 2

When temperature is increased by 50°, rate becomes

$$= 2^{(50/10)} = 2^5 \text{ times}$$

$$= 32 \text{ times}$$

33. $A \xrightarrow{k_1} B, A \xrightarrow{k_2} C,$

By Arrhenius equation,

$$k_1 = A' \, e^{-E_{a_1}/RT}$$

and $$k_2 = A' \, e^{-E_{a2}/RT}.$$

(A' is Arrhenius constant.)

$$(\text{Since, } E_{a_2} = 2E_{a_1})$$

$\therefore$ $$k_2 = A' \, e^{-2E_a/RT}$$

$$\frac{k_1}{k_2} = \frac{A' \, e^{-E_{a_1}/RT}}{A' \, e^{-2E_{a_1}/RT}} = e^{E_{a_1}/RT}$$

$\therefore$ $$k_1 = k_2 e^{E_{a\,1}/RT}$$

34. For a zero order reaction,

$$k_0 = \frac{[A]_0}{2t_{1/2}}$$

Since, $[A]_0 = 2 \text{ M}, t_{1/2} = 1 \text{h}$

So, $k_0 = 1$

and $$k_0 = \frac{\Delta x}{t}$$

or $$t = \frac{0.50 - 0.25}{1} = 0.25 \text{ h}$$

35. Slowest step is the rate determining step. Thus, in case (A), rate law is given as rate $= k[Cl_2][H_2S]$

While for the reaction given in case (*B*), rate law is given as

$$\text{rate} = k[H_2S][Cl_2][H^+]^{-1}.$$

Hence, only mechanism (A) is consistent with the given rate law.

36. Half-life $= 6.93$ min $\quad k_1 = \dfrac{0.693}{6.93} = 0.1$

We know, k_1 for per cent completion

$$k_1 = \frac{2.303}{t} \log\left(\frac{100}{100 - x}\right)$$

$$0.1 = \frac{2.303}{t} \times \log \frac{100}{1}$$

$$0.1 = \frac{2.303}{t} \log 10^2$$

$$t = \frac{2.303 \times 2}{0.1}$$

$$= 46.06 \text{ min}$$

37. $$\frac{1}{2} A \longrightarrow 2B$$

For the given reaction

$$-\frac{2d\,[A]}{dt} = \frac{1}{2}\frac{d\,[B]}{dt} = \text{Rate of reaction}$$

Rate of disappearance of *A*

$$= -\frac{d\,[A]}{dt} = \frac{1}{2 \times 2}\frac{d[B]}{dt} = \frac{1}{4}\frac{d\,[B]}{dt}$$

38. $$2A + B \longrightarrow \text{products}$$

[*B*] is doubled, half-life didn't change, *i.e.*, half-life is independent of change in conc of reactant *i.e.*, first order. First order *wrt* to *B*

When [*A*] is doubled, rate increased by two times

$\Rightarrow$ First order *wrt A*

Hence, net order of reaction $= 1 + 1 = 2$

Unit for the rate constant $= \text{conc}^{(1-n)}\, t^{-1}$

$$= (\text{mol L}^{-1})^{-1} \cdot \text{s}^{-1}$$

$$= \text{L} \cdot \text{mol}^{-1} \text{ s}^{-1}$$

39. $A_2 + B_2 \rightleftharpoons 2AB$

$$E_a \text{ (forward)} = 180 \text{ kJ mol}^{-1}$$

$$E_a \text{ (backward)} = 200 \text{ kJ mol}^{-1}$$

In the presence of catalyst :

$$E_a \text{ (forward)} = 180 - 100 = 80 \text{ kJ mol}^{-1}$$

$$E_a \text{ (backward)} = 200 - 100 = 100 \text{ kJ mol}^{-1}$$

$$\Delta H = E_a \text{ (forward)} - E_a \text{ (backward)}$$

$$= 80 - 100 = -20 \text{ kJ mol}^{-1}$$

40. $$\text{Rate} = k\,[NOBr_2]\,[NO] \qquad \text{...(i)}$$

But $NOBr_2$ is in equilibrium

$$K_{eq} = \frac{[NOBr_2]}{[NO]\,[Br_2]}$$

$$[NOBr_2] = K_{eq}\,[NO]\,[Br_2] \qquad \text{...(ii)}$$

Putting the value of $[NOBr_2]$ in Eq (i)

$$\text{Rate} = k \cdot K_{eq}\,[NO]\,[Br_2]\,[NO]$$

Hence, $$\text{Rate} = k \cdot K_{eq}\,[NO]^2\,[Br_2]$$

$$\text{Rate} = k'\,[NO]^2\,[Br_2]$$

where $$k' = k \cdot K_{eq}$$

41. $k = Ae^{-E/RT}$

E is activation energy. It is that energy, which molecule must have to give the product.

42. There are two different reactants (say *A* and *B*).

$$A + B \longrightarrow \text{product}$$

Thus, it is a bimolecular reaction.

If $$\frac{dx}{dt} = k\,[A]\,[B]$$

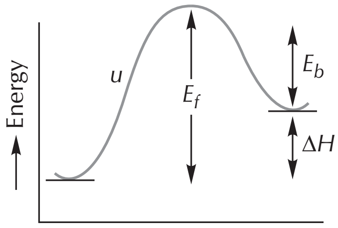
it is second order reaction

If $$\left(\frac{dx}{dt}\right) = k\,[A] \quad \text{or} \quad = k\,[B]$$

it is first order reaction.

Molecularity is independent of rate, but is the sum of the reacting substances, thus it cannot be unimolecular reaction.

43. $X \rightarrow Y$ is an endothermic reaction, $\Delta H = +$ ve



E_b = energy of activation of backward reaction

E_f = energy of activation of forward reaction

ΔH = heat of reaction

Thus, $\quad E_f = E_b + \Delta H$

Thus, $\quad E_f > E_b$

44. Variation of K_{eq} with temperature T is given by van't Hoff equation.

$$\log K_{eq} = -\underset{A}{\frac{\Delta H^\circ}{2.303\,RT}} + \underset{B}{\frac{\Delta S^\circ}{R}}$$

Slope of the given line is positive indicating that term A is positive, thus ΔH° is negative.

Thus, reaction is exothermic.

45. $2A + B \longrightarrow C$

$$\text{Rate} = k\,[A]\,[B]$$

It represents second order reaction.

Thus, unit of k is $M^{-1}\ s^{-1}$

$t_{1/2}$ is dependent of concentration but not constant.

and $\quad -\frac{1}{2}\frac{d\,[A]}{dt} = \frac{d\,[C]}{dt}$

46. Order = 1

Concentration changes from 0.8 M to 0.4 M in (50%) 15 min, thus half-life = 15 min = T_{50}

A change from 0.1 M to 0.025 M is 75% and for first order reaction

$$T_{75} = 2 \times T_{50} = 2 \times 15 = 30 \text{ min}$$

or $\quad T_{50} = 15$ min

$$k = \frac{2.303 \log 2}{T_{50}} = \frac{2.303 \log 2}{15}$$

$$a = 0.1 \text{ M}$$

$$(a - x) = 0.025 \text{ M}$$

For first order :

$$k = \frac{2.303}{t} \log \left(\frac{a}{a - x}\right)$$

$$\frac{2.303 \log 2}{15} = \frac{2.303}{t} \log \frac{0.1}{0.025}$$

$$= \frac{2.303}{t} \log 4$$

$$\therefore \quad \frac{2.303 \log 2}{15} = \frac{2 \times 2.303 \log 2}{t}$$

$$\therefore \quad t = 30 \text{ min}$$

47.

$$\left(\frac{dx}{dt}\right) = k\,[\text{NO}]^2\,[O_2]$$

$$= k\left(\frac{n_{\text{NO}}}{V}\right)^2\left(\frac{n_{O_2}}{V}\right)$$

$$\left(\frac{dx}{dt}\right) = \frac{k}{V^3}\,(n_{\text{NO}})^2\,(n_{O_2})$$

$$\left(\frac{dx}{dt}\right) = \frac{k\,(n_{\text{NO}})^2\,(n_{O_2})}{\left(\frac{V}{2}\right)^3} = 8\left(\frac{dx}{dt}\right)$$

48. $H_2 + I_2 \longrightarrow 2HI$

$$\text{Rate of reaction} = \frac{-d\,[H_2]}{dt} = \frac{-d\,[I_2]}{dt} = \frac{1}{2}\frac{d\,[HI]}{dt}$$

or $\quad \frac{-2d\,[H_2]}{dt} = \frac{-2d\,[I_2]}{dt} = \frac{d\,[HI]}{dt}$

49. $kt = -\log_e C_t + \log_e C_0$

$$t = -\frac{1}{k}\log_e C_t + \log_e C_0$$

$y = mx + c$, straight line, negative slope.

5 Surface Chemistry

JEE Main MILESTONE

- Adsorption
- Catalysis
- Enzyme Catalysis
- Colloidal State
- Classification of Colloids
- Preparation of Colloids
- Properties of Colloids
- Protective Colloids
- Emulsion
- Applications of Colloids

5.1 Adsorption

When a solid surface is exposed to a gas or a liquid, molecules from the gas or the liquid accumulate at the surface. The phenomenon of concentration of molecules of a gas or a liquid at a solid surface rather than in its bulk is called adsorption. The substance that concentrates at the surface is called **adsorbate** and the solid at the surface of which the concentration occurs, is called **adsorbent.**

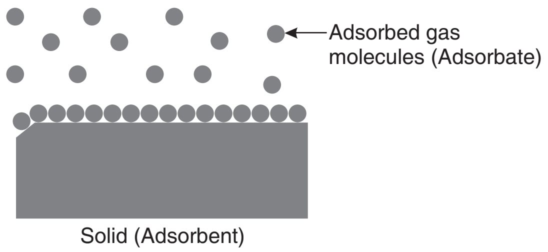


Fig. 5.1 Adsorption of gas molecules over solid surface

Surface chemistry deals with the phenomenon that occurs at the surface or interfaces. There are several properties of substances, particularly of solids and liquids and solids and gases, which depend upon the nature of the surface of interface.

Some examples of adsorption are

(i) Finely divided charcoal if stirred into a dilute solution of methylene blue, the dye molecules are adsorbed by the charcoal particles and the depth of colour of the solution decreases appreciably.

(ii) If a gas (SO_2, Cl_2, NH_3) is treated with powdered charcoal in a closed vessel, the gas molecules adsorb on charcoal surface and the gas pressure is reduced.

The common adsorbents are **charcoal** (vegetable and animal), **silica gel** (prepared by heating a mixture of sodium silicate and 10% HCl at 50°C), **metals** such as Ni, Cu, Ag, Au, Pt and colloids.

Distinction between Adsorption and Absorption

1. Adsorption implies concentration at the surface only while absorption implies penetration into the body of the solid.
2. Absorption is a rapid process and equilibrium is maintained in a short time. While in adsorption, the equilibrium is reached slowly.
3. Both adsorption and absorption often take place side by side and it is difficult to distinguish between two processes.
4. Mc Bain introduced the general term **sorption,** which includes both the processes.

Characteristics of Adsorption

Important characteristics of adsorption are as follows

(a) Specificity and Selectivity

Adsorption is specific and selective phenomenon, which strictly refers to the existence of a higher concentration of any particular component at the surface of a liquid or a solid phase.

(b) Exothermic Process

Adsorption is accompanied with decrease in free energy of the system. In adsorption, there is a decrease in entropy of the system.

As, $\Delta G < 0$

and $\Delta S < 0$,

Therefore, $\Delta H < 0$ $(\Delta H = \Delta G + T\Delta S)$

Hence, the adsorption is associated with decrease in enthalpy of the system. Thus, *adsorption is always an exothermic process.*

(c) Residual Valency Bonds

The atoms or molecules of a solid surface have unbalanced or residual attractive forces on the surface, which can hold adsorbate particles together. Thus, the adsorbed atoms or molecule can be held on the surface of a metal by physical van der Waals' forces or chemical forces due to residual valence bonds.

Molecular adsorption

Atomic adsorption

(d) Extent of Adsorption

All solids adsorb gases to some extent. Adsorption is not very pronounced unless an adsorbent possesses a large surface area for a given mass. Various types of charcoals, silica gels, metal, etc., are used as adsorbents. Appreciable adsorption also takes place on some smooth surfaces, such as those of platinum and glass. Charcoal and other solids gain increased power of adsorption on heating at low pressure with various gases or in air or vacuum at temperature varying from 350–1000°C. Such treated charcoal is called **activated charcoal** and the process is called **activation**. On activation

1. the hydrocarbons and other impurities are removed from charcoal.
2. the surface area may increase due to chemical interaction with the oxidising agent which is used as **activator.**
3. the degree of unsaturation of the surface atoms may be increased.

Different Types of Adsorption

Adsorption may be classified into the following two types

On the basis of Concentration

On the basis of concentration of adsorbates adsorption can be of following two types

(a) Positive Adsorption

If the concentration of adsorbate is more on the surface as compared to its concentration in the bulk phase then it is called positive adsorption. *e.g.*, when a concentrated solution of KCl is shaken with blood charcoal, it shows positive adsorption.

(b) Negative Adsorption

If the concentration of the adsorbate is less than its concentration in the bulk then it is called negative adsorption. *e.g.,* when a dilute solution of KCl is shaken with blood charcoal, it shows negative adsorption.

Hot Spot 1

PHYSICAL and Chemical Adsorption

It is an important topic of the chapter for JEE Main examination. The questions, if asked, from this chapter may be from this topic. The level of questions is easy to average and its nature is generally theoretical.

On the basis of nature of force existing between adsorbate and adsorbent adsorption again of the following two types

(a) Physical Adsorption or van der Waals' Adsorption

If the physical or van der Waals' forces of attraction hold the adsorbate molecules to the surface of adsorbent, it is termed as physical adsorption (physisorption). Since physical forces involves, van der Waals' forces, it is

1. Reversible
2. Involves physical forces
3. Appreciable only at low temperature below the boiling point of adsorbate
4. Not very specific
5. Cause multilayer adsorption
6. Generally has heat of adsorption less than 10 kcal/mol

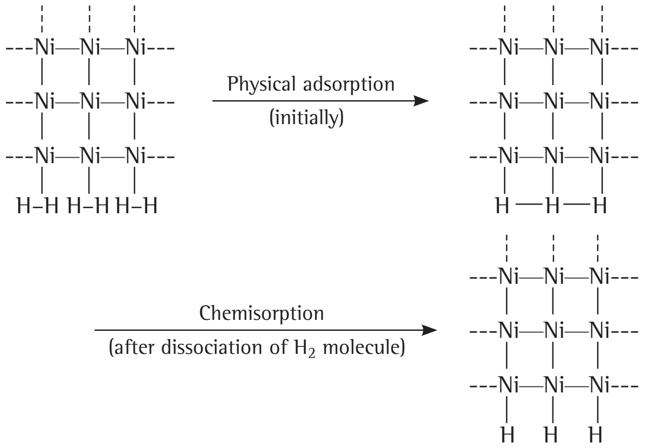
Due to the formation of multilayers, physical adsorption decreases after sometimes.

(b) Chemical Adsorption or Activated Adsorption

If the chemical forces hold the gas molecules to the surface of the adsorbent, the adsorption is termed as chemical adsorption (chemisorption). Since activated chemisorbent involves a high degree of specificity like chemical forces, thus chemisorption is

1. Irreversible
2. Involves transfer of electrons between gas and solid
3. Appreciable at high temperatures
4. May be rapid as well as slow
5. May involve activation energy in the adsorption process
6. Highly specific
7. Leads almost to a monolayer
8. Generally has heat of adsorption greater than about 20 kcal/mol

Often adsorption is a combination of both the two types of adsorptions. *e.g.,* hydrogen molecules are first adsorbed by van der Waals' forces on a nickel surface and then dissociate. The hydrogen atoms are thus adsorbed on nickel as



Comparison between physical and chemical adsorption is tabulated below

Table 5.1 **Comparison between Physisorption and Chemisorption**

S.N.	Physisorption	Chemisorption
1.	It is caused by intermolecular van der Waals' forces	It is caused by chemical bond formation
2.	It is not specific	It is highly specific
3.	It is reversible	It is irreversible
4.	It depends on the nature of gas. More easily liquefiable gases get adsorbed readily	It depends on the nature of gas. Gases which form compounds with the adsorbent exhibit it
5.	Heat of adsorption is low. (about 5 kcal mol^{-1})	Heat of adsorption is high (20 to 100 kcal mol^{-1})
6.	Low temperature is favourable. It decreases with increase of temperature	High temperature is favourable. It increases with increase of temperature
7.	No appreciable activation energy is involved	High activation energy is involved
8.	High pressure is favourable. Decrease of pressure causes desorption	High pressure is favourable. Decrease of pressure does not cause desorption
9.	It depends on the surface area. It increases with increase of surface area	It also depends on the surface area. It increases with increase of surface area

Factors Affecting the Extent of Adsorption

The extent of adsorption is affected by following factors

(a) Nature of Adsorbent

A gas is adsorbed in different amounts on different adsorbents. *e.g.,* hydrogen is strongly adsorbed on nickel surface, while it is weakly adsorbed on alumina surface under identical conditions.

(b) Surface Area

Increase in the surface area of the adsorbent, increases the total amount of the gas adsorbed because number of adsorbing sites increases. Thus, finely divided metals (Pt, Ni) and porous substance (charcoal, silica gel) are best solid adsorbents.

(c) Nature of the Gas

In general, the more liquifiable a gas is, the more readily will it be adsorbed. Thus, the amount of adsorption of gas on same mass of charcoal follows the following order

$$SO_2(T_c = 157°C) > CH_4(T_c = -83°C) > H_2(T_c = -120°C).$$

Easily liquifiable gases, such as NH_3, HCl, Cl_2, SO_2, CO_2 etc., are readily adsorbed than the permanent gases, such as O_2, N_2, H_2 etc. *The higher the critical temperature of the gas, the greater the extent of adsorption.*

Caution Point *Nature of adsorption of nitrogen on the surface of iron depends on the temperature. AT 83 K, nitrogen is physisorbed on iron surface as N_2 molecules. The degree of adsorption decreases rapidly as the temperature increases. At room temperature, there is no adsorption of N_2 on iron. When temperature is further increased up to 773 K and above, then nitrogen is chemisorbed on the iron surface as nitrogen atom.*

(d) Exothermic Nature

The energy liberated when 1 g mol of a gas is adsorbed on a solid surface is defined as **heat of adsorption.**

(e) Pressure

At the surface of adsorbent, a fix number of adsorption sites are available where only gaseous molecules can be adsorbed. Initially as pressure is increased, the number of molecules which strike the unit area of the surface increases in proportion to the increase of pressure and hence adsorption increases almost linearly with pressure. Since a fixed number of adsorption sites are available, eventually at some high pressure, a stage would be reached where all the sites are occupied and hence further increase in pressure would not cause any further adsorption to occur, *i.e.,* extent of adsorption becomes independent of pressure after a certain high pressure. In the intermediate range of pressure, the increase in adsorption is not as fast as in the beginning. This can be understood on the basis that the phenomenon of adsorption and desorption proceed simultaneously due to its reversible nature.

Adsorption Isotherms

The amount of gas adsorbed depends on equilibrium pressure and temperature. The relationship between the equilibrium pressure (p) of a gas and its amount adsorbed on the solid adsorbent at any constant temperature is called an adsorption isotherm.

Two such isotherms are given below.

(a) Freundlich Adsorption Isotherm

Freundlich gave the relationship between the gas adsorbed by solid adsorbent surface and pressure of the gas at a particular temperature. He proposed the following empirical equation

$$\frac{x}{m} = kp^{1/n} \quad \text{...(i)}$$

where, x is the mass of gas adsorbed on a mass m of adsorbent at a pressure p. k and n are constant, which depend upon the nature of the gas and the adsorbent and upon temperature. From the relationship curves,

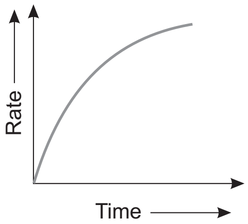


Fig. 5.2 Rate *vs T* graph

When $n = 1, \frac{x}{m} = kp$ or $\frac{x}{m} \propto p$ (at low pressure)

When $n > 1,$ $\frac{x}{m} = k$ (independent of pressure)

It is observed that at high pressure when saturation point is reached, logarithmic form of Eq. (i) is

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$$

Graph between $\log \frac{x}{m}$ and $\log p$ is a straight line with slope $\frac{1}{n}$ and intercept $\log k$.

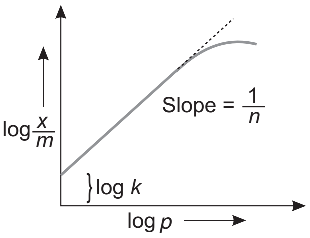
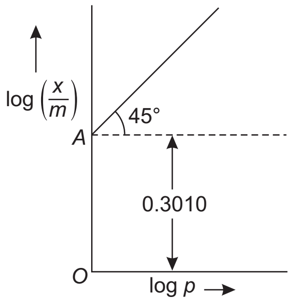


Fig. 5.3 Graph between log *x/m* and log *p*

The limitations of Freundlich isotherm are as

1. Concept of Freundlich adsorption is purely empirical.
2. It is not applicable at high pressure.
3. It does not consider the role of surface area of adsorbent in the process of adsorption.

Sample Problem 1 *Graph between* $\log\left(\frac{x}{m}\right)$ *and* $\log p$ *is a straight line at angle 45° with intercept as shown in the figure. Hence,* $\left(\frac{x}{m}\right)$ *at a pressure of 0.2 atm is*



(a) 0.2 (b) 0.4
(c) 0.6 (d) 0.8

Interpret (b) $\log\left(\frac{x}{m}\right) = \log k + \frac{1}{x}\log p$

Here, $\frac{1}{n} = \tan 45° = 1 \Rightarrow n = 1$

and $\log k = 0.3010 \Rightarrow k = 2$

Again, since, $\left(\frac{x}{m}\right) = kp^{1/n}$

therefore, $\left(\frac{x}{m}\right) = 2(0.2)^1 = 0.4$

(b) Langmuir Adsorption Isotherm

Langmuir developed adsorption isotherm on the basis of the following assumptions

1. The layer of gas adsorbed on the solid adsorbent is one molecule thick.
2. The adsorbed layer is uniform all over the adsorbent.
3. There is no interaction between the adjacent adsorbed molecules.

If 'θ' is the fraction of surface covered by the adsorbed molecules, the fraction of naked area is $(1-\theta)$.

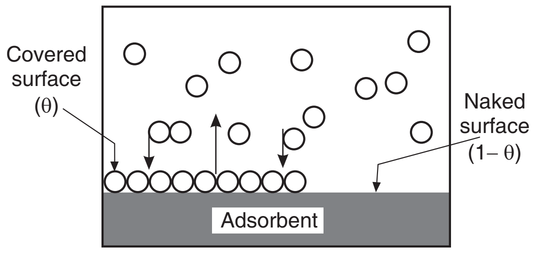


Fig. 5.4 Unimolecular adsorption on solid surface

Rate of desorption,

$$R_d \propto \theta$$

$$\Rightarrow \quad R_d = k_d\,\theta$$

Rate of adsorption,

$$R_a \propto (1-\theta) \Rightarrow R_a = k_a(1-\theta)p$$

where, k_d and k_a are the rate constants for desorption and adsorption processes respectively.

At equilibrium, $R_a = R_d$, giving

$$k_d\theta = k_a(1-\theta)p$$

or

$$\theta = \frac{k_a\,p}{k_d + k_a\,p}$$

$$= \frac{k_a/k_d p}{1 + k_a/k_d p} = \frac{Kp}{1+Kp}$$

where, $K = \frac{k_a}{k_d}$ is the equilibrium constant referred to as **adsorption coefficient.**

According to Langmuir, the degree of adsorption is directly proportional to the θ, *i.e.*, the fraction of surface area occupied,

i.e., $$\frac{x}{m} \propto \theta = k\theta$$

$$\frac{x}{m} = \frac{kKp}{1+Kp}$$

$$\frac{x}{m} = \frac{K'p}{1+kp} \qquad \text{...(i)}$$

where, $K' = kK$ = constant

This relationship is called Langmuir adsorption isotherm.

Eq. (i) may be written as

$$\frac{p}{(x/m)} = \frac{1}{K'} + \left(\frac{k}{K'}\right)p$$

$$\frac{p}{(x/m)} = \frac{1}{K'} + \frac{p}{K''}$$

where, $K'' = k/K'$ = constant

It is of the form $(y = c + mx)$, *i.e.*, equation of straight line but not passing through origin.

Thus, if $\frac{p}{(x/m)}$ is plotted against p, it will result in a straight line.

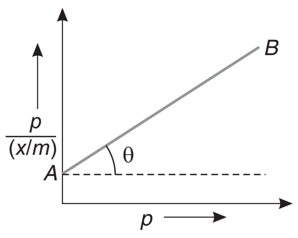


Fig. 5.5 Plot of $\frac{p}{x/m}$ vs p

Slope of the line $AB = \frac{k}{K'} = \tan\theta$

Interpretation of Langmuir Adsorption Isotherm Let us consider the mathematical relation

$$\frac{x}{m}=\frac{K'p}{1+kp}$$

Case I When pressure is very high

then $1+Kp=Kp$

$$\therefore \qquad \frac{x}{m}=\frac{K'p}{Kp}=\text{constant}$$

Thus, at high pressure, the degree of adsorption approaches to a limiting value.

Case II When pressure is low then $1+Kp=1$

$$\therefore \qquad \frac{x}{m}=K'p \quad \text{or} \quad \frac{x}{m}\propto p$$

Thus, degree of adsorption is directly proportional to pressure.

Case III When pressure is moderate then expression is of the form $\frac{x}{m}=Kp^{1/n}$;

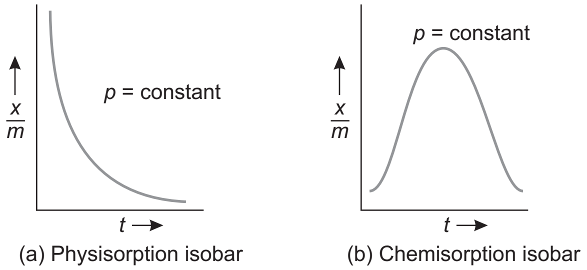
where $\frac{1}{n}$ lies between 0 and 1.

The limitations of Langmuir isotherm is that (i) this isotherm holds good at low pressure but fails at high pressure.

Caution Point *The Langmuir adsorption isotherm is restricted to the formation of unimolecular layer of gas molecules on the surface of solids. However, it was suggested that there is possibility of multimolecular layer of gas molecules on the surface of the solids rather than single layer. On this basis Brunauer, Emmelt and Teller proposed a new theory known as BET theory.*

Adsorption Isobars

A graph drawn between extent of adsorption $\left(\frac{x}{m}\right)$ and temperature '*t*' at a constant pressure of adsorbate gas is known as adsorption isobar.



(a) Physisorption isobar (b) Chemisorption isobar

Fig. 5.6 Adsorption isobars

Adsorption isobars of physical and chemical adsorption show an important difference and this difference is helpful in distinguishing these two types of adsorption.

Adsorption Isostere

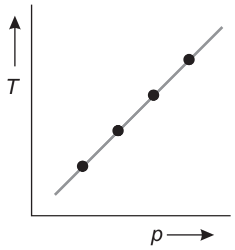


Fig 5.7 Adsorption isostere

Degree of adsorption depends on temperature as well as on pressure. When temperature increases, the extent of adsorption decreases. A linear relationship should exist between temperature and pressure with a certain amount of adsorption. The plot of temperature *versus* pressure for a given amount of adsorption is called adsorption isostere.

Adsorption From Solution

Solids can adsorb solutes from solution also. The following observations have been made in the case of adsorption from solution phase

(i) The extent of adsorption decreases with the increase of temperature.

(ii) The extent of adsorption increases with the increase of surface area of the adsorbent.

(iii) The extent of adsorption depends on the concentration of the solute in solution.

(iv) The extent of adsorption depends on the nature of the adsorption and the adsorbate.

The precise mechanism of adsorption from solution is not known. Freundlich's equation approximately describes the behaviour of adsorption from solution with the difference that instead of pressure, concentration of the solution is taken into account, *i.e.,*

$$\frac{x}{m}=kC^{1/n}$$

(C is the equilibrium concentration, *i.e.,* when adsorption is complete.)

On taking logarithm we get

$$\log\frac{x}{m}=\log k+\frac{1}{n}\log C$$

Plotting $\log x/m$ against $\log C$ gives a straight line which shows the validity of Freundlich isotherm.

This can be tested experimentally by taking solutions of different concentration of acetic acid. Equal volumes of solutions are added to equal amounts of charcoal in different flasks. The final concentration is determined in each flask after adsorption.

The difference in the initial concentration and final concentration gives the value of x. Using the above equation, validity of Freundlich isotherm can be established.

Sample **Problem 2** *The mass x of a solute adsorbed per gram of a solid adsorbent is given by Freundlich isotherm* $x = kC^n$ *where* $(k = 0.160$ *and* $n = 0.431)$. *Calculate the amount of the acetic acid that 1 kg charcoal would adsorb from a 0.837 M acetic acid solution.*

(a) 2.47 (b) 3.25 (c) 4.28 (d) 5.24

Interpret (a) $x = kC^n$

$$= 0.160(0.837)^{0.431}$$

$$= 0.1482 \text{ g acetic acid per gram charcoal}$$

$$-148.2 \text{ g acetic acid per kg charcoal}$$

$$= \frac{148.2}{60} \text{ mol acetic acid per kg charcoal}$$

$$= 2.47 \text{ mol acetic acid per kg charcoal.}$$

Ion-Exchange Adsorption

The specialised specific application of adsorption is seen in the cases of ion-exchangers where ion-exchange adsorption play its role. e.g., synthetic resin are utilised as ion-exchangers. The resin has one ion adsorbed on them, which afterwards releases this ion and adsorbs another like ion. This process is called ion-exchange adsorption.

There may be two types of ionic exchanges

(a) Cationic Exchange

The resin which exchanges cations is called cationic exchanger. These are high polymers containing acidic groups (*e.g.*, sulphonic acid group, SO_3H). The resulting macroanion has adsorbed H^+ ions, which are exchanged when solution of another cation is allowed to flow over it.

$$R^-H^+ + Na^+ \rightleftharpoons R^-Na^+ + H^+$$

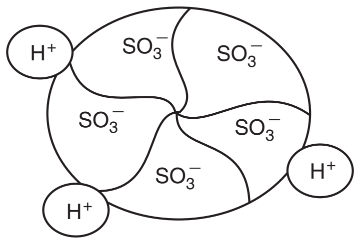


Fig. 5.8 Cationic exchange

(b) Anionic Exchange

The resin which exchanges anions is called anionic exchanger. It contains a basic group (*e.g.,* quaternary ammonium hydroxides, $—N^+R_3OH$). The macrocation has adsorbed OH^- ions, which are exchanged by another anion.

$$R^+OH^- + Cl^- \rightleftharpoons R^+Cl^- + OH^-$$

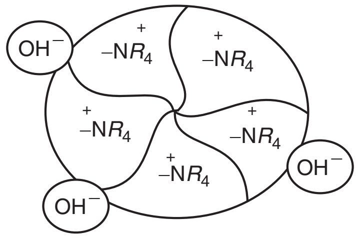


Fig. 5.9 Anionic exchange

The ionic exchangers are reversible and the original exchange resin can be regenerated by the treatment of the exchange resin with suitable acid or base.

Applications of Ion-exchange Adsorption

Ion-exchange adsorption is widely used as

(a) Water Softening

Hard water is softened by passing through a column packed with sodium cation exchanger resin, R^-Na^+.

$$2R^-Na^+ + Ca^{2+} \longrightarrow R_2^-Ca^{2+} + Na^+$$

(b) Deionisation of Water

Using a cation and an anion-exchanger resins, all dissolved ions in water can be removed. Such water is referred to as **deionised** or **demineralised water.**

(c) Medical Uses

Excess sodium salts can be removed from the body fluids by giving the patient a suitable ion-exchanger to eat. Weakly basic anion-exchangers are used to remove excess acid or **acidity** in stomach.

Applications of Adsorption

Adsorption is utilised in several processes, some important of which are as follows :

(a) Production of High Vacuum

A partially evacuated vessel is connected to a container of activated charcoal cooled with liquid air, which adsorbs all the gas molecules in the vessel resulting in a very high vacuum.

(b) Gas Masks

All gas masks contain an adsorbent (finely divided charcoal or activated charcoal) or a series of adsorbents, which remove poisonous gases by adsorption.

(c) Heterogeneous Catalysis

The reactant molecules are expected to be adsorbed on the catalyst surface and decompose later on to yield product molecules.

(d) Removal of Colouring Matter from Solutions

Animal charcoal removes colours of solutions by adsorbing coloured impurities.

(e) In Froth Floatation Process

The low-grade sulphide ores (PbS, ZnS, Cu_2S) are made free from silica and other earthly matters by froth floatation process. Finely divided ore particles mixed with oil are adsorbed on air bubbles created in water with detergent and rise to the surface.

(f) Chromatographic Analysis

Chromatography involves the principal of selective adsorption.

(g) Removal of Impurities

Colloidal silica is used to adsorb impurities from petroleum oils, motor sprits and waxes. Fuller's earth is also used for the same purpose.

(h) Miscellaneous Uses

Ferric hydroxide is used as an antidote adsorbent in case of arsenic poisoning. Many drugs are selectively adsorbed. Various adsorbents are used in industry to recover solvent vapour from air or particular solvents from a mixture.

Silica gel and alumina are used as good drying agents.

Check Point 1

1. Which will absorb more, a lump of charcoal or charcoal powder and why?
2. Why are all adsorption processes exothermic?
3. What is the sign of ΔH and ΔS when a gas gets adsorbed on a solid?
4. Why physisorption is multimolecular whereas chemisorption is unimolecular?
5. Activated charcoal is used in gas masks, why?

5.2 Catalysis

A substance that alters the rate of a reaction without being consumed in the reaction is called **catalyst** and the phenomenon is known as catalysis. As these are not consumed in a reaction that means these are required in very small quantities in the reaction. The term catalyst was given by Berzelius.

Types of Catalysis

Catalysis may be classified into the following classes

(a) Homogeneous Catalysis

If the catalyst is present in the same phase as reactants, it is called **homogeneous catalyst** and the phenomenon is known as homogeneous catalysis. *e.g.,*

(i) Hydrolysis of ester in the presence of mineral acid, *i.e.,*

$$RCOOR'(l) + H_2O(l) \xrightleftharpoons{H_2SO_4(s)} RCOOH + R'OH$$

(ii) Catalytic decomposition of ozone by chlorine atoms in gaseous phase, *i.e.,*

$$O_3(g) + O(g) \xrightarrow{Cl(g)} 2O_2$$

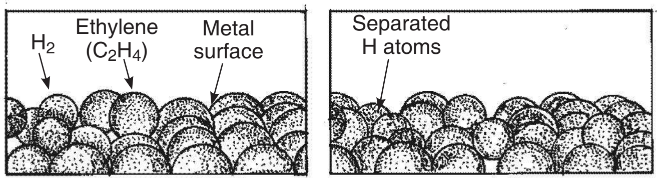
(iii) Oxidation of CO by O_2 in the presence of NO as a catalyst,

i.e., $$2CO(g) + O_2(g) \xrightarrow{NO(g)} 2CO_2(g)$$

(b) Heterogeneous Catalysis

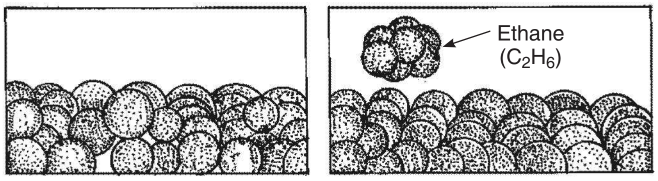
In **heterogeneous catalysis,** the catalyst is present in a different phase from that of reactants. Here, the catalyst is generally a solid (sometimes liquid) and the reactants are generally gaseous. *e.g.,*

(i) Hydrogenation of unsaturated hydrocarbons in the presence of metals like Ni, Pt or Pd at 250°C near about. The process can be seen as



1. H_2 and C_2H_4 approach and adsorb to metal surface

2. Rate-limiting step is H-H bond breakage



3. One H atom bonds to adsorbed C_2H_4

4. Another C-H bond forms and C_2H_6 leaves the surface

Fig. 5.10 Procedure of heterogeneous catalysis

(ii) NH_3 is manufactured from N_2 and H_2 (Haber's process) using Fe as catalyst.

$$N_2(g) + 3H_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$$

(iii) Methyl alcohol synthesis from water gas and H_2 using CuO, ZnO and Cr_2O_3 as catalyst.

$$\underbrace{CO(g) + H_2(g)}_{\text{water gas}} + H_2(g) \xrightarrow{Cu/ZnO-Cr_2O_3(s)} CH_3OH(l)$$

Sample **Problem 3** *Which reaction represents homogeneous catalysis?*

(*a*) $2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$

(*b*) $N_2(g) + 3H_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$

(*c*) $4NH_3(g) + 5O_2(g) \xrightarrow{Pt(s)} 4NO(g) + 6H_2O(g)$

(*d*) $4HCl(g) + O_2(g) \xrightarrow{Cu_2Cl_2(s)} 2H_2O(g) + 2Cl_2(g)$

Interpret (*a*) In reaction given in option (a), the state of reactants SO_2, O_2 and catalyst NO are same, so this is an example of homogeneous catalysis.

In other given reactions, the state of reactants and catalyst used are not same, so these are examples of heterogeneous catalysis.

(c) Positive Catalysis

When the rate of reaction is accelerated by the foreign substance, it is said to be a *positive catalyst* and the phenomenon is known as *positive catalysis. e.g.,*

(i) Oxidation of ammonia in the presence of platinum gauze.

$$4NH_3(g) + 5O_2(g) \xrightarrow[300°C]{Pt(s)} 4NO(g) + 6H_2O(g)$$

(ii) Decomposition of H_2O_2 in the presence of colloidal platinum.

$$2H_2O_2(l) \xrightarrow{Pt} 2H_2O(l) + O_2(g)$$

(iii) Synthesis of ammonia by Haber's process in the presence of a mixture of iron and molybdenum.

$$N_2(g) + 3H_2(g) \xrightarrow[450-500°C]{Fe(s),\ MO} 2NH_3(g)$$

(iv) Oxidation of hydrochloric acid into chlorine by Deacon's process in the presence of $CuCl_2$.

$$4HCl(g) + O_2(g) \xrightarrow[450°C]{CuCl_2(s)} 2Cl_2(g) + 2H_2O(g)$$

(d) Negative Catalysis

When the rate of reaction is retarded by the foreign substance, it is said to be a **negative catalyst** and the phenomenon is called negative catalysis. *e.g.,*

(i) The oxidation of chloroform by air is retarded if some alcohol is added to it.

$$2CHCl_3(l) + O_2(g) \xrightarrow{Alcohol(l)} 2COCl_2(g) + 2HCl(g)$$

(ii) The decomposition of hydrogen peroxide decreases in the presence of glycerine.

$$2H_2O_2(l) \xrightarrow{Glycerine\ (l)} 2H_2O(l) + O_2(g)$$

(iii) The oxidation of sodium sulphite by air is retarded by alcohol.

$$2Na_2SO_3(s) + O_2(g) \xrightarrow{Alcohol(l)} 2Na_2SO_4(s)$$

(iv) The oxidation of benzaldehyde is retarded if some diphenyl amine is added.

$$2C_6H_5CHO(l) + O_2(g) \xrightarrow{Diphenyl\ amine(l)} 2C_6H_5COOH(l)$$

(e) Auto Catalysis

In certain reactions, one of the product acts as catalyst. This type of phenomenon in which one of the products itself acts as a catalyst is known as auto catalysis. *e.g.,*

During hydrolysis of ethyl acetate, acetic acid and ethyl alcohol are formed. The reaction is initially very slow but gradually its rate increases. This is due to the formation of acetic acid which acts as an auto catalyst in this reaction.

$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$$

In the case of homogeneous auto catalytic reaction, rate increases with passage of time because in such cases rate of reaction is directly proportional to concentration of catalyst, *e.g.,*

$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$$

$$\text{Rate} = k\underbrace{[CH_3COOC_2H_5]}_{\text{reactant}}\underbrace{[CH_3COOH]}_{\text{catalyst}}$$

(f) Induced Catalysis

When one reaction does not occur under ordinary conditions, but influenced by other reaction, the phenomeonon is termed as induced catalysis. *e.g.,*

Sodium arsenite solution is not oxidised by air. If, however air is passed through a mixture of the solution of sodium arsenite and sodium sulphite, both of them undergo simultaneous oxidation. The oxidation of sodium sulphite, thus, induces the oxidation of sodium arsenite.

Catalytic Promoters or Activators

It has been observed in a number of cases that the activity of a catalyst is considerably increased by the addition of a second substance which by itself has no catalytic property. Such a substance, which (though not a catalyst by itself) promotes the activity of a catalyst, is called a **promoter.** *e.g.,* Molybdenum (Mo) promotes the catalytic activity of iron in the **Haber process** for the manufacture of ammonia.

$$N_2 + 3H_2 \xrightarrow[Mo]{Fe} 2NH_3$$

Oxides of aluminium, thorium also have the same role in this process.

Catalytic Poisons

When the activity of a catalyst is decreased by the addition of a second substance which by itself has no catalytic property, such a substance is called catalytic poison. *e.g.,* The activity of iron catalyst is decreased (even stop) by the presence of H_2S or CO in the synthesis of ammonia by Haber's process.

$$N_2 + 3H_2 \xrightarrow[H_2S]{Fe} 2NH_3$$

Characteristics of Catalysts

Some important characteristics of catalysts are discussed below

1. They become temporarily involved in a reaction, providing an alternative reaction path of lower activation energy than that for the uncatalysed reaction.
2. They catalyse both forward and backward reactions to the same extent in a reversible reaction and thus have no effect on the equilibrium constant.
3. The catalyst remains unchanged in amount and chemical composition at the end of the reaction. It may undergo some physical change.
4. Only a small quantity of the catalyst is generally needed. One mole of colloidal platinum in 10^8 L can catalyse decomposition of H_2O_2.
5. In certain reactions, the rate of the reaction is dependent on the concentration of the catalyst. *e.g.,* Rate of inversion of cane sugar is dependent on the concentration of H^+ used as catalyst.
6. Rate of the reaction in certain heterogeneous reaction varies with surface area of the catalyst. Hence, finely divided metals are preferred in the form of catalyst.
7. The catalyst does not initiate the reaction and are specific in their action. *e.g.,* starting from H_2 and CO, 3 different products are possible using different catalysts as

   (i) $CO(g) + 3H_2(g) \xrightarrow{Ni} CH_4(g) + H_2O(g)$

   (ii) $CO(g) + 2H_2(g) \xrightarrow{Cu/ZnO—Cr_2O_3} CH_3OH(g)$

   (iii) $CO(g) + H_2(g) \xrightarrow[250°C]{Cu} HCHO$

   The catalyst cannot alter the nature of the products of the reaction.

Activity and Selectivity of Catalyst

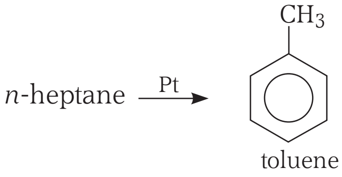
Catalysts possess unique property of activity and selectivity which are discussed below

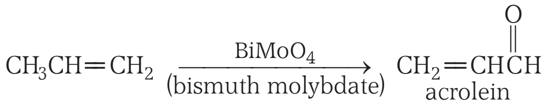
(a) Activity

Activity is the ability of catalysts to accelerate chemical reactions. The degree of acceleration can be as high as 10^{10} times in certain reactions. *e.g.,* Reaction between H_2 and O_2 to form H_2O in the presence of platinum as catalyst takes place with explosive violence. In the absence of catalyst, H_2 and O_2 can be stored indefinitely without any reaction.

(b) Selectivity

It is the ability of catalysts to direct reaction to yield particular products (excluding other). *e.g.,*





$$CH_3CH{=}CH_2 \xrightarrow[\text{(bismuth molybdate)}]{BiMoO_4} \underset{\text{acrolein}}{CH_2{=}CH\overset{\overset{\Large O}{\|}}{C}H}$$

Similarly, acetylene on hydrogenation in the presence of Pt or Ni or Pd catalyst gives ethane.

$$H—C{\equiv}C—H + 2H_2(g) \xrightarrow{Pt/Pd/Ni} \underset{\text{ethane}}{CH_3—CH_3}$$

Hydrogenation of acetylene in the presence of Lindlar's catalyst gives ethylene.

$$H—C{\equiv}C—H + H_2 \xrightarrow[\substack{\text{Sulphur or}\\ \text{quinoline}}]{Pd\text{-}BaSO_4} \underset{\text{ethylene}}{CH_2{=}CH_2}$$

Zeolite : Shape Selective Catalysts

Zeolites are alumino-silicates of the general formula

$$M_{x/n}[(AlO_2)_x \cdot (SiO_2)_y] \cdot mH_2O$$

where, M may be simple cation like Na^+, K^+ or Ca^{2+},

n is the charge on the simple cation.

m is the number of molecules of water of crystallisation.

Some well known zeolites are

Erionite : $Na_2K_2CaMg(AlO_2)_2(SiO_2)_2 \cdot 6H_2O$
Gemelinite : $Na_2Ca(AlO_2)_2(SiO_2)_4 \cdot 6H_2O$
Fauzasite (natural) : $Na_{56}[(Al_2O)_{56}(SiO_2)_{136}] \cdot 250H_2O$
ZSM–5 :$H_x[(AlO_2)_x \cdot (SiO_2)_{96-x}] \cdot 16H_2O$

The characteristic feature of zeolites is the openness of the structure, which permits cavities of different sizes. The open structure is provided by silica in which aluminium occupies $x/(x+y)$ fraction of the tetrahedral sites.

The negative charge of the alumino silicate framework is neutralised by the replaceable cations. The void space forms more than 50% of the total volume, which is occupied by water molecules. The reaction selectivity of zeolites depends upon the size of cavities (cages), pores (apertures) and the distribution of pores in the structure. The pore size in zeolites generally varies from 260 pm to 740 pm.

There is a new class of highly siliceous zeolites with an optimal pore diameter of 550 pm. ZSM-5 is one such zeolite. This converts alcohol to gasoline (petrol) by dehydrating the alcohol and producing a mixture of wide variety of hydrocarbons. The product distribution depends on the ability of the pores to accommodate linear, branched, *iso*-alkanes as well as benzene derivatives.

Theories of Catalysis

The theories explaining the mechanism of catalysis are discussed below

(a) Intermediate Compound Formation Theory

According to this theory, the catalyst first forms an intermediate compound with one of the reactants. The intermediate compound is formed with less energy consumption than needed for the actual reaction. The intermediate compound being unstable combines with other reactant to form the desired product and the catalyst is regenerated.

e.g., a reaction of the type

$$A + B \xrightarrow{K} AB$$

which occurs in the presence of a catalyst *K,* may takes place as

$$\underset{\text{}}{A} + \underset{\text{catalyst}}{K} \longrightarrow \underset{\text{intermediate compound}}{AK} \quad \text{(Slow reaction)}$$

$$AK + B \longrightarrow \underset{\text{product}}{AB} + \underset{\text{catalyst}}{K} \quad \text{(Fast reaction)}$$

Many catalytic reactions can be explained on the basis of this theory. The catalytic oxidation of sulphur dioxide to sulphur trioxide in the lead chamber process probably takes place as

$$\underset{\text{catalyst}}{2NO} + O_2 \longrightarrow \underset{\text{intermediate product}}{2NO_2}$$

$$NO_2 + SO_2 \longrightarrow \underset{\text{product}}{SO_3} + \underset{\text{catalyst}}{NO}$$

This theory explains why the catalyst remains unchanged in mass and chemical composition at the end of the reaction and is effective even in small quantities.

Limitations of this theory are

1. Intermediate compound is formed only in case of homogeneous catalysis only.
2. It cannot explain the action of catalytic promotors, poisions and finely divided catalysts.

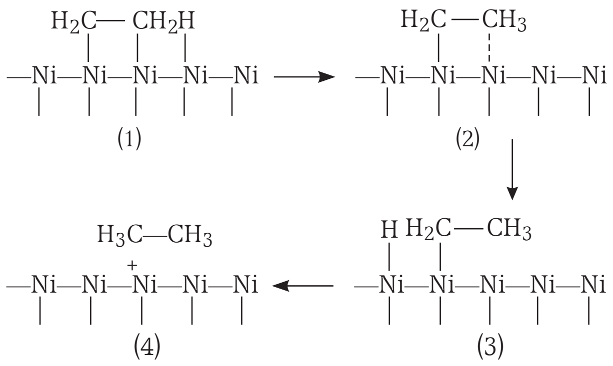
(b) Adsorption Theory

According to this theory, the catalytic activity is localised on the surface of the catalyst. *This theory proposed following steps of mechanism.*

1. Firstly reactants on the solid surface are adsorbed (chemisorption). The adsorption step is thought to involve chemical bonding of reactants to the highly reactive metal atoms on the surface which accompanying breaking or at least weakening of bonds in the reactants.
2. Diffusion of reactants along the surface.
3. Reaction at an active site to form adsorbed product called the **activated surface complex.**
4. Desorption of the product and the catalyst surface is regenerated.

   e.g., hydrogenation of ethene at nickel surface at 400 K takes place in the following stages (1) to (4)

$$CH_2{=}CH_2(g) + H_2(g) \xrightarrow{Ni(s)} CH_3{-}CH_3(g)$$



Applications of Catalysis

Some of the important catalytic processes are listed below

Table 5.2 **Catalysts in Industry**

S.N.	Industrial process	Catalyst used
1.	Acetic acid from acetaldehyde by oxidation with air	V_2O_5
2.	Bosch process for the manufacture of H_2	$Fe_2O_3 + Cr_2O_3$
3.	Contact process for the manufacture of H_2SO_4	V_2O_5, Pt
4.	Dacon's process for the manufacture of Cl_2	$CuCl_2$
5.	Dehydrogenation of alcohol to aldehyde	Cu
6.	Haber's process for the synthesis of NH_3	Fe_2O_3 or Fe + Mo
7.	Lead chamber process for the manufacture of H_2SO_4	NO
8.	Manufacture of vegetable ghee	Ni
9.	Methanol from water gas and H_2	ZnO, Cr_2O_3
10.	Ostwald's process for the manufacture of HNO_3	Pt gauze
11.	Polymerisation of alkenes	H_3PO_4 on Kieselguhr
12.	Preparation of O_2 from $KClO_3$	MnO_2
13.	Synthetic petrol from coal (Bergius process)	Iron oxalate

5.3 Enzyme Catalysis

Enzymes are complex nitrogenous substances secreted by low forms of vegetable and animal organisms. Either the organisms in bulk (like yeast) or the chemicals synthesised by and extracted from them (like yeast extract) may be used for catalysing certain reactions.

Table 5.3 **Examples of Enzyme Catalysts**

S.N.	Reaction	Catalyst used
1.	$\underset{\text{glucose}}{C_6H_{12}O_6} \longrightarrow \underset{\text{ethanol}}{2C_2H_5OH} + 2CO_2$	Zymase
2.	$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$	Invertase
3.	$\underset{\text{maltose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{glucose}}{2C_6H_{12}O_6}$	Maltase
4.	$\underset{\text{starch}}{(C_6H_{10}O_5)_n} + nH_2O \longrightarrow \underset{\text{maltose}}{C_{12}H_{22}O_{11}}$	Diastase
5.	$\underset{\text{urea}}{NH_2CONH_2} + H_2O \longrightarrow 2NH_3 + CO_2$	Urease
6.	$N_2\text{(atmospheric)} \longrightarrow NH_3$	Nitrogenase
7.	$CO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$	Carbonic anhydrase (in human body)

Characteristics of Enzyme Catalysis

Some important characteristics of enzyme catalysis are listed below

1. In the case of enzyme catalysis, the rate of the reaction is much more dependent on the amount of the catalyst (enzyme) than it is in the case of the other types of catalysis.
2. The enzyme reactions are sensitive to temperature, optimum temperature for maximum enzyme activity varies between 15°C to 25°C.
3. The activators or promoters for enzyme reactions are called **co-enzymes** and for every enzyme there is a co-enzyme. If co-enzyme is separated from the enzyme, the activity of the enzyme is paralysed.
4. The addition of electrolyte deactivates enzyme. It is due to coagulation of enzymes.

Mechanism of Enzyme Catalysis

Enzymes are highly specific in their function because of the presence of active site on their surface such as $—NH_2$, —COOH, —SH, —OH, etc. These are actually the active centers on the surface of enzyme particles; when the reactant molecules, called the substance of the reaction,bind at the active site, a chemical change is initiated and an activated complex is formed which then decomposes to yield the products. In most cases, the substrate binds to the active site through intermolecular forces: H-bonds, dipole forces, and other weak attractions.

Two models of enzyme action have been proposed. These are

(a) Lock and key model
(b) Induced fit model

(a) **Lock and Key Model**

According to this model, every lock (active site) has a particular shape and when a particular key (subtrate), which has complementary shape, fits into a lock, the chemical change begins, which finally results into a product (Fig. 5.11)

$$E + S \rightleftharpoons [E - S] \longrightarrow E + P$$

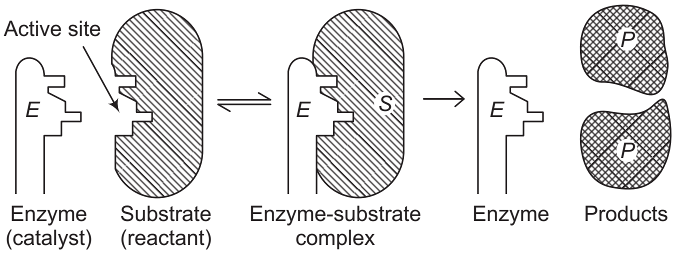


Fig. 5.11 Mechanism of enzyme-catalyzed reaction

(b) Induced Fit Model

Modern X-ray crystallographic and spectroscopic methods have shown that in many cases, unlike an ordinary lock, the protein molecules (enzyme) slightly change the shape when a substrate lands at the active site. The ability of an enzyme to undergo the correct distortion also determines whether the key will fit or not. This refinement of the original lock and key model is known as induced fit model. According to which, a substrate induces the active site to adopt a perfect fit rather than a rigidly shaped lock and key. Therefore, we can picture this model as *hand in a glove,* in which the glove (active site) does not attain its functional shape until the hand (substrate) moves into place.

Check Point 2

1. Explain why rough surface of a catalyst is more effective than smooth surface?
2. Chloroform, an anaesthetic, is kept in dark-coloured bottles and mixed with ethyl alcohol. Explain, why?
3. What is the role of a catalyst in establishing equilibrium?
4. Why is it necessary to remove CO when ammonia is obtained by Haber's process?
5. Why is ester hydrolysis slow in the beginning and becomes faster after sometime?
6. How does BF_3 act as a catalyst in industrial process?
   (Hint because of Lewis acidity)

5.4 Colloidal State

Thomas Graham observed that crystalline substances, such as sugar, urea, sodium chloride etc., could diffuse very readily in solution and could pass through animal and vegetable membranes, while others like glue, gelatin, gum, starch, proteins, etc., did not. He named the former **crystalloids** and the latter **colloids.** According to Graham, the inability of the colloids towards diffusion is due to their high molecular weights (big particle size, thus low osmotic pressure).

However, the term colloid does not apply to a particular class of substances. It is a state and any substance, regardless of its nature, could be converted into a colloid by subdividing it into particles of colloidal size.

Classification of Solution

On the basis of size of particles of dispersed phase (internal phase or discontinuous phase) and dispersion medium (external phase or continuous phase), a solution may be divided into following classes

(a) True Solution

In a true solution (*e.g.,* sugar or salt in water), the dispersed particles are as single molecules or ions. Thus, the diameter of the dispersed particles ranges from 1Å to 10Å (0.1 – 1 mμ).

(b) Suspension

In a suspension (*e.g.,* sand stirred into water), the dispersed particles are aggregates of millions of molecules. The diameter of these particles is of the order of 2000Å (0.2 μ).

(c) Colloidal Solutions

The colloidal solutions are intermediate between true solutions and suspensions.

Thus, the diameter of dispersed particles range from 10 Å to 2000 Å (1 mμ – 0.2 μ).

In fact, the upper limit of colloidal range is fixed as the lower limit of microscopic visibility. *It is not possible to see any particle whose diameter is less than half of the wavelength of light used.*

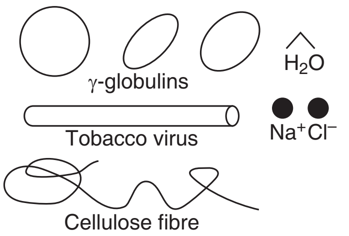


Fig. 5.12 Substances of different diameter

The lowest wavelength of visible light = 4000Å = 0.4 μ (approx.) and thus,

The upper limit of colloidal particles = 2000 Å = 0.2 μ.

The colloidal particles are not necessarily corpuscular in shape, but may be rod-like, disc-like, thin films or long filaments.Thus, *at least one of the dimensions has to be in colloidal range so that the system may be classified as a colloidal one.*

A colloidal system is made of two phases. The substance distributed as the colloidal particles is called the *dispersed phase, discontinuous phase* or *internal phase.* The second phase in which the colloidal particles are scattered is called the *dispersion medium, continuous phase* or *external phase. e.g.,* for a colloidal solution of copper in water, copper particles form dispersed phase and water is dispersion medium.

Sample Problem 4 *Select the correct statement.* **[NCERT]**

(*a*) *colloid is a substance*
(*b*) *colloid is a state of substance*
(*c*) *colloid is state as well as substance*
(*d*) *None of the above*

Interpret (*b*) Colloid is not a substance but a state of substance is a true statement. Because there are some substances which are crystalloid under certain conditions but colloid under the other. *e.g.*, NaCl is such substance which is called a crystalloid and behaves as a crystalloid in aqueous medium. But when mixed with benzene, it behaves as colloid. So, the above statement is correct.

Moreover, the diameter of colloidal particles ranges from 1 to1000 nm.

If particle diameter is lesser than 1 nm, the solution is true solution and if it is more than 1000 nm, the solution is a suspension.

The colloidal state is an intermediate state between these two.

Table 5.4 **Distinction among True, Colloids and Suspensions Solutions**

S.N.	Property	True solutions	Colloids	Suspensions
1.	Particle size	$< 10^{-7}$ cm or 10 Å or 1 mμ	10^{-7} cm to 10^{-5} cm or 10 Å to 10^3 Å or 1 m μ to 100 mμ	$> 10^{-5}$ cm or 10^3 Å or 100 mμ
2.	Visibility	Not visible with any of the optical means	Visible with ultra microscope	Visible with naked eye
3.	Separtion			
	(i) with filter paper	Not possible	Not possible	Possible
	(ii) with membranes	Not possible	Possible	Possible
4.	Diffusion	Diffuses rapidly	Diffuses very slowly	Does not diffuse
5.	Settling	Does not settle	Does not settle but it may settle under centrifuge	Settles under gravity
6.	Nature	Homogeneous	Heterogeneous	Heterogeneous
7.	Appearance	Clear	Generally clear	Opaque

5.5 Classification of Colloids

Colloids are classified on several basis which are given below

On the Basis of Physical States of the Dispersed Phase and Dispersion Medium

On the above basis, colloidal solutions are of following eight types (colloidal dispersion of one gas in another is not possible). These are as tabulated below

Table 5.5 **Different Types of Colloidal Systems**

S.N.	Type name	Dispersed phase	Dispersion medium	Examples
1.	Foam	Gas	Liquid	Whipped cream, shaving cream, soda-water froth
2.	Solid foam	Gas	Solid	Cork, pumice stone, foam rubber.
3.	Aerosol	Liquid	Gas	Fog, mist and clouds.
4.	Emulsion	Liquid	Liquid	Milk, hair cream
5.	Solid emulsion (Gel)	Liquid	Solid	Butter, cheese
6.	Smoke	Solid	Gas	Dust in air
7.	Sol	Solid	Liquid	Paint, ink, colloidal gold, protein, starch ruby glass (gold dispersed in glass), alloys, rock salt
8.	Solid sol	Solid	Solid	Salt

The colloidal solutions in water are termed as **hydrosols** or **aquasols.**

When the dispersion medium in alcohol or benzene, the sols are termed as **alcosols** and **benzosols,** respectively.

Caution Point *A colloidal system of gas in gas is not possible as gases are completely miscible and always form homogeneous true solution.*

On the Basis of Nature of Interaction Between Dispersed Phase and Dispersion Medium

On this basis, colloidal solutions are of the following types

(a) Lyophilic Colloids

Lyophilic colloides are those in which the dispersed phase exhibits a difinite affinity for the medium or the solvent. These are also known as **emulsoids.** Such colloids are more stable and may be taken as reversible colloids. *e.g.*, Dispersion of starch, gum rubber and protein in water form lyophilic colloids.

(b) Lyophobic Colloids

Lyophobic colloids are those in which the dispersed phase has no attraction for the medium or the solvent. These are also known as **suspensoids.** These are generally less stable and regarded as irreversible colloids. *e.g.*, Dispersion of gold, silver, AgCl, $Fe(OH)_3$ and sulphur in water form lyophobic colloids.

Most inorganic colloids are hydrophobic (or lyophobic), while most organic colloids are lyophilic.

The affinity of the sol particles for the medium, in a lyophilic sol, is due to hydrogen bonding in water.

Table 5.6 **Difference between Lyophilic and Lyophobic Colloids**

Property	Lyophilic colloids	Lyophobic colloids
Preparation	Prepared by direct mixing with dispersion medium.	Cannot be prepared by direct mixing with the medium
Charge on particles	Particles carry little or no charge	Particles carry characteristic positive or negative charges
Solvation	Particles are generally solvated	No solvation of particles
Viscosity	Viscosity higher than the dispersion medium as the particles size increases due to solvation. Warm solutions of the dispersed phase on cooling set to a gel	Viscosity is almost same as of medium and do not set to a gel
Surface tension	Surface tension is usually low.	Surface tension is almost the same as that of the solvent
Precipitation	Precipitated by high concentration of electrolytes, when the sol particle's are desolvated. Hence, coagulation is difficult	Precipitated by low concentration of electrolytes. These are easily coagulated
Reversibility	Reversible	Irreversible
Tyndall effect	Do not exhibit Tyndall effect, as they do not scatter light due to relatively small particles size	Exhibit Tyndall effect
Migration in electric field	Particles migrate to anode or cathode, or not at all	Particles migrate to either anode or cathode
Stability	Are more stable	Are less stable

On the Basis of Types of Particles of Dispersed Phase

On the above basis colloidal solutions are of the following types

(a) Multimolecular Colloids

When on dissolution, atoms of smaller molecules of substances (having diameter less than 1 nm) aggregate together to form particles of colloidal dimensions, the particles thus formed are **multimolecular colloids.** These atoms or molecules are held together by van der Waals' forces. They show generally lyophilic character. *e.g.,*

(i) Gold sol contains particles of various sizes having several atoms of gold.

(ii) Sulphur sol consists of particles containing about a thousand of S_8 molecules.

(b) Macromolecular Colloids

In macromolecular type of colloids, the particles are themselves large molecules (usually polymers) which on dissolution form size in the colloidal range. They show generally lyophobic character. *e.g.,*

(i) Starch, cellulose, proteins, enzymes geletin etc., are the examples of naturally occurring macromolecules.

(ii) Nylon, polythene, plastics, polystyrene etc., are examples of synthetic macromolecules.

(c) Associated Colloids

Substance whose molecules aggregate spontaneously in a given solvent to form particles of colloidal dimensions are called **associated colloids**. Such colloids occur in case of soap or detergents, whose molecules are smaller than colloidal size but they aggregate in concentrated solution to colloid size. The colloidal aggregates of soap or detergent molecules formed in the solvent are referred to as **micelles.**

Their molecules contain both lyophilic and lyophobic behaviour. These are the cluster or aggregated particles formed by association of colloids in solution. Micelles may contain 100 or more molecules. These are capable of forming ions. *e.g.,* Soap (sodium stearate, $C_{17}H_{35}COONa$) is a typical example of micelles. When soap is dissolved in water, it gives Na^+ and $C_{17}H_{35}COO^-$ ions.

$$\underset{\text{(sodium stearate)}}{C_{17}H_{35}COONa} \rightleftharpoons \underset{\text{stearate ion}}{C_{17}H_{35}COO^-} + Na^+$$

The stearate ions associated to form **ionic micelles** of colloidal size. It has long hydrocarbon part of $C_{17}H_{35}$ radical which is **lyophobic** and COO^- part which is **lyophilic.** In the figure, the chain corresponds to stearate ion, ($C_{17}H_{35}COO^-$). When the concentration of the solution is below from its CMC (10^{-3} mol L^{-1}), it behaves as **normal electrolyte.** But above this concentration, it aggregates to behave as **micelles.**

The main function of a soap is to reduce oily and greasy dirt to colloidal particles (as emulsion). Soap therefore, are known is **emulsifying agent.**

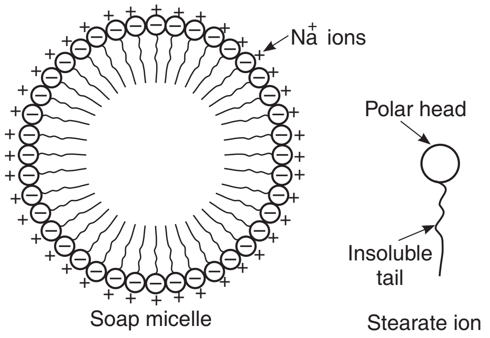


Fig. 5.13 Micelle formation

The cleaning action of soap may be due to

(i) **Solubilisation of grease into the micelle** The grease stain is absorbed into the interior of the micelle, which behaves like liquid hydrocarbon. As the stain is detached from the fabric, the dirt particles sticking to the stain are also removed.

(ii) **Emulsification of grease** When soap solution is added to a fabric, the tails of the soap anions are pegged into the grease stain. The polar heads protrude from the grease surface and form a charged layer around it. Thus, by mutual repulsion, the grease droplets are suspended in water. This emulsified greases stains are washed away.

Some other examples of micelles are sodium palmitate ($C_{15}H_{31}COONa$), sodium lauryl sulphate $[CH_3(CH_2)_{11}SO_3O^-Na^+]$, cetyl trimethyl ammonium bromide $[CH_3(CH_2)_{15}(CH_2)_3N^+Br^-]$ etc.

Critical micelle concentration (CMC)

It is the lowest concentration at which micelle formation apears. It increases with the total surfactant concentration. At concentration higher than CMC, they form extended parallel sheets, known as **lamellar micelles** which resemble biological membranes with two molecular thick. The individual molecule is perpendicular to the sheets such that hydrophilic groups are towards outside in aqueous solution and towards inside in non-polar medium.

Increasing the hydrophobic part of the surfactant molecules favours micelle formation. Micelle formation is opposed by thermal agitation and CMC would thus be expected to increase with increasing temperature.

With ionic micelles, the addition of simple electrolyte reduces the repulsion between the charged groups at the surface of the micelle by the screening action of the added ions. The CMC is, therefore lowered.

Kraft point The temperature above which a surfactant forms micelle is called kraft point.

5.6 Preparation of Colloids

Lyophilic colloids may be prepared by simply warming the solid with the liquid dispersion medium. On the other hand, lyophobic colloids have to be prepared by special methods.

There are in general two methods for the preparation of lyophobic colloids. These are

Dispersion Methods

In these methods the larger particles are broken down to the particles of colloidal size.

Some dispersion methods are discussed below

(a) Mechanical Dispersion

Here **colloidal mill** is used to prepare colloidal sol. In this, the solid along with the liquid dispersion medium is fed into a colloid mill. Colloidal graphite (a lubricant) and printing inks are prepared by this method.

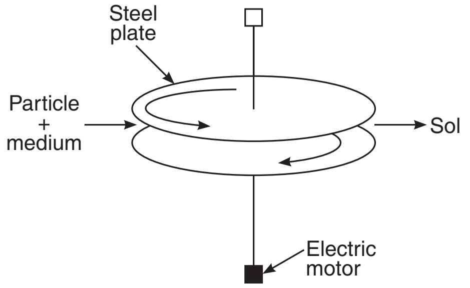


Fig. 5.14 Mechanical dispersion

(b) Bredig's Arc Method [Electro-dispersion]

It is used to prepare hydrosols of metals, *e.g.*, silver, gold, platinum. An arc is struck between the two metal electrodes held close together beneath deionised water. The intense heat of the spark vaporises some of the metal and the vapour condenses under water. Traces of KOH are added to water as stabilising agent.

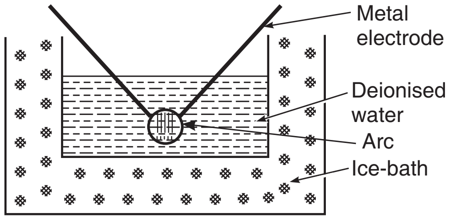


Fig. 5.15 Bredig's arc method

(c) Peptisation

In peptisation, some freshly precipitated ionic solids are dispersed into colloidal solution in water by the addition of small quantities of electrolytes, particularly containing a common ion. The precipitate adsorbs the common ions and electrically charged particles then split from the precipitate as colloidal particles.

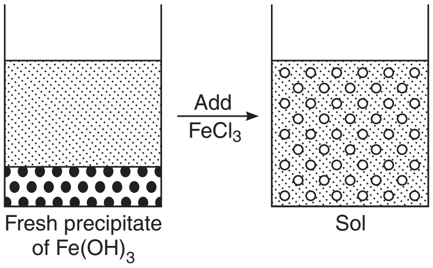


Fig. 5.16 Procedure of peptisation

The dispersal of a precipitated material into colloidal solution by the action of an electrolyte in solution is termed as **peptisation** and the electrolyte is called a **peptising agent.** *e.g.,*

(i) AgCl can be converted into a sol by adding HCl.

(ii) $Fe(OH)_3$ yields a sol by adding $FeCl_3$.

Aggregation Methods

In these methods, colloidal size particles (or molecules) are built up by aggregating ions or smaller particles.

Some important aggregation methods are as follows

(a) Double Decomposition

e.g., the arsenic sulphide sol is prepared by passing a slow stream of H_2S gas through a cold solution of arsenious oxide.

$$As_2O_3 + 3H_2S \longrightarrow \underset{\text{(yellow)}}{As_2S_3\text{(sol)}} + 3H_2O$$

Excess of H_2S is removed by passing in a stream of hydrogen.

(b) Reduction

e.g., Sols of noble metals (Au, Ag, Pt, Pb) can be obtained by treating dilute solutions of their salts with organic reducing agents like tannic acid, ethanol, formaldehyde or phenyl hydrazine etc.

$$AgNO_3 + \text{tannic acid} \longrightarrow \text{Ag} - \text{sol}$$

$$AuCl_3 + \text{tannic acid} \longrightarrow \text{Au} - \text{sol}$$

$$\underset{\text{chloroauric acid}}{2H[AuCl_4]} + 5K_2CO_3 \longrightarrow \underset{\substack{\text{potassium}\\ \text{aurate}}}{2KAuO_2} + 5CO_2 + 8KCl$$

$$2KAuO_2 + \underset{\text{formaldehyde}}{2HCHO} + K_2CO_3 \xrightarrow{\Delta} 2Au\text{(sol)} + 3HCOOK + KHCO_3$$

$KAuO_2$ acts as the stabiliser of the red gold sol obtained represented as

$$m[\text{Au}]\ n\text{auO}_2^-\ (n-x)\ \text{K}^+]\ x\text{K}^+$$

(c) Oxidation

e.g., A sol of sulphur is produced by passing H_2S into a solution of sulphur dioxide.

$$2H_2S + SO_2 \longrightarrow 2H_2O + S\downarrow$$

(d) Hydrolysis

e.g., Sols of the hydroxides of iron, chromium and aluminium are readily prepared by the hydrolysis of salts of respective metals.

$$FeCl_3 + 3H_2O \longrightarrow \underset{\text{(red sol)}}{Fe(OH)_3} + 3HCl$$

(e) Change of Solvent

e.g., When a solution of sulphur or resin in ethanol is added to an excess of water, the sulphur or resin sol is formed owing to decrease in solubility.

(f) Change of Physical State

e.g., Colloidal solutions of certain elements such as mercury and sulphur are obtained by passing their vapour through cold water containing a stabilizer.

Caution Point *The colloidal sol of ice in an organic solvent (as $CHCl_3$ or ether) can be obtained by freezing a solution of water in the solvent. The molecules of water which can no longer be held in solution separately combine to form particles of colloidal size. (Excessive cooling).*

Purification of Colloidal Solution

(a) Dialysis

The process of removing ions (or molecules) from a sol by diffusion through a permeable membrane is called **dialysis.**

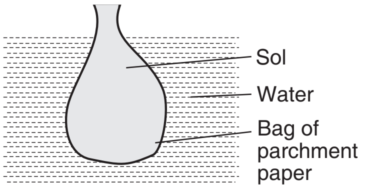


Fig. 5.17 Dialysis

In this process a sol containing dissolved ions or molecules is placed in a bag of permeable membrane (animal bladder, parchment paper and cellophone sheet), dipping in water, the ions diffuse through the membrane. By using a continuous flow of water, the concentration of electrolyte outside the membrane is made zero. *e.g.,* A ferric hydroxide sol can be purified by this method.

(b) Electrodialysis

In this process, dialysis is carried under the influence of electric field. Potential is applied between the metal screen supporting the membranes. This speeds up the migration of ions to the opposite electrodes. Hence, dialysis is greatly accelerated.

This method is not suitable for non-electrolyte impurities like urea etc.

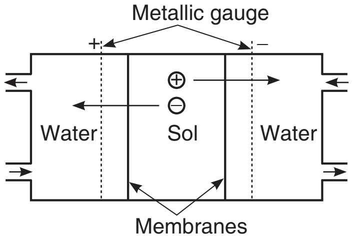


Fig. 5.18 Electrodialysis

(c) Ultrafiltration

If filter paper is impregnated with colloidion (a 4% solution of nitrocellulose in a mixture of alcohol and ether is usually applied) or regenerated cellulose such as cellophone, the pores size is much reduced. Such a modified filter paper is called an **ultrafilter.** The separation of the sol particles from the liquid medium and electrolytes by filtration through an ultra-filter is called **ultrafiltration.**

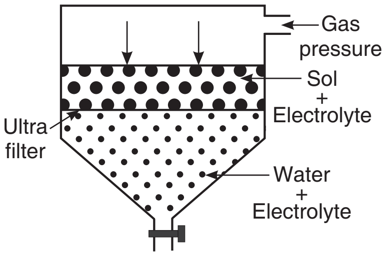


Fig. 5.19 Ultrafiltration of colloidal sol

Ultrafiltration is a slow process. Gas pressure has to be applied to speed it up. The colloidal particles left on the ultra-filter (in form of slime) is stirred onto fresh medium to get back the pure solution.

(d) Electrodecantation

It is used for purification as well as for concentration of the sol. When the **electrodialysis** is carried without stirring, the bottom layer gradually become settled while the top layer, containing pure and concentrated colloid, may be siphoned off.

5.7 Properties of Colloids

The important characteristics exhibited by colloids are as follows

1. General Properties

Some of the general characteristics of colloids are as follows

(a) Heterogeneity

Colloidal system is a heterogeneous system and consist of two phases *viz.* dispersed phase and dispersion medium.

(b) Filtrability

Colloids particles cannot be filtered by ordinary filter papers but can be filtered by ultra-filters.

(c) Diffusibility

Colloidal suspensions, unlike true solutions do not diffuse readily through membranes.

(d) Surface Area

The total surface area of the particles in a colloidal system is enormous, compared with an equal mass of the matter in the usual coarse-grained size. Due to large surface area, colloidal system show extensive adsorption of foreign materials.

(e) Concentration and Density of Sols

The concentration of most of the colloids is small. Most metal sols usually contain 0.1–0.5% metal. Sols of hydroxides and sulphides contains 1–5% of the solid. Concentration of fibrous molecule colloids is also small and usually lies between 0.2–1%.

(f) Colligative Properties

Like true solution, colloidal solution also exhibits colligative properties, but the effects observed are much smaller and except the osmotic pressure, the effects are practically negligible. This is because of their bigger size.

(g) Colour

The colour of a colloidal solution depends on the wavelength of the light scattered by the dispersed particles, which in turn depends on the size and the nature of the particles. *e.g.,* gold sol may be either red or a mixture of red and blue depending upon the size of the particles. Sulphur sol may be colourless, faint yellow or dark yellow in reflected light, while reddish in transmitted light. Dilute milk gives a bluish tinge in reflected light and reddish tinge in transmitted light.

2. Optical Properties (Tyndall effect)

When a strong beam of light is passed through a sol and viewed at right angles, the path of light shows up as a hazy beam or cone. This is due to the fact that sol particles absorb light energy and then emit light in all directions in space (scattering of light). This illuminates the path of the beam in the colloidal dispersion. The phenomenon of the scattering of light by the particles is called Tyndall effect. The illuminated beam or cone formed by the scattering of light by the sol particles is reffered as **Tyndall beam** or **Tyndall cone.**

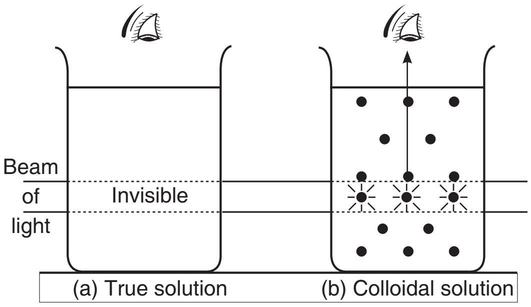


Fig. 5.20 Tyndall effect

True solutions do not exhibit Tyndall effect due to too small size of the ions or absolute molecules.

In order that a system would show Tyndall effect

(i) The refractive index of the dispersed phase and dispersion medium must differ considerably.

(ii) The diameter of the particles of the dispersed phase must not be much smaller than the wavelength of light used.

Examples of Tyndall effects are blue appearance of sky and sea water, visibility of tails of comets, twinkling of stars.

In lyophilic sols, the particles are largely solvated, and so the difference in refractive index is very small, hence Tyndall effect is weak.

3. Electrical Properties of Sols

Stern showed that the double layer is a bit different and made up of

(i) A **compact layer** of positive and negative charges fixed firmly on the particle's surface.

(ii) A **diffused layer** of counter ions diffused into the medium.

The combination of the compact and diffused layers is referred to as **stern double layer.** The diffused layer is only loosely attached to the particle surface.

Because of the distribution of charge around the particles, there is a potential difference between the compact layer and the bulk of solution across the diffuse layer. This is called **electrokinetic** or **zeta potential.** The presence of double layer accounts for the electric properties like **cataphoresis** and **electro-osmosis.**

(a) Electrophoresis or Cataphoresis

The movement of sol particles under an applied potential is called electrophoresis. By noting the direction of movements of the sol particle, it can be determined whether they carry a positive or negative charge.

(b) Electro-osmosis

Electro-osmosis is the movement of the dispersion medium under the influence of applied potential. When the applied potential exceeds the zeta potential, the diffused layer moves and causes electro-osmosis.

4. Kinetic Properties of Sols
(Brownian Motion)

Brownian motion the continuous rapid *zig-zag* movement executed by a colloidal particle in the dispersion medium.

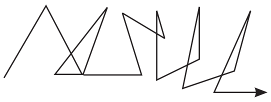


Fig. 5.21 Brownian motion

Suspensions and true solutions do not exhibit Brownian motion. Brownian motion is independent of the nature of colloid but depends on the size of the particles and the viscosity of solution. Smaller the size and lesser the viscosity, faster is the motion.

The Brownian movement is due to the unbalanced bombardment of the particles by the molecules of the dispersion medium. The Brownian movement has a stirring effect which does not permit the particles to settle and thus, is responsible for the stability of sols.

The motion becomes intense at high temperature. The distance between two points decreases at elevated temperature.

5. Charge on Colloidal Particles

The sol particles carry an electric charge *i.e.*, acquire positive or negative charge by preferrential adsorption of positive or negative ions from dispersion medium. *e.g.*,

(i) $Fe(OH)_3$ sol prepared by the hydrolysis of $FeCl_3$ solution adsorbs Fe^{3+} and thus is positively charged.

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl$$

$$Fe(OH)_3 + FeCl_3 \longrightarrow \underset{\text{fixed part}}{[Fe(OH)_3]Fe^{3+}} : \underset{\text{diffused part}}{3Cl^-}$$

Positive charge on colloidal sol is due to adsorption of Fe^{3+} ion [common between $Fe(OH)_3$ and $FeCl_3$].

(ii) As_2S_3 colloidal sol is obtained when As_2O_3 is saturated with H_2S.

$$As_2O_3 + 3H_2S \longrightarrow As_2S_3 + 3H_2O$$

As_2S_3 adsorbs S^{2-} ion (common between $H_2S$and As_2S_3) and thus is negatively charged.

$$As_2S_3 + H_2S \longrightarrow \underset{\text{fixed part}}{[As_2S_3]S^2} : \underset{\text{diffused part}}{2H^+}$$

(iii) AgI in contact with $AgNO_3$ forms positively charged colloidal sol due to adsorption of Ag^+ ion.

$$\underset{\text{fixed part}}{AgI + AgNO_3 \longrightarrow [AgI]Ag^+} : \underset{\text{duffused part}}{NO_3^-}$$

(iv) AgI in contact with KI forms negatively charged colloidal sol due to adsorption of I^- ion.

$$\underset{\text{fixed part}}{AgI + KI \longrightarrow [AgI]I^-} : \underset{\text{diffused part}}{K^+}$$

(v) SnO_2 is acidic medium forms positively charged colloidal sol due to adsorption of Sn^{4+} formed.

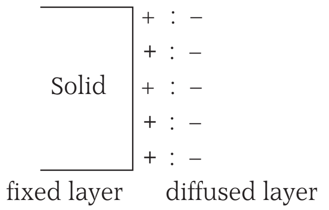
$$SnO_2 + 4H^+ \longrightarrow Sn^{4+} + 2H_2O$$
$$SnO_2 + Sn^{4+} \longrightarrow [SnO_2]Sn^{4+}$$

SnO_2 in alkaline medium forms negatively charged colloidal sol due to adsorption of SnO_3^{2-} formed.

$$SnO_2 + 2OH^- \longrightarrow SnO_3^{2-} + H_2O$$
$$SnO_2 + SnO_3^{2-} \longrightarrow [SnO_2]SnO_3^{2-}$$

There is formation of an **electrical double layer** of opposite charges on the surface of colloidal particles.

$$[AgI]I^- : K^+$$
$$[AgI]Ag^+ : NO_3^-$$
$$[Fe(OH)_3]Fe^{3+} : 3Cl^-$$



The combination of the two layers of positive and negative charges around the sol particles is called **Helmholtz electrical double layer.**

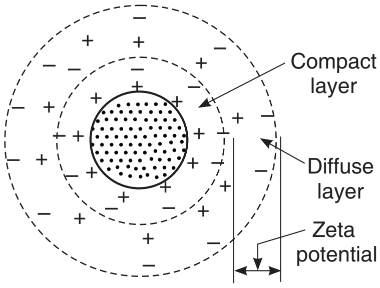


Fig. 5.22 Formation of electrical double layer

Potential difference of this electrical double layer is called **zeta potential** or **electrokinetic potential,** Z, given by

$$Z = \frac{4\pi\eta u}{D}$$

where η is called the coefficient of viscosity, D is the dielectric constant of the medium and u is the velocity of the colloidal particles when an electric field is applied.

Using water as the dispersion medium, the charges on some common sols are as

Negatively charged → Metals, *e.g.,* Au, Ag, Pt; arsenic sulphide, starch, clay

Positively charged → Ferric hydroxide; aluminium hydroxide, basic dyes, haemoglobin.

Sample **Problem 5** *Which of the following process is not responsible for the presence of electric charge on the sol particles?* **[NCERT Exemplar]**

(*a*) *Electron capture by sol particles.*
(*b*) *Adsorption of ionic species from solution.*
(*c*) *Formation of Helmholtz electrical double layer.*
(*d*) *Adsorption of ionic species from solution.*

Interpret (*d*) In adsorption, the ionic species is distributed evenly throughout the solution, so no charge is developed at the surface. Hence, it is not responsible for the presence of electric charge on the sol particles.

Hot Spot 2

COAGULATION or Precipitation

It is also an important topic of the chapter for JEE Main examination. The level of questions is generally average.

The colloidal particles contain positive or negative charges. The repulsive forces between them do not allow them to settle. If, some how, the charge is removed, they aggregate (or flocculate) and settle down under the action of gravity. The flocculation and settling down of the discharged sol particles is called **coagulation** or **precipitation.**

The coagulation of given colloid can be brought about in many ways

1. By addition of electrolytes
2. By electrophoresis
3. By boiling
4. By persistent dialysis
5. By mixing two oppositely charged sols, called **mutual coagulation**

The most important method among these is precipitation by adding some suitable electrolyte. The coagulating power of ion is decided by **Hardy-Schulze Rule.** According to Hardy and Schulze, *"the precipitating effect of an ion on dispersed phase of opposite charge increases with the valence of the ions".*

e.g., For precipitating an As_2S_3 sol (–ve), the precipitating power of Al^{3+}, Ba^{2+}, Na^+ ions (+ve) is in the order

$$Al^{3+} > Ba^{2+} > Na^+$$

Similarly, for precipitating $Fe(OH)_3$ sol (+ve), the precipitating power of anions $[Fe(CN)_6]^{3-}$, SO_4^{2-}, Cl^- (–ve) is in the order

$$[Fe(CN)_6]^{3-} > SO_4^{2-} > Cl^-.$$

The minimum concentration of an electrolyte in millimoles per litre required to cause precipitation of a sol is called **flocculation value.** The smaller the flocculating value, the higher will be the coagulating power of an ion.

Sample Problem 6 *In the coagulation of a positive sol, the focculation powers of* Cl^-, SO_4^{2-}, PO_4^{3-} *and* $[Fe(CN)_6]^{4-}$ *are in the order of*

(a) $Cl^- > SO_4^{2-} > [Fe(CN)_6]^{4-} > PO_4^{3-}$
(b) $Cl^- > PO_4^{3-} > SO_4^{2-} > [Fe(CN)_6]^{4-}$
(c) $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^-$
(d) $Cl^- > SO_4^{2-} > PO_4^{3-} > [Fe(CN)_6]^{4-}$

Interpret (c) According to Hardy-Schulze rule, the flocculation power is directly proportional to the charge. Thus, correct order is

$$[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^-$$

Sample Problem 7 *Number of moles of* $[NH_4OH]$ *required to coagulate* 1 *mole of* $[Fe(OH)_3]Fe^{3+}$ *are*

(a) 1 (b) 2
(c) 3 (d) 4

Interpret (c) $3NH_4OH + [Fe(OH)_3]Fe^{3+} \longrightarrow Fe(OH)_3 \downarrow$

$\therefore$ Moles of NH_4OH required to coagulate $[Fe(OH)_3]Fe^{3+}$ ion = 3

5.8 Protective Colloids

Lyophobic colloids are readily precipitated by small amounts of electrolytes. However, these colloids are often stabilised by the addition of lyophilic colloids, which form a layer around particles, thus, protect them from electrolytes. The property of lyophilic colloids to prevent the precipitation of lyophobic colloid is called **protection.** The lyophilic colloid used is called protective colloid.

Gold Number

The protective power of lyophilic colloids is measured in terms of gold number. This terms was introduced by **Zsigmondy** and can be defined as : *"the number of milligrams of a hydrophilic colloid that will just prevent the precipitation of* 10 *mL of a gold sol on the addition of* 1 *mL of* 10% *sodium chloride solution".* The smaller the gold number of hydrophilic colloids, the greater is its protective power.

Sample Problem 8 *The gold numbers of three protective colloids x, y and z are* 0.1, 0.01, *and* 0.001 *respectively. The increasing order of their protective power is*

(a) *x, y, z*
(b) *z, y, x*
(c) *x, z, y*
(d) *y, z, x*

Interpret (a) $\because$ Protective power $\propto \dfrac{1}{\text{Gold number}}$

$\therefore$ The increasing order of protective power

$$\underset{(0.1)}{x} < \underset{(0.01)}{y} < \underset{(0.001)}{z}$$

Rubbin Number

It is the mass in milligrams of a colloid per 100 cc of solution which just prevents the colour change of standard sol of dye congo-Rubbin from red to violet when 0.16 g equivalent KCN is added to it.

5.9 Emulsion

An **emulsion** is a dispersion of finely divided droplets in another liquid. Thus, these are liquid-liquid colloidal systems. Generally, one of two liquids is water and the other, which is immiscible with water, is designated as oil.

Types of Emulsions

Two types of emulsions may be formed with two types of liquids.

(a) Oils Dispersed in Water (O/W type)

In this system, water acts as dispersion medium. *e.g.,* milk, in which tiny droplets of liquid fat are dispersed in water.

(b) Water Dispersed in Oil (W/O type)

In this system, oil acts as dispersion medium. *e.g.,* stiff greases, in which water being dispersed in lubricating oil.

Preparation of Emulsion

The dispersion of a liquid in the form of an emulsion is called **emulsification.** This is done by agitating a small proportion of one liquid with the bulk of the other, or by passing a mixture of two liquids through a colloidal mill known as **homogenizer.**

Emulsifying Agent

The emulsions obtained by shaking the two liquids are unstable. A small amount of a third substance is added during the preparation to stabilise the emulsion. These are called **emulsifiers** or emulsifying agents. These may be a soap, synthetic detergent or a hydrophilic colloid, protein, gum and agar. The emulsifier concentrates at the interface and reduces surface tension on the side of one liquid, which rolls into droplets.

Emulsions can be diluted with any amount of the dispersion medium. On the other hand, the dispersed liquid when mixed with it, at once form a separate layer.

Breaking of Emulsions

Emulsions can be broken to get the constituent liquids by heating, freezing, centrifuging or by addition of appreciable amounts of electrolytes. They are also broken by destroying the emulsifying agent.

5.10 Applications of Colloids

Most of the substances, we come across in our daily life, are colloidal in nature. The meal we eat, the clothes we wear, the wooden are largely composed of colloids.

The applications of colloids are limitless. *In general, these can be divided into following two classes*

1. Natural Applications

The natural applications of colloids include.

(a) Blue Colour of The Sky

Colloidal particles scatter blue light. Dust particles along with water suspended in air scatter blue light which reaches our eyes and the sky looks blue to us.

(b) Foods

Many of foods are colloids, *e.g.,* milk, salad deserts, fruit jellies and whipped cream. Bread is a dispersion of air in baked dough.

(c) Soils

Fertile soils are colloidal in nature in which humus acts as a protective colloid.
On account of colloidal nature, soils absorb moisture and nourishing materials.

(d) Formation of Delta

River water is a colloidal solution of clay. Seawater contains a number of electrolytes. When river water meets the seawater, the electrolytes present in seawater coagulate the colloidal solution of clay which gets deposited with the formation of delta.

(e) Artificial Rain

Artificial rain is caused by spraying oppositely charged colloidal dust or sand particles over the clouds by aeroplanes. The colloidal water particles of the clouds are neutralised and coagulate to bigger water drops which cause artificial rain.

(f) Digestion of Fats

Digestion of fats in intestines is aided by emulsification. A little amount of fat forms a sodium soap with alkaline medium of intestine and this soap emulsifies rest of fat. It is easier for digestive enzymes to carry out their function on emulsified fat.

2. Technical Applications

These technical applications of colloids include.

(a) Electrical Precipitation of Smoke

Smoke is a colloidal solution of solid particles such as carbon, arsenic compounds, dust, etc., in air. The smoke, before it comes out from the chimney, is led throughout a chamber containing plates having a charge opposite to that carried by smoke particles. The particles on coming in contact with these plates lost their charge and get precipitated. The particles thus, settle down on the floor of the chamber. The precipitator is called **cottrell precipitator.**

(b) In Disinfectants

Dettol and lysol give oil in water type emulsion with water.

(c) In Metallurgical Operations

Metal ores are concentrated by froth floatation process, which involves the treatment of pulverized ore in emulsion of pine oil.

(d) Rubber Plating

The negatively charged rubber particles from the rubber sol are deposited on wires, handles of different tools, rubber gloves, etc., by electroplating.

(e) Sewage Disposal

Sewage water contains particles of dirt, rubbish etc., which are of colloidal size, carry charge and therefore, do not settle down easily. These particles can be removed by electrophoresis. The deposited matter is used as manure and the water left behind is used for irrigation.

(f) Medicines

Colloidal medicines being finely divided, are more effective and are easily absorbed in our system. Halibut-liver oil and cod-liver oil are emulsions of the respective oils in water. Many ointments are physiologically active components dissolved in oil and made into an emulsion with water. Antibiotics such as penicillin and streptomycin are produced in colloidal form which are suitable for injections.

Following are some commonly used medicines in colloidal forms.

(i) **Aragrol and Protargol** used as eye lotions and are protected silver solution.
(ii) **Colloidal metals** Au, Mn, Ca used in intramuscular injections.
(iii) **Colloidal antimony** curing kalazar.
(iv) **Colloidal sulphur** germ killer in plants.
(v) **Cod liver oil** tonic in nature.

(g) Purification of Municipal Water

Colloidal particles in water are removed by coagulating with aluminium sulphate (alum).

$$Al^{3+} + 3H_2O \longrightarrow Al(OH)_3 + 3H^+$$

$$Al(OH)_3 + 4H_2O + H^+ \longrightarrow Al(OH)_3(H_2O)_4^+$$

(h) Adsorption Indicators

They function by preferential adsorption of ions onto sol particles, *e.g.,* fluorescein used in titration of NaCl against $AgNO_3$ solution.

(i) Photographic Plates and Films

The photographic plates or films are precipitated by coating an emulsion of the light sensitive silver bromide in gelatin over glass plates or celluloid films.

(j) Disinfectants

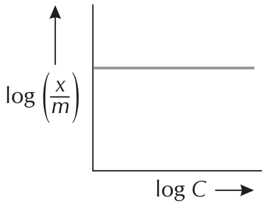
The disinfectants such as dettol and lysol give emulsion of oil in water type when mixed with water.

Check Point 3

1. How can one distinguish colloidal solution from true solution?
2. Colloidal sulphur exhibits Brownian movement while a solution of sulphur in CS_2 does not. Explain it.
3. Explain how is a delta formed?
4. Explain why medicines in colloidal state are more effective?
5. Why does sky appear blue?
6. Tyndall effect is not exhibited by a sugar solution but milk exhibits it. Explain.

WORKED **OUT**
Examples

Example 1 *For the adsorption of solution on a solid surface* $\frac{x}{m} = kC^{1/n}$ *adsorption isotherm of* $\log\left(\frac{x}{m}\right)$ *and* $\log C$ *was found the following type*



This is when

(a) $C = 0$ (b) $C = 2\,M$

(c) C = *constant* (d) $\frac{1}{n} = 0$

Solution (d) Here, $\theta = 0 \Rightarrow \tan\theta = \tan 0 = 0$

$$\because \quad \frac{1}{n} = \tan\theta \quad \therefore \quad \frac{1}{n} = 0$$

Example 2 *It is said that finely divided catalyst has greater catalytic activity than the solid in compact form. For a catalysed reactions, a total surface area of* $6291456\ \text{cm}^2$ *is required for adsorption of gaseous reactants. How many splits should be made of a cube exactly 1 cm in length?*

(a) 10 (b) 15 (c) 20 (d) 30

Solution (c) Total surface area of six faces of a cube $= 6 \times (1 \times 1) = 6\ \text{cm}^2$

now suppose that we divide each side in two equal halves, then there will be total of eight cubes each of side 0.5 cm.

then total surface area $= 8 \times 6 \times \left(\frac{1}{2} \times \frac{1}{2}\right) = 12\ \text{cm}^2$

General formula of surface area on n splits (cube) is

$$= 8^n \times 6 \times \left(\frac{1}{2}\right)^{2n} = 2^n \times 6$$

$$2^n \times 6 = 6291456\ \text{cm}^2$$

On solving $\quad n = 20$

Thus, total of 20 splits are to be made of a cube of 1 cm length.

Example 3 *A sample of charcoal weighing 6.00 g was brought into contact with a gas contained in a vessel of 1 L capacity at 27°C. The pressure of the gas was found to fall from 700 to 400 mm. Calculate the volume of the gas (reduced to STP) that is adsorbed per gram of the adsorbent under the condition of the experiment (density of charcoal sample is* $1.5\ g\ cm^{-3}$*)*

(a) 30 *mL* (b) 60 *mL* (c) 90 *mL* (d) 120 *mL*

Solution (b) The adsorption is taking place in a closed vessel hence as pressure falls, there is correspondingly increase in volume and to keep volume constant, excess of the volume of the gas would be adsorbed.

Using $\quad p_1V_1 = p_2V_2$

$$V_2 = p_1\frac{V_1}{p_2} = 700 \times \frac{1000}{400} = 1750\ \text{mL}$$

Actual volume of the flask $= 1000 -$ volume of charcoal

$$= 1000 - \frac{6.00}{1.50} = 996\ \text{mL}$$

Volume of the gas adsorbed $= 1750 - 996 = 754$ mL

Volume of the gas adsorbed per gram of charcoal

$$= \frac{754}{6} = 125.67\ \text{mL g}^{-1}$$

Volume of the gas adsorbed per gram at STP $\left(\text{Using } \frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}\right)$

$$= \frac{125.67 \times 400 \times 273}{300 \times 760} = 60.19\ \text{mL}$$

Example 4 *The density of gold is* $19\ g/cm^3$. *If* 1.9×10^{-4} *g of gold is dispersed in one litre of water to give a sol having spherical gold particles of radius 10 nm, then the number of gold particles per* mm^3 *of the sol will be*

(a) 1.9×10^{12} (b) 6.3×10^{14}

(c) 6.3×10^{10} (d) 2.4×10^{6}

Solution (d) Volume of the gold dispersed in 1 L water

$$= \frac{\text{Mass}}{\text{Density}} = \frac{1.9 \times 10^{-4}}{19} = 1 \times 10^{-5}\ \text{cm}^3$$

Radius of gold sol particle $= 10\ \text{nm} = 10 \times 10^{-9}$ m

$$= 10 \times 10^{-7}\ \text{cm} = 10^{-6}\ \text{cm}$$

Volume of the gold sol particle $= \frac{4}{3}\pi r^3 = \frac{4}{3} \times \frac{22}{7} \times (10^{-6})^3$

$$= 4.19 \times 10^{-18}\ \text{cm}^3$$

No. of gold sol particles in $1 \times 10^{-5}\ \text{cm}^3 = \frac{1 \times 10^{-5}}{4.19 \times 10^{-18}}$

$$= 2.38 \times 10^{12}$$

No. of gold sol particles in one $\text{mm}^3 = \frac{2.38 \times 10^{12}}{10^6} = 2.38 \times 10^6$

Start Practice for JEE Main

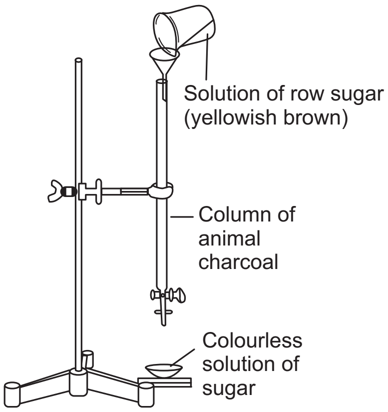
Round I (Topically Divided Problems)

Adsorption

1. Which of the following is an example of absorption? [NCERT Exemplar]

(a) Water on silica gel
(b) Water on calcium chloride
(c) Hydrogen on finely divided nickel
(d) Oxygen on metal surface

2. Which of the following phenomenon is applicable to the process shown in the figure? [NCERT Exemplar]



(a) Absorption (b) Adsorption
(c) Coagulation (d) Emulsification

3. The substance that gets adsorbed on the surface of solid is called

(a) adsorbate (b) adsorbent
(c) micelle (d) absorbent

4. Which of the following is not a favourable condition for physical adsorption? [NCERT Exemplar]

(a) High pressure
(b) Negative ΔH
(c) Higher critical temperature of adsorbate
(d) High temperature

5. Extent of physisorption of a gas increases with [NCERT Exemplar]

(a) increase in temperature
(b) decrease in temperature
(c) decrease in surface area of adsorbent
(d) decrease in strength of van der Waals' forces

6. Which of the following is adsorbed greatly by activated charcoal?

(a) SO_2 (b) CO_2
(c) NO_2 (d) Water vapours

7. Which of the following statements is correct about Langmuir's adsorption isotherm?

(a) It forms monolayer
(b) It is reversible in nature
(c) It occurs at low temperature
(d) None of the above

8. Which of the following is less than zero during adsorption?

(a) ΔG (b) ΔS
(c) ΔH (d) All of these

9. At the equilibrium position in the process of adsorption [NCERT Exemplar]

(a) $\Delta H > 0$ (b) $\Delta H = T\Delta S$
(c) $\Delta H > T\Delta S$ (d) $\Delta H < T\Delta S$

10. Indicate the correct statement

(a) In chemisorption, there is no disruption of bonding in an adsorbed molecule
(b) The rate of decomposition of the substance adsorbed on a surface depends on the surface coverage
(c) In heterogeneous catalytic reaction, no surface reaction occurs
(d) Increase in surface area of catalyst reduces the surface phase reactions

11. Extent of adsorption of adsorbate from solution phase increases with **[NCERT Exemplar]**
(a) increase in amount of adsorbate in solution
(b) decrease in surface area of adsorbent
(c) increase in temperature of solution
(d) decrease in amount of adsorbate in solution

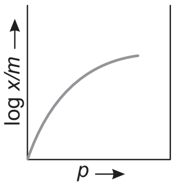
12. Which is correct in the case of van der Waals' adsorption?
(a) High temperature, low pressure
(b) Low temperature, high pressure
(c) Low temperature, low pressure
(d) All of the above

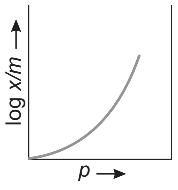
13. Adsorption is accompanied by
(a) ΔS of system is negative
(b) decrease in enthalpy of system
(c) $T\Delta S$ for the process is negative
(d) All of the above

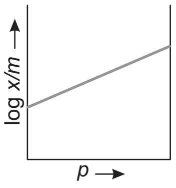
14. Which of the following statements is incorrect?
(a) Physical adsorption occurs at very low temperature and chemisorption occur at all temperature
(b) The magnitude of chemisorption decreases with rise in temperature and physisorption increases with rise in temperature
(c) Chemisorption is irreversible and physisorption is reversible
(d) In physisorption, the activation energy of desorption is very low and in chemisorption, the activation energy of desorption is very high

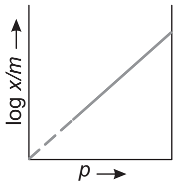
15. What will be the Freundlich adsorption isotherm equation at high pressure ?
(a) $\frac{x}{m} = k$
(b) $\frac{x}{m} = kp^{1/n}$
(c) $\frac{x}{m} = kp$
(d) None of these

16. Which of the following curves is in accordance with Freundlich adsorption isotherm? **[NCERT Exemplar]**

(a)


(b)


(c)


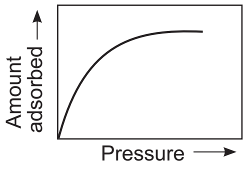
(d)


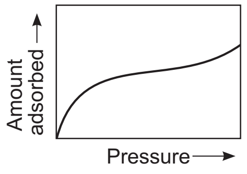
17. Which among the following statements is false?
(a) Adsorption may be monolayered or multilayered
(b) Particle size of adsorbent will not effect the amount of adsorption
(c) Increase of pressure increases the amount of adsorption
(d) Increase of temperature may decrease the amount of adsorption

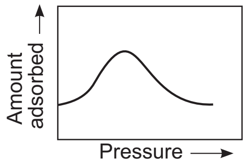
18. In Langmuir's model of adsorption of a gas on a solid surface,
(a) the rate of dissociation of adsorbed molecules from the surface does not depend on the surface covered
(b) the adsorption at a single site on the surface may involve multiple molecules at the same time
(c) the mass of gas striking a given area of surface is proportional to the pressure of the gas
(d) the mass of gas striking a given area of surface is independent of the pressure of the gas

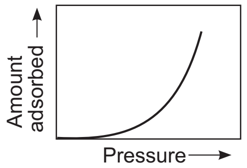
19. According to Freundlich adsorption isotherm, which of the following is correct?
(a) $\frac{x}{m} \propto p^1$
(b) $\frac{x}{m} \propto p^{1/n}$
(c) $\frac{x}{m} \propto p^0$
(d) All of the above are correct for different ranges of pressure

20. Which of the following curves do not correspond to adsorption isotherms?

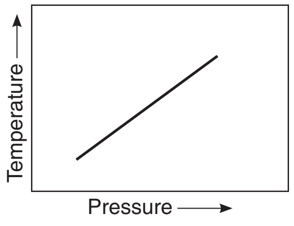
(a)


(b)


(c)


(d)


21. The curve showing the variation of pressure with temperature for a given amount of adsorption is called



(a) adsorption isobar
(b) adsorption isotherm
(c) adsorption isostere
(d) adsorption isochore

22. What is the role of activated charcoal in gas mask used in coal mines? **[NCERT Exemplar]**
(a) Absorption of poisonous gases
(b) Adsorption of poisonous gases
(c) Neutralisation of gases
(d) None of the above

23. On the basis of data given below predict which of the following gases shows least adsorption on a definite amount of charcoal? **[NCERT Exemplar]**

Gas	CO_2	SO_2	CH_4	H_2
Critical temp/K	304	630	190	33

(a) CO_2 (b) SO_2 (c) CH_4 (d) H_2

Catalysis (Including Enzyme Catalysis)

24. Term catalyst was given by
(a) Rutherford (b) Berzilius
(c) Wohler (d) Kolbe

25. Catalysis is a phenomenon in which
(a) a substance alters the speed of the chemical reaction
(b) heat is evolved in a chemical reaction
(c) the reaction is induced by light
(d) None of the above

26. In chemical reaction, catalyst
(a) alters the amount of the products
(b) lowers the activation energy
(c) decreases the ΔH of forward reaction
(d) increases the ΔH of forward reaction

27. A catalyst in finely divided state is more efficient because in this state
(a) it has larger activation energy
(b) it can react with one of the reactants more efficiently
(c) it has large surface area
(d) All of the above

28. Which of the following reactions is an example of negative catalysis?
(a) $2H_2O_2 \xrightarrow{Pt} 2H_2O + O_2$
(b) $N_2 + 3H_2 \xrightarrow{Fe} 2NH_3$
(c) $2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$
(d) $4CHCl_3 + 3O_2 \xrightarrow{C_2H_5OH} 4COCl_2 + 2Cl_2 + 2H_2O$

29. Which of the following is a heterogeneous catalysis?
(a) $2C_2H_5OH \xrightarrow{\text{Conc } H_2SO_4} C_2H_5OC_2H_5 + H_2O$
(b) $2CO + O_2 \xrightarrow{NO} CO_2$
(c) $SO_2 + \frac{1}{2} O_2 \xrightarrow{NO_2} SO_3$
(d) $SO_2 + \frac{1}{2} O_2 \xrightarrow{V_2O_5} SO_3$

30. By dividing the catalyst into fine powder there will be increase in
(a) surface area
(b) free valancies
(c) active centres
(d) All of these

31. Which of the following process does not occur at the interface of phases? **[NCERT Exemplar]**
(a) Crystallisation
(b) Heterogenous catalysis
(c) Homogeneous catalysis
(d) Corrosion

32. Which of the following acts as a catalyst?
(a) Metals with variable valency
(b) Metals with non-variable valency
(c) Non-metals with fixed valency
(d) Inert gases

33. According to the adsorption theory of catalysis, the speed of the reaction increases because
(a) the concentration of reactant molecules at the active centres of the catalyst becomes high due to adsorption
(b) in the process of adsorption, the activation energy of the molecules becomes large
(c) adsorption produces heat which increases the speed of the reaction
(d) adsorption lowers the activation energy of the reaction

34. Shape selective catalysts are so called because of
(a) the shape of the catalyst
(b) the specificity of the catalyst
(c) the size of the pores of catalyst which can trap selective molecules only
(d) their use for only some selected reaction

35. Catalyst used in Haber's process is
(a) nickel powder
(b) iron and molybdenum powder
(c) black lead
(d) iodine

36. In contact process of manufacture of H_2SO_4, the catalyst used is
(a) iron
(b) V_2O_5
(c) chromium
(d) oxides of nitrogen

37. A biological catalyst is
(a) an amino acid
(b) a carbohydrate
(c) a nitrogen molecule
(d) an enzyme

Colloids and their Applications

38. Point out the false statement.
(a) The size range of colloidal particles is 10–2000Å
(b) Colloidal solutions are homogeneous systems
(c) Colloids carry charge
(d) Colloids show Tyndall effect

39. A colloidal system having a solid substance as a dispersed phase and a liquid as a dispersion medium is classified as **[NCERT Exemplar]**
(a) solid sol (b) gel
(c) emulsion (d) sol

40. Which of the following is mismatched?

	Dispersed phase	Dispersed medium	Specific name
(a)	liquid	liquid	emulsion
(b)	solid	solid	solid sol
(c)	liquid	gas	aerosol
(d)	gas	solid	foam

41. Fog is a colloidal solution of
(a) liquid particles dispersed in a gas
(b) gaseous particles dispersed in a liquid
(c) solid particles dispersed in a liquid
(d) solid particles dispersed in a gas

42. Which will not form colloidal solution?

(Where DP = Dispersed phase and DM = Dispersion medium)
(a) DP–gas, DM–liquid (b) DP–liquid DM–solid
(c) DP–gas, DM–gas (d) DP–solid, DM–solid

43. Multimolecular colloids are present in
(a) soap solution (b) sol of proteins
(c) sol of gold (d) All of these

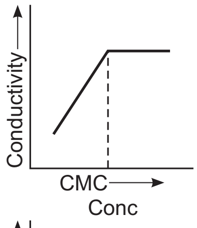
44. Which of the following is not the property of hydrophilic sol?
(a) Coagulation is reversible
(b) Viscosity and surface tension are equal to that of water
(c) Charge on the particle depends upon pH of the medium. It may be positive, negative or zero
(d) Dispersed phase acquires higher concentration easily

45. Micelles have
(a) same colligative property as that of common colloidal solution
(b) lower colligative property as that of common colloidal solution
(c) higher colligative property as that of common colloidal solution
(d) None of the above

46. At high concentration of soap in water, soap behaves as **[NCERT Exemplar]**
(a) molecular colloid (b) associated colloid
(c) macromolecular colloid (d) lyophilic colloid

47. Choose macromolecular colloids among the following
(a) soap (b) detergent
(c) starch and cellulose (d) All of these

48. Which graph is correct for critical micelle concentration (CMC)?

(a)


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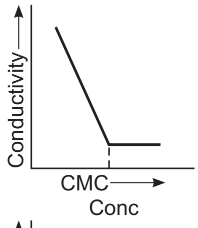

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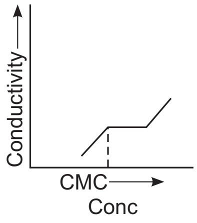

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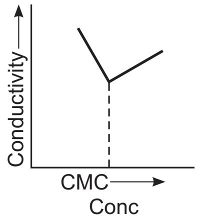


49. Match Column I with Column II and select the correct match.

	Column I		Column II
A.	Rain cloud	1.	Sol
B.	Milk of magnesia	2.	Foam
C.	Whipped cream	3.	Micelles
D.	Soap in water	4.	Aerosol

Codes

	A	B	C	D		A	B	C	D
(a)	1	2	3	4	(b)	4	1	2	3
(c)	4	2	3	1	(d)	3	1	2	4

50. Purple of cassius is
(a) colloidal solution of Au
(b) colloidal solution of Pt
(c) colloidal solution of Ag
(d) colloidal solution of As

51. Choose the intrinsic colloids among the following
(a) sulphur (b) arsenic sulphide
(c) egg albumen (d) ferric hydroxide

52. Surfactant molecules or ions cluster together as micelles
(a) due to their hydrophilic tails tend to congregate
(b) due to their hydrophobic heads provide protection
(c) which are colloid sized clusters of molecules
(d) None of the above

53. Freshly prepared precipitate sometimes gets converted to colloidal solution by **[NCERT Exemplar]**

(a) coagulation (b) electrolysis
(c) diffusion (d) peptisation

54. Which of the following reactions lead to the formation of colloidal solution?

(a) $Cu + HgCl_2 \longrightarrow CuCl_2 + Hg$
(b) $2HNO_3 + 3H_2S \longrightarrow 3S + H_2O + 2NO$
(c) $2Mg + CO_2 \longrightarrow 2MgO + C$
(d) $Cu + CuCl_2 \longrightarrow 2CuCl$

55. Peptisation involves

(a) precipitation of colloidal particles
(b) disintegration of colloidal aggregates
(c) evaporation of dispersion medium
(d) impact of molecules of the dispersion medium on the colloidal particles

56. Blood may be purified by

(a) dialysis (b) electroosmosis
(c) coagulation (d) filtration

57. The values of colligative properties of colloidal solution are of small order in comparison to those shown by true solutions of same concentration because of colloidal particles **[NCERT Exemplar]**

(a) exhibit enormous surface area
(b) remain suspended in the dispersion medium
(c) form lyophilic colloids
(d) are comparatively less in number

58. The Brownian movement is due to

(a) enthalpy change during the formation of colloids
(b) attractive forces between the colloidal particles and the molecules of dispersion medium
(c) the impact of molecules of the dispersion medium on the colloidal particles
(d) the movement of positively charged colloidal particle to negatively charged particle

59. Sedimentation potential is the reverse of

(a) electrosmosis
(b) electrophoresis
(c) electrokinetic potential
(d) dorn potential

60. Which of the following is incorrect for electrophoresis?

(a) In electrophoresis, solution migrates either to anode or to the cathode depending upon the positively or negatively charged solution
(b) Electrophoresis is a useful method for finding the charge of a solution
(c) Electrophoresis with a high potential is helpful in destroying an emulsion
(d) Colloids are uncharged particles and do not migrate towards the electrodes when electric field is applied

61. Which of the following statements is correct for Tyndall effect ?

(a) Scattering and polarising of light by small suspended particles is called Tyndall effect
(b) Tyndall effect of colloidal particles is due to dispersion of light
(c) Tyndall effect is due to refraction of light
(d) *Zig-zag* motion of suspended particles

62. Method by which lyophobic sol can be protected, is. **[NCERT Exemplar]**

(a) by addition of oppositely charged sol
(b) by addition of an electrolyte
(c) by addition of lyophilic sol
(d) by boiling

63. Hardy-Schulze law states that

(a) higher the charge of the coagulating ions, greater its coagulating power, having opposite sign of solution
(b) solution must have zero gold number
(c) disperse phase and dispersion medium must be of the same sign
(d) micelles coagulate in the presence of surfactants

64. Which of the following is the most effective in the coagulation of gold sol?

(a) $NaNO_3$ (b) $MgCl_2$
(c) Na_3PO_4 (d) $K_4[Fe(CN)_6]$

65. Colloidal gold is given by injection to act as

(a) disinfectant
(b) anticancer agent
(c) germ killer
(d) tonic to raise vitality of human systems

66. Which of the following process is responsible for the formation of delta at a place where rivers meet the sea? **[NCERT Exemplar]**

(a) Emulsification
(b) Colloid formation
(c) Coagulation
(d) Peptisation

67. Ferric chloride is applied to stop bleeding because

(a) Fe^{3+} ions coagulate negatively charged blood solution
(b) Fe^{3+} ions coagulate positively charged blood solution
(c) Cl^- ions coagulate positively charged blood solution
(d) Cl^- ions coagulate negatively charged blood solution

68. The leather get hardened after tanning because of **[NCERT Exemplar]**

(a) coagulation (b) peptisation
(c) oxidation (d) reduction

69. How does it become possible to cause artificial rain by spraying silver iodide on the clouds? [**NCERT** Exemplar]

(a) Due to coagulation
(b) Due to peptisation
(c) Due to development of charge
(d) Both (a) and (c)

70. Gelatin which is peptide is added to ice creams. What can be its role? [**NCERT** Exemplar]

(a) As coagulating agent
(b) As pepting agent
(c) As emulsifying agent
(d) As floculating agent

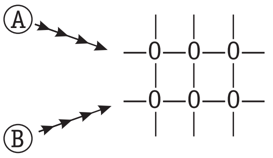
Round II (Mixed Bag)

Single Option Correct

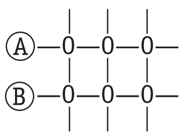
1. In physisorption, adsorbent does not show specificity for any particular gas because .... [**NCERT** Exemplar]

(a) involved van der Waals' forces are universal
(b) gases involved behave like ideal gases
(c) enthalpy of adsorption is low
(d) it is a reversible process

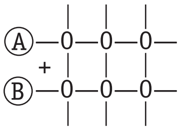
2. Arrange the following diagrams in correct sequence of steps involved in the mechanism of catalysis, in accordance with modern adsorption theory. [**NCERT** Exemplar]



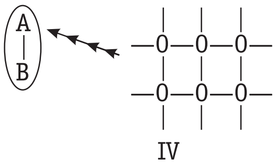
I



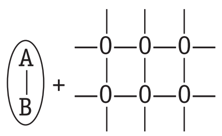
II



III



IV



V

(a) I $\longrightarrow$ II $\longrightarrow$ III $\longrightarrow$ IV $\longrightarrow$ V
(b) I $\longrightarrow$ III $\longrightarrow$ II $\longrightarrow$ IV $\longrightarrow$ V
(c) I $\longrightarrow$ III $\longrightarrow$ II $\longrightarrow$ V $\longrightarrow$ IV
(d) I $\longrightarrow$ II $\longrightarrow$ III $\longrightarrow$ V $\longrightarrow$ IV

3. Which one of the following is not applicable to the phenomenon of adsorption? [**NCERT** Exemplar]

(a) $\Delta H > 0$ (b) $\Delta G < 0$
(c) $\Delta S < 0$ (d) $\Delta H < 0$

4. Identify the gas which is readily adsorbed by activated charcoal

(a) H_2 (b) N_2 (c) SO_2 (d) O_2

5. For adsorption of a gas on a solid, the plot of $\log \frac{x}{m}$ *vs* $\log p$ is linear with slope equal to (n being whole number)

(a) K (b) $\log k$
(c) n (d) $\frac{1}{n}$

6. Plot of $\log \frac{x}{m}$ against $\log p$ is a straight line inclined at an angle of 45°. When the pressure is 0.5 atm and Freundlich parameter, k is 10, the amount of solute adsorbed per gram of adsorbent will be ($\log 5 = 0.6990$)

(a) 1 g (b) 2 g
(c) 3 g (d) 5 g

7. 50 mL of 1 M oxalic acid is shaken with 0.5g wood charcoal. The final concentration of the solution after adsorption is 0.5 M. What is the amount of oxalic acid absorbed per gram of carbon ?

(a) 3.15 g (b) 3.45 g
(c) 6.30 g (d) None of these

8. Pd can adsorb in the space between its atoms, 900 times its volume of hydrogen. This process is called

(a) absorption (b) desorption
(c) adsorption (d) chemisorption

9. Which of the following processes does not involve a catalyst?

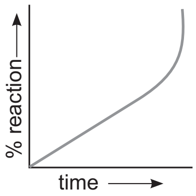
(a) Ostwald process (b) Contact process
(c) Thermite process (d) None of these

10. In Haber's process for the manufacture of ammonia, the reaction is usually carried at about 500°C. If a temperature of about 250°C was used then

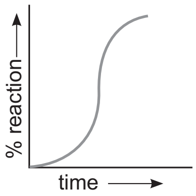
(a) a catalyst would be of no use at all at this temperature
(b) the rate of formation of ammonia would be too slow
(c) no ammonia would be formed at all
(d) the percentage of ammonia in the equilibrium mixture would be too low

11. Which graph represents auto catalysis?

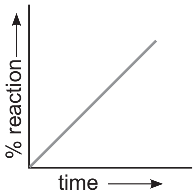
(a)



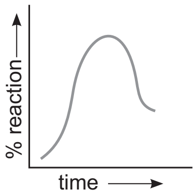
(b)



(c)



(d)



12. In which of the following reactions heterogeneous catalysis is involved? **[NCERT Exemplar]**

I. $2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$

II. $2SO_2(g) \xrightarrow{Pt(s)} 2SO_3(g)$

III. $N_2(g) + 3H_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$

IV. $CH_3COOCH_3(l) + H_2O(l) \xrightarrow{HCl(l)} CH_3COOH(aq) + CH_3OH(aq)$

(a) II, III (b) II, III, IV (c) I, II, III (d) IV

13. Choose the incorrect statement.

(a) If the mutual affinity between the dispersed phase and the dispersion medium is small, the system will be lyophobic

(b) If the mutual affinity between the dispersed phase and dispersion medium is great, the system will be lyophilic

(c) In a system, when water is the dispersion medium, the system may be hydrophobic or hydrophilic

(d) Ionic surfactant molecules cluster together in clumps

14. Match the statement given in Column I with the phenomenon given in Column II.

	Column I		Column II
A.	Dispersion medium moves in an electric field	1.	Osmosis
B.	Solvent molecules pass through semi permeable membrane towards solvent side.	2.	Electrophoresis
C.	Movement of charged colloidal particles under the influence of applied electric potential towards oppositely charged electrodes	3.	Electroosmosis
D.	Solvent molecules pass through semi permeable membranes towards solution side	4.	Reverse osmosis

Codes

	A	B	C	D
(a)	3	4	2	1
(b)	3	1	2	4
(c)	3	4	1	2
(d)	3	2	1	4

15. Match the following.

	Column I		Column II
A.	Smoke	1.	Aerosol of liquid
B.	Milk	2.	Aerosol of solid
C.	Butter	3.	Emulsion
D.	Fog	4.	Gel

Codes

	A	B	C	D		A	B	C	D
(a)	2	1	3	4	(b)	3	2	4	1
(c)	1	2	3	4	(d)	2	3	4	1

16. Match the following.

	Column I		Column II
A.	Protective colloid	1.	$FeCl_3$ + NaOH
B.	Liquid-liquid colloid	2.	Lyophilic colloids
C.	Positively charged colloid	3.	Emulsion
D.	Negatively charged colloid	4.	$FeCl_3$ + hot water

Codes

	A	B	C	D
(a)	1	2	3	4
(b)	2	3	1	4
(c)	2	3	4	1
(d)	3	2	1	4

17. Match the following.

	Column I		Column II
A.	Dialysis	1.	Precipitate converts to colloidal solution
B.	Peptisation	2.	Precipitation of colloidal solution
C.	Flocculation	3.	Protective power
D.	Gold number	4.	Purification of colloidal solution

Codes

	A	B	C	D		A	B	C	D
(a)	1	3	2	4	(b)	4	1	2	3
(c)	2	4	3	1	(d)	3	2	4	1

18. In which of the following reactions colloids are not prepared by the double decomposition method?

(a) $2H_3AsO_4 + 3H_2S \longrightarrow As_2S_3 + 6H_2O$

(b) $3K_4[Fe(CN)_6] + 4FeCl_3 \longrightarrow Fe_4[Fe(CN)_6]_3 + 12KCl$

(c) $Mg(CN)_2 + H_2S \longrightarrow HgS + 2HCN$

(d) $Cu + HgCl_2 \longrightarrow CuCl_2 + Hg$

19. Which of the following substances will precipitate the negatively charged emulsions? **[NCERT Exemplar]**

I. KCl II. glucose
III. urea IV. NaCl

The correct answer is

(a) I and II (b) I and III
(c) I and IV (d) II and III

20. An emulsion cannot be broken by …… and …… . **[NCERT Exemplar]**

I. heating
II. adding more amount of dispersion medium
III. freezing
IV. adding emulsifying agent

The correct answer is

(a) I and II (b) II and III
(c) II and IV (d) I, II and III

21. Which of the following will show Tyndall effect? **[NCERT Exemplar]**

(a) Aqueous solution of soap below critical micelle concentration
(b) Aqueous solution of soap above critical micelle concentration
(c) Aqueous solution of sodium chloride
(d) Aqueous solution of sugar

22. Which of the following electrolytes will have maximum coagulating value for AgI/Ag^+ sol? **[NCERT Exemplar]**

(a) Na_2S (b) Na_3PO_4
(c) Na_2SO_4 (d) NaCl

23. The minimum flocculation power of KCl, $MgCl_2$, $CrCl_3$ and $SnCl_4$ for a positively charged sol are in the order of

(a) $KCl < MgCl_2 < CrCl_3 < SnCl_4$
(b) $KCl = MgCl_2 = CrCl_3 = SnCl_4$
(c) $MgCl_2 < KCl < CrCl_3 < SnCl_4$
(d) $SnCl_4 < CrCl_3 < MgCl_2 < KCl$

24. The gold number of gelatin, haemoglobin and sodium acetate are 0.005, 0.05 and 0.7 respectively. The protective actions will be in the order of

(a) Gelatin < haemoglobin < sodium acetate
(b) Gelatin > haemoglobin > sodium acetate
(c) Haemoglobin > gelatin > sodium acetate
(d) Sodium acetate > gelatin > haemoglobin

25. Which of the following forms cationic micelles above certain concentration?

(a) Urea
(b) Sodium dodecyl sulphate
(c) Sodium acetate
(d) Cetyltrimethylammonium bromide

26. The coagulation of 10 cm^3 of gold sol is completely prevented by addition of 0.025 g of starch to it. The gold number of starch is

(a) 0.025 (b) 0.25
(c) 2.55 (d) 25

27. Which one of the following impurities present in colloidal solution cannot be remove by electrodialysis?

(a) Sodium chloride
(b) Potassium sulphate
(c) Urea
(d) Calcium chloride

28. Blue colour of the sky and red colour of the sunsets are due to

(a) scattering of light from the sun
(b) scattering of light from particles of dust in the atmosphere
(c) refraction of blue light by impurities in sea water
(d) scattering of light due to ozone layer

29. The Rubin number which was proposed by Ostwald as an alternative to the gold number in order to measure the protective efficiency of a lyophilic colloid may be defined as the

(a) mass in milligrams of a colloid per 100 cc of solution which just prevents the colour change of standard sol of dye Congo-Rubin from red to violet when 0.16 g aq. KCl is added to it
(b) mass in grams of a colloid per 100 cc of solution which just prevents the colour change of standard sol of dye Congo-Rubin from red to violet when 0.1 M KCl is added to it
(c) mass in grams of a colloid per 100 cc of solution which just prevents the colour change of standard sol of dye Congo-Rubin from red to violet when 0.2 M KCl is added to it
(d) mass in grams of a colloid per 100 cc of solution which just prevents the colour change of standard sol of dye Congo-Rubin from red to violet when 1 M KCl is added to it

More than One Correct Option

30. Which of the following options are correct? **[NCERT Exemplar]**

(a) Micelle formation by soap in aqueous solution is possible at all temperatures
(b) Micelle formation by soap in aqueous solution occurs above a particular concentration
(c) On dilution of soap solution micelles may revert to individual ions
(d) Soap solution behaves as a normal strong electrolyte at all concentrations

31. Which of the following statements are correct about solid catalyst? **[NCERT Exemplar]**

(a) Same reactants may give different product by using different catalysts

(b) Catalyst does not change ΔH of reaction

(c) Catalyst is required in large quantities to catalyse reactions

(d) Catalytic activity of a solid catalyst does not depend upon the strength of chemisorption

32. Which phenomenon occurs when an electric field is applied to a colloidal solution and electrophoresis is prevented? **[NCERT Exemplar]**

(a) Reverse osmosis takes place

(b) Electroosmosis takes place

(c) Dispersion medium begins to move

(d) Dispersion medium becomes stationary

33. Freundlich adsorption isotherm is given by the expression $\frac{x}{m} = kp^{1/n}$ which of the following conclusions can be drawn from this expression? **[NCERT Exemplar]**

(a) When $\frac{1}{n} = 0$, the adsorption is independent of pressure

(b) When $\frac{1}{n} = 0$, the adsorption is directly proportional to pressure

(c) When $n = 0$, $\frac{x}{m}$ *vs* p graph is a line parallel to x-axis

(d) When $n = 0$, plot of $\frac{x}{m}$ *vs* p is a curve

34. Which of the following statements is/are correct about physical adsorption?

(a) It is a selective and specific process

(b) It is a reversible process

(c) An increase in the gaseous adsorbate causes increase in adsorption. However, at higher pressure the adsorption become constant

(d) It is an endothermic process

35. Which is/are correct statement about the role of a catalyst in a reaction?

(a) It is reactant in a rate-determining step and then a product of some subsequent steps

(b) It provides an alternate mechanism with a lower energy of activation

(c) It increases the rate of chemical reaction but does not itself undergo a permanent change during the course of the reaction

(d) It increases quantity of the product

36. H_2 gas is adsorbed on activated charcoal to a very little extent in comparison to easily liquefiable gases due to **[NCERT Exemplar]**

(a) very strong van der Waals' interaction

(b) very weak van der Waals' forces

(c) very low critical temperature

(d) very high critical temperature

37. 1 mole of $[AgI]Ag^+$ sol is coagulated by

(a) 1 mol of KI (b) 500 mL of 1 M K_2SO_4

(c) 1 L of 1 M KI (d) None of these

38. On adding $AgNO_3$ solution into KI solution, a negative charged colloidal sol is obtained when they are in

(a) 100 mL of 0.1 M $AgNO_3$ + 100 mL of 0.1 M KI

(b) 100 mL of 0.1 M $AgNO_3$ + 100 mL of 0.2 M KI

(c) 100 mL of 0.2 M $AgNO_3$ + 100 mL of 0.1 M KI

(d) 100 mL of 0.15 $AgNO_3$ + 100 mL of 0.25 M KI

Assertion and Reason

Directions (Q. Nos. 39 to 43) *Each of these questions contains two statements : Statement* I (*Assertion*) *and Statement* II (*Reason*). *Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes* (*a*), (*b*), (*c*), (*d*) *given below.*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I.

(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.

(c) Statement I is true; Statement II is false.

(d) Statement I is false; Statement II is true.

39. **Statement I** According to Freundlich, $\frac{x}{m} = k \cdot p^{1/n}$.

Statement II The isotherm shows variation of the amount of gas adsorbed by the adsorbent with temperature.

40. **Statement I** Detergents with low CMC are more economical to use. **[NCERT Exemplar]**

Statement II Cleansing action of detergents involves the formation of micelles. These are formed when the concentration of detergents becomes equal to CMC.

41. **Statement I** An ordinary filter paper impregnated with collodion solution stops the flow of colloidal particles. **[NCERT Exemplar]**

Statement II Pore size of the filter paper becomes more than the size of colloidal particle.

42. **Statement I** Coagulation power of Al^{3+} is more than Na^+. **[NCERT Exemplar]**

Statement II Greater the valency of the flocculating ion added, greater is its power to cause precipitation (Hardy Schulze rule).

43. **Statement I** ZSM–5 is used as a catalyst in petrochemical industries.

Statement II Zeolites are three dimensional network silicates in which some silicon atoms are replaced by aluminium atoms.

Comprehension Based Questions

Directions (Q. Nos. 44 to 46) Freundlich adsorption isotherm is obeyed by the adsorptions where the adsorbate forms a multimolecular layer on the surface of adsorbent. In such case, the degree of adsorption varies linearly with pressure but at high pressure, it becomes independent of pressure. It is given as

$$\frac{x}{m} = kp^{1/n}$$

where, k and n are constants.

Langmuir adsorption isotherm is obeyed by the adsorption where the adsorbate forms only a unimolecular adsorbed layer. The mathematical relation of Langmuir adsorption isotherm is

$$\frac{x}{m} = \frac{ap}{1+bp}$$

44. When $\log\left(\frac{x}{m}\right)$ is plotted against $\log p$, we get a straight line with slope

(a) $\frac{1}{n}$ (b) n

(c) x (d) m

45. The degree of adsorption $\left(\frac{x}{m}\right)$ at low pressure will be

(a) $\frac{x}{m} = n$ (b) $\frac{x}{m} = ap$

(c) Both (a) and (b) (d) None of these

46. Freundlich adsorption isotherm is valid for

(a) physisorption (b) chemisorption

(c) Both (a) and (b) (d) None of these

Directions (Q. Nos. 47 to 49) Emulsions are also the colloidal solutions in which disperse phase as well as dispersion medium are liquids. It may be oil in water or water in oil type. Bancroft proposed that the phase in which the emulsifier is more soluble becomes the outer phase of the emulsion. Emulsifiers can be used to stabilise the emulsion. Soaps, detergents, proteins and gum etc, are used as emulsifiers.

47. Addition of lyophilic solution to the emulsion forms

(a) a protective film around the dispersed phase

(b) a protective film around the dispersion medium

(c) an aerosol

(d) true solution

48. Which of the following is homogeneous?

(a) Milk (b) Paint

(c) Shampoo (d) None of these

49. Milk is an emulsion in which

(a) a gas is dispersed in water

(b) a solid is dispersed in water

(c) fat is dispersed in water

(d) lactose is dispersed in water

Previous Years' Questions

50. Which of the following statement is incorrect regarding physisorptions?

(a) It occurs because of van der Waals' forces

(b) More easily liquefiable gases are adsorbed readily

(c) Under high pressure it results into multimolecular layer on adsorbent surface

(d) Enthalpy of adsorption ($\Delta H_{\text{adsorption}}$) is slow and positive

51. Gold numbers of protective colloids A, B, C and D are 0.50, 0.01, 0.10 and 0.005, respectively. The correct order of their protective powers is [AIEEE 2008]

(a) $D < A < C < B$ (b) $C < B < D < A$

(c) $A < C < B < D$ (d) $B < D < A < C$

52. In Langmuir's model of adsorption of a gas on a solid surface, [AIEEE 2006]

(a) the rate of dissociation of adsorbed molecules from the surface does not depend on the surface covered

(b) the adsorption at a single site on the surface may involve multiple molecules at the same time

(c) the mass of gas striking a given area of surface is proportional to the pressure of the gas

(d) the mass of gas striking a given area of surface is independent of the pressure of the gas

53. The disperse phase in colloidal iron (III) hydroxide and colloidal gold is positively and negatively charged respectively. Which of the following statement is not correct? [AIEEE 2005]

(a) Coagulation in both sols can be brought about by electrophoresis

(b) Mixing the sols has no effect

(c) Sodium sulphate solution causes coagulation in both sols

(d) Magnesium chloride solution coagulates the gold sol more readily than the iron (III) hydroxide sol

54. The volume of a colloidal particle, V_C as compared to the volume of a solute particle in a true solution V_S, could be [AIEEE 2005]

(a) $\frac{V_C}{V_S} \approx 10^3$ (b) $\frac{V_C}{V_S} \approx 10^{-3}$

(c) $\frac{V_C}{V_S} \approx 10^{23}$ (d) $\frac{V_C}{V_S} \approx 1$

55. Which one of the following characteristics is not correct for physical adsorption ? **[AIEEE 2003]**

(a) Adsorption on solids is reversible

(b) Adsorption increases with increase in temperature

(c) Adsorption is spontaneous

(d) Both enthalpy and entropy of adsorption are negative

Answers

Round I

1. (b) **2.** (b) **3.** (a) **4.** (d) **5.** (b) **6.** (d) **7.** (a) **8.** (d) **9.** (b) **10.** (b)
11. (a) **12.** (b) **13.** (d) **14.** (b) **15.** (a) **16.** (c) **17.** (b) **18.** (c) **19.** (d) **20.** (c)
21. (c) **22.** (b) **23.** (d) **24.** (b) **25.** (a) **26.** (b) **27.** (c) **28.** (c) **29.** (d) **30.** (d)
31. (c) **32.** (a) **33.** (d) **34.** (c) **35.** (b) **36.** (b) **37.** (d) **38.** (b) **39.** (d) **40.** (d)
41. (a) **42.** (c) **43.** (c) **44.** (b) **45.** (b) **46.** (b) **47.** (c) **48.** (b) **49.** (b) **50.** (a)
51. (c) **52.** (c) **53.** (d) **54.** (b) **55.** (b) **56.** (a) **57.** (d) **58.** (c) **59.** (b) **60.** (d)
61. (a) **62.** (c) **63.** (a) **64.** (b) **65.** (d) **66.** (c) **67.** (a) **68.** (a) **69.** (a) **70.** (c)

Round II

1. (a) **2.** (b) **3.** (a) **4.** (c) **5.** (d) **6.** (d) **7.** (c) **8.** (d) **9.** (c) **10.** (b)
11. (b) **12.** (a) **13.** (d) **14.** (a) **15.** (d) **16.** (c) **17.** (b) **18.** (d) **19.** (c) **20.** (c)
21. (b) **22.** (b) **23.** (b) **24.** (b) **25.** (d) **26.** (d) **27.** (c) **28.** (b) **29.** (a) **30.** (b,c)
31. (a,b) **32.** (b,c) **33.** (a,c) **34.** (a,b,c) **35.** (a,b,c) **36.** (b,c) **37.** (a,b,c) **38.** (b,d) **39.** (c) **40.** (a)
41. (c) **42.** (a) **43.** (b) **44.** (a) **45.** (b) **46.** (a) **47.** (a) **48.** (d) **49.** (c) **50.** (d)
51. (c) **52.** (c) **53.** (b) **54.** (a) **55.** (b)

the Guidance

Round I

1. Water on calcium chloride is an example of absorption as water is also distributed in the bulk.

3. The substance that gets adsorbed on the surface of solid is called adsorbate and the solid on which adsorption occurs is called adsorbent.

4. High temperature is not a favourable condition for physical adsorption as it is an exothermic process.

5. Extent physisorption of a gas increase with decrease in temperature because of its exothermic nature.

6. Activated charcoal has great affinity for water vapour as they easily form hydrogen bond among themselves.

7. Langmuir's adsorption is monomolecular, *i.e.,* the gas adsorbed forms unimolecular layer.

8. Adsorption is a process where randomness decreases and energy is released hence ΔS, ΔH and ΔG, all have negative values.

9. At the equilibrium position in the process of adsorption $\Delta H = T\Delta S$

11. Extent of adsorption of adsorbate from solution phase increase with increase an amount of adsorbate in solution.

13. In adsorption, due to forces of attraction, ΔH is negative and as the particles came closer entropy of the system decrease, *i.e.,* ΔS is negative, hence $T\Delta S$ is also negative.

14. For chemisorption, high temperature is favourable. It increases with rise in temperature. On the other hand low temperature is favourable for physisorption so it decreases with rise in temperature.

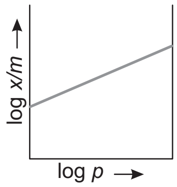
15. Freundlich adsorption isotherm is given as

$$\frac{x}{m} = kp^{1/n} \text{ (at a particular pressure)}$$

When $x = 1, \frac{x}{m} = kp$ (at low pressure)

When $n > 1, \frac{x}{m} = k$ (at high pressure)

16. Curve (c) is in accordance with Freundlich adsorption isotherm as $\frac{x}{m} = kp^{1/n}$ or $\log \frac{x}{m} = \log k + \frac{1}{n} \log p$



18. In Langmuir's adsorption isotherm, the mass of gas striking a given area of surface is proportional to the pressure of the gas as

$$\frac{x}{m} = \frac{k'p}{1+kp}$$

21. The plot of temperature *versus* pressure for a given amount of adsorption is called adsorption isostere.

22. Activated charcoal adsorbs various poisonous gases on its surface present in coal mines, so it is used in gas masks.

23. Extent of adsorption depends upon the liquefication or critical temperature of a gas.

Since H_2 has lower critical temperature than the others, it exhibits least adsorption.

26. A catalyst alters the nature of chemical reaction by lowering the activation energy of the rectants and products.

29. Equation, $SO_2(g) + \frac{1}{2} O_2(g) \xrightarrow{V_2O_5(l)} SO_3(g)$ is only example of heterogeneous catalysis.

31. Homogeneous catalysis does not occur at the interface of phases.

32. Transitional metals, showing variable valency in finely divided state mostly acts as catalyst.

35. In Haber's process, a mixture of iron powder and molybdenum powder is used as catalyst.

$$N_2 + 3H_2 \underset{Mo}{\overset{Fe}{\rightleftharpoons}} 2NH_3$$

36. The reaction in contact process is

$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$$

37. Enzymes are biological catalyst, as they catalyse the biological processes.

38. Colloidal solutions are heterogeneous in nature.

39. A colloidal system having a solid substance as a dispersed phase and a liquid as a dispersion medium is classified as sol.

40. When dispersed phase is gas and dispersion medium is solid the colloidal sol obtained is termed as solid foam.

41. Fog is a colloidal solution in which water (liquid, dispersed phase) is dispersed in air (gas, dispersion medium).

42. A colloidal solution cannot form when dispersion medium as well as dispersion medium both are gases.

44. For hydrophilic sol, viscosity is higher than water whereas surface tension is low.

45. Micelles show lower colligative properties as that of common colloidal solution.

46. At high concentration of soap in water, soap behaves as associated colloid.

47. Starch and cellulose are macromolecular particles.

49. Rain cloud is an example of aerosol. Milk of magnesia is a sol. Whipped cream is foam and soap in water is a form of associated colloids, *i.e.,* micelles.

50. Colloidal solution of gold is called purple of cassius.

53. The dispersal of a precipitated material into colloidal solution by the action of an electrolyte in the solution is termed as peptisation and the electrolyte is called a peptising agent. Thus, freshly prepared precipitate sometimes gets converted to colloidal solution by peptisation.

54. $2HNO_3 + 3H_2S \longrightarrow 3S + H_2O + 2NO$

This equation is used for the preparation of sulphur sol.

55. Peptisation is a process in which freshly prepared precipitate disintegrates into colloidal solution.

57. The values of colligative properties of colloidal solution are of small order in comparison to those shown by true solutions of same concentration because colloidal particles because of their large size are comparatively less in number.

58. The continuous rapid *zig-zag* motion by a colloidal particle in the dispersion medium is called Brownian movement.

61. The phenomenon of the scattering of light by the particles is called Tyndall effect.

64. Among Na^+, K^+, Mg^{2+} ions, Mg^{2+} ion has maximum valency, thus it will be the most effective in the coagulation of gold sol.

65. In medical field, colloidal gold is used as tonic to raise vitality of human systems.

66. Coagulation process is responsible for the formation of delta at a place where rivers meet the sea.

68. Animal leather is colloidal in nature and has positively charged particles. When it is soaked in tanin (negatively charged), a colloid, it results in mutual coagulation and gets harden.

69. Clouds are colloidal in nature and carry charge. Spray of silver iodide, an electrolyte, results in coagulation leading to rain.

70. Ice cream (emulsion) is stabilised by emulsifying agents like gelatin.

Round II

1. In physisorption, adsorbent does not show specificity for any particular gas because it involve van der Waals' forces which are universal.

2. In the mechanism of catalysis in accordance with modern adsorption theory the correct sequence of steps involved are $\text{I} \rightarrow \text{III} \rightarrow \text{II} \rightarrow \text{IV} \rightarrow \text{V}$.

3. $\Delta G < 0$, $\Delta S < 0$ and $\Delta H < 0$ are applicable to the phenomenon of adsorption but $\Delta H > 0$ is not applicable to the phenomenon of adsorption.

4. Easily liquefiable gases like SO_2, NH_3, CO_2 are adsorbed to a greater extent than the elemental gases like N_2, O_2, H_2.

5. According to Freundlich adsorption isotherm,

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$$

It is clear from the above equation that slope is equal to $\frac{1}{n}$.

6. Freundlich adsorption isotherm equation is

$$\frac{x}{m} = kp^{1/n}$$

On taking log both sides

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$$

$$\log \frac{x}{m} = \log 10 + 1 \cdot \log 0.5$$

$$(\because \text{ slope} = \frac{1}{n} = \tan \theta = \tan 45° = 1)$$

$$\log \frac{x}{m} = 1 + \log (5 \times 10^{-1})$$

$$\log \frac{x}{m} = 1 + 0.6990 - 1$$

$$= 0.6990$$

$$\frac{x}{m} = 5.00 = 5 \text{ g}$$

7. 50 mL of 1 M oxalic acid $[(COOH)_2 \cdot 2H_2O] = 50$ millimol

$$= 0.050 \text{ mol}$$

$$= 0.050 \times 126 \text{ g}$$

$$= 6.3 \text{ g}$$

50 mL of 0.5 M oxalic acid = 3.15 g

$\therefore$ Oxalic acid adsorbed on 0.5 g charcoal = 6.3 – 3.15

$$= 3.15 \text{ g}$$

$\therefore$ Amount of oxalic acid adsorbed per gram of charcoal

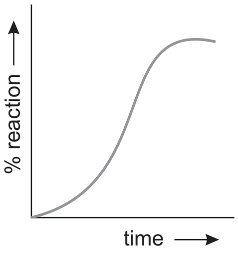
$$= \frac{3.19}{0.5} = 6.3$$

8. Palladium being a transition element, adsorbs the hydrogen gas to a greater extent and the molecules of H_2 are held to the surface of the metal by chemical forces.

9. Catalysis is a process where the rate of a chemical reaction alters due to mere presence of foreign substance. In thermite process, no other substance present except the reacting substances.

10. The optimum temperature for the production of ammonia by Haber's process is 500°C. If the temperature is lowered down then production of ammonia becomes slow down.

11.



12. In the heterogeneous catalysis, the catalyst is present in a different phase from that of reactants. Here the catalyst is generally a solid (sometimes liquid) and the reactants are generally gaseous. Thus, in the reaction II and III, reactants and the catalyst are in different phase, *i.e.,* in these reactions, heterogeneous catalysis is involved.

13. Ionic surfactant molecules are preferentially adsorbed at the interfaces.

14. In electrosmosis, dispersion medium moves in an electric field. When solvent molecules pass through semipermeable membrane towards solvent side, the process is called reverse osmosis.

Electrophoresis is the process of movement of charged colloidal particles under the influence of applied electric potential towards oppositely charged electrodes.

In osmosis, solvent molecule pass through semipermeable membrane towards solution side.

15. Smoke is an aerosol of solid, milk is an emulsion, butter is a gel and fog is an aerosol of liquid.

16. (A) Protective colloids are infact lyophilic colloids which being stable stabilises the lyophobic colloids if added from coagulation.

(B) Liquid-liquid colloids are called emulsion.

$$FeCl_3 + \underset{\text{excess}}{3NaOH} \longrightarrow Fe(OH)_3 + 3NaCl$$

$$Fe(OH)_3 + OH^- \longrightarrow Fe(OH)_3 : OH^-$$

(C) $FeCl_3 + 3H_2O \longrightarrow Fe(OH)_3 + 3HCl$

(D) $Fe(OH)_3 + FeCl_3 \longrightarrow [Fe(OH)_3]Fe^{3+} : 3Cl^-$

17. (A) Dialysis is used for the purification of colloidal solution.

(B) In peptisation, freshly prepared precipitates converted in to colloidal solution.

(C) Flocculation is precipitation of colloidal solution.

(D) Gold number is a scale of protective power.

18. Colloidal solution of $CuCl_2$ is not prepared by double decomposition method.

19. Potassium chloride (KCl) and sodium chloride (NaCl) will precipitate the negatively charged emulsions as they provide positive ions (K^+, Na^+).

20. An emulsion cannot be broken by adding more amount of dispersion medium and adding emulsifying agent.

21. Aqueous solution of soap above critical micelle concentration shows Tyndall effect.

22. Na_3PO_4 electrolytes have the maximum coagulating value for AgI/Ag^+ sol.

23. The order of minimum flocculation power KCl, $MgCl_2$, $CrCl_3$ and $SnCl_4$ for a positively charged sol are

$$KCl = MgCl_2 = CrCl_3 = SnCl_4$$

24. $\because$ Protective power $\propto \dfrac{1}{\text{gold number}}$

$\therefore$ Order of protective power will be

$$\underset{(0.005)}{\text{Gelatin}} > \underset{(0.05)}{\text{haemoglobin}} > \underset{(0.7)}{\text{sodium acetate}}$$

25. $R(NH_3)_3Br \longrightarrow R(NH_3)_3^+ + Br^-$

Alkyl trimethyl ammonium ions aggregates to form cationic micelles.

26. Gold number is the amount of substance in milligram that is required to prevent coagulation of 10 cm^3 of gold sol by addition of 1 mL of 10% NaCl solution.

Convert 0.025 g into milligram = 25

$$0.025 \text{ g starch} = 0.025 \times 1000 = 25 \text{ mg}$$

Thus, the gold number of starch = 25

27. Electrodialysis is the technique by which electrolytic impurities can be removed. Hence, urea, being non-elecrolyte cannot be removed by this method.

28. Blue colour of the sky and red colour of the red sun sets are due to scattering of light from particles of dust in the atmosphere.

29. A new definition for protective power of a lyophobic sol as given by Ostwald and known as Rubin number. It is the mass (in mg) of a colloid per 100 cc of solution which just prevents the colour change of standard sol of dye Congo-Rubin from red to violet when 0.16 g eq. KCl is added to it.

30. The colloidal aggregates of soap or detergent molecules formed in the solvent are referred to as micelles. The formation of micelle by soap in aqueous solution occurs above a particular concentration. And on dilution of soap solution, micelles may revert to individual ions.

31. In solid catalyst same reactants may give different products by using different catalysts. A catalyst does not change ΔH of reaction.

32. Electroosmosis takes place and dispersion medium begins to move when an electric field is applied to a colloidal solution and electrophoresis is prevented.

33. Freundlich adsorption isotherm is given by the expression $\dfrac{x}{m} = kp^{1/n}$

And when $\dfrac{1}{n} = 0$, the adsorption is independent of pressure and when $n = 0$, $\dfrac{x}{m}$ *vs* p graph is a line parallel to x-axis.

34. Adsorption is a selective, specific and reversible process. It increases in the gaseous adsorbate. But it is an exothermic process.

35. A catalyst is reactant in a rate-determining (r/d) step and then a product of some subsequent step. It also provides an alternate mechanism with a lower energy of activation. It alters rate of chemical reaction but cannot change quantity of the product.

36. H_2 gas is adsorbed on activated charcoal to a very little extent in comparison to easily liquefiable gases due to very weak van der Waals' forces and very low critical temperature.

37. One mole of $[AgI]Ag^+$ is coagulated by 1 mole of I^-.

$$[AgI]Ag^+ + I^- \longrightarrow AgI + AgI$$

$$\underset{\substack{2 \text{ mol} \\ 1 \text{ mol}}}{2[AgI]Ag^+} + \underset{\substack{1 \text{ mol} \\ 0.5 \text{ mol}}}{SO_4^{2-}} \longrightarrow 2AgI + Ag_2SO_4$$

$$500 \text{ mL of } 1 \text{ M } K_2SO_4 = 0.5 \text{ mol}$$

Thus, (b) is not true.

$$1 \text{ L of } 1 \text{ M KI} = 1 \text{ mol } I^-$$

Thus, (c) is also true.

38. AgI is precipitated by reaction of equivalent amount of Ag^+ and I^-. I^- is adsorbed (if present in excess) on the surface of AgI forming negatively charged colloidal sol. Thus,

$$Ag^+ + I^- \longrightarrow AgI$$

$$AgI + I^- \longrightarrow [AgI]I^-$$

(a) 100 mL of 0.1 M $AgNO_3$ = 10 millimol Ag^+

100 mL of 0.01 M KI = 10 millimol I^-

AgI is only precipitated.

(b) 20 millimol I^- > 10 millimol Ag^+

Thus, AgI is precipitated and then $[AgI]I^-$ colloidal sol is formed.

(c) 20 millimole of Ag^+ > 10 millimole of I^-

AgI is precipitated and then $[AgI]Ag^+$ colloidal sol is formed.

(d) 25 millimole I^- > 15 millimole of Ag^+

Thus, $[AgI]I^-$ colloidal sol is formed.

39. Freundlich adsorption isotherm gives an empirical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature.

40. Detergents with low CMC are more economical to use. Cleansing action of detergent involves the formation of micelles. These are formed when the concentration of detergent becomes equal to CMC.

41. An ordinary filter paper impregnated with colloidion solution stops the flow of colloidal particles because the pore size of the filter paper becomes less than the size of colloidal particles.

42. Coagulation power of Al^{3+} is more than Na^+ because according to Hardy Schulze rule, greater the valency of the flocculating ion added, greater is its power to cause precipitation.

43. ZSM-5 converts alcohols directly into gasoline (petrol) by dehydrating them so that a mixture of hydrocarbons is formed.

44. Freundlich adsorption isotherm is given as

$$\frac{x}{m} = kp^{1/n}$$

or, $$\log\frac{x}{m} = \log k + \frac{1}{n}\log p$$

Thus, when $\log\left(\frac{x}{m}\right)$ is plotted against $\log p$, we have a straight line with slope $\left(\frac{1}{n}\right)$ and intercept $\log k$.

45. From Langmuir adsorption isotherm,

$$\frac{x}{m} = \frac{ap}{1+bp}$$

When pressure is low then $1 + bp \approx 1$

$$\therefore \qquad \frac{x}{m} = ap$$

46. Decrease of pressure does not cause desorption in chemisorption, while it causes desorption in physisorption. In Freundlich adsorption isotherm, the degree of adsorption varies linear with pressure.

Thus, this isotherm is valid only for chemisorption.

47. Addition of lyophilic solution to the emulsion forms a protective film around the dispersed phase.

48. Milk, paint and shampoo are examples of colloidal solutions. A colloidal solution is always a heterogeneous system instead of homogeneous system.

49. In milk, milk fat (dispersed phase) is dispersed in water (dispersion medium).

50. Adsorption is an exothermic process *i.e.,* energy is released against van der Waals' force of attraction (physisorptions).

Hence, ΔH is always negative.

51. Higher the gold number, lesser will be the protective power of colloid. Therefore, the correct order of protective powers of colloids is $A < C < B < D$.

52. The adsorption of a gas is directly proportional to the pressure of the gas.

53. Mixing the soles together can cause coagulation, since the charges are neutralised.

54. Size of colloidal particles $= 1$ to 100 nm

(say 10 nm)

$$V_C = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(10)^3$$

Size of true solution particles ≈ 1 nm

$$V_S = \frac{4}{3}\pi(1)^3$$

Thus, $$\frac{V_C}{V_S} = 10^3$$

55. As temperature increases desorption increases.

$$\text{Adsorbent} + \text{Adsorbate} \rightleftharpoons \text{Adsorbed state} + \Delta E$$

Adsorption is an exothermic process (forward direction), desorption is endothermic process (backward direction).

According to Le-Chatelier's principle, increase in temperature favours endothermic process.

6

General Principles and Processes of Isolation of Metals

JEE Main MILESTONE

- Modes of Occurrence of Elements in Nature
- Metallurgy
- Steps Involved in the Extraction of Metals
- Principles Involved in the Extraction of Metals
- Extraction Schemes of Some Metals

6.1 Modes of Occurrence of Elements in Nature

Based on their reactivity elements (metals) generally occurs in two forms in nature

(i) In native state

(ii) In combined state

Less reactive metals are found in **native state** (free state) in nature. Such metals are not attacked by O_2, H_2O, CO_2 etc. Examples of such metals include Ag, Au, Pt etc. Sometimes, Cu is also found in free state.

Reactive metals are found in **combined state** in nature. Such metals are attacked by O_2, H_2O, CO_2 etc. Examples of such metals include Na, Ca, Mg, Fe, Cu, Zn, Al etc.

Earth crust is a source of many elements. Oxygen is present in the most abundance in the earth crust. Among metals, Al is the most abundant metal of earth crust and Fe comes second. The percentage of different elements in the earth crust is O–49%; Si–26%; Al–7.5%; Fe–4.2%; Ca–3.2%; Na–2.4%; K–2.3%; Mg–2.3%; H–1%; other elements–2%. Besides earth crust, some soluble salts of metals, such as NaCl, $MgCl_2$, KBr, $CaBr_2$, KI etc., are also found in sea water.

Metals in their pure form are of great importance because of their utilisation for the synthesise of several compounds, for making articles (as alloys) etc. But most of metals due to their high reactivity found in the combined form. So, it is necessary to extract metal from the compound. This chapter deals with the various principles and processes used during extraction process.

Caution Point *In earth crust metals generally not found as their nitrates because of their high solubility in water.*

Minerals, Ores and Matrix

The natural material in the form of which the metal is found in nature is called mineral and those minerals from which a metal can be extracted conveniently, economically and in large quantity are called ores. Thus, we can say that *all the ores are minerals but all the minerals are not ores.*

Common ores/minerals of some important metals are given as follows

Table 6.1 **Ores of Some Metals**

Metal	Ore/mineral	Formula
Li	Spodumene	$LiAlSi_2O_6$
	Lepidolite	$(Li, Na, K)_2Al_2(SiO_2)_3F(OH)$
Na	Common salt	$NaCl$ (rock salt)
	Chile salt petre	$NaNO_3$
	Glauberite	$Na_2SO_4 \cdot 10H_2O$ (Glauber's salt)
	Borax	$Na_2B_4O_7 \cdot 10H_2O$
	Trona	$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$
	Soda ash	Na_2CO_3
	Feldspar	$NaAlSi_3O_8$
K	Sylvine	KCl
	Nitre	KNO_3 (salt petre)
	Schonite	$K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$
Mg	Magnesite	$MgCO_3$
	Dolomite	$MgCO_3 \cdot CaCO_3$
	Carnallite	$KCl \cdot MgCl_2 \cdot 6H_2O$
	Epsom salt	$MgSO_4 \cdot 7H_2O$
	Asbestos	$CaMg_3(SiO_3)_4$
	Talc	$Mg_2(Si_2O_5)_2Mg(OH)_2$
Ca	Gypsum	$CaSO_4 \cdot 2H_2O$
	Limestone	$CaCO_3$
	Phosphorite	$Ca_3(PO_4)_2$
	Fluorspar	CaF_2
Al	Bauxite	$Al_2O_3 \cdot 2H_2O$
	Diaspore	$Al_2O_3 \cdot H_2O$
	Corundum	Al_2O_3
	Cryolite	Na_3AlF_6
	Kaolinite	$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$
	Mica	$K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$
Sn	Cassiterite	SnO_2 (tin stone)
Pb	Galena	PbS
	Cerussite	$PbCO_3$
	Anglesite	$PbSO_4$
	Lanarkite	$PbO \cdot PbSO_4$
Cu	Chalcopyrite	$CuFeS_2$ (copper pyrites)
	Chalcocite	Cu_2S (copper glance)
	Cuperite	Cu_2O (rubby copper)
	Azurite	$2CuCO_3 \cdot Cu(OH)_2$
	Malachite	$CuCO_3 \cdot Cu(OH)_2$
Ag	Argentite	Ag_2S (silver glance)
	Cerargyrite	$AgCl$ (horn silver)
	Pyrargyrite	$Ag_2S \cdot Sb_2S_3$ (ruby silver)
Fe	Haematite	Fe_2O_3 (red haematite)
	Limonite	$Fe_2O_3 \cdot 3H_2O$ (brown haematite)
	Magnetite (load stone)	Fe_3O_4 (magnetic oxide of iron)
	Siderite	$FeCO_3$
	Iron pyrite	FeS_2
Hg	Cinnabar	HgS
Zn	Zinc blende	ZnS (black zinc or sphalerite)
	Calamine	$ZnCO_3$
	Zincite	ZnO (red zinc)
	Willemite	Zn_2SiO_4
Mn	Pyrolusite	MnO_2
	Manganite	$Mn_2O_3 \cdot H_2O$
Cr	Chromite	$Cr_2O_3 \cdot FeO$

Metallic ores are often found to contain certain non-metallic rocky substances in them, *e.g.,* sand, clay, quartz, feldspar, silicates, mica, etc. These unwanted impurities are called **gangue** or **matrix.** Thus, the waste material present in an ore is called **gangue.**

6.2 Metallurgy

The process of extracting a metal in pure form from its ores is known as metallurgy. Metallurgical processes can be of following three types : hydrometallurgy, pyrometallurgy and electrometallurgy.

In **hydrometallurgy** the concentrated ore is treated with aqueous solution of some reagent, *e.g.,* NaCN or Cl_2 in the presence of water etc. The metal present in ore forms soluble salt and comes in solution which is then recovered from the solution either by electrolysis or through precipitation by adding some suitable more electropositive metal in the solution. It is generally applicable for less reactive metals like AgBr or highly reactive metals like Al.

Pyrometallurgy generally refers to the extraction through heat. Roasting, calcination, smelting etc., processes are included in it. Generally it is applicable for moderately active metals like Cu, Pb, Zn, Fe, etc.

In **electrometallurgy**, metal is generally extracted with the help of electrolysis. It is applicable for highly reactive metals like Na, K, Al, etc.

6.3 Steps Involved in the Extraction of Metals

It is not possible to chalk out a universal scheme for the extraction of all metals since the extraction of each metal is an individual problem and the line of treatment depends upon the nature of the ore, impurities and the metal.

The various metallurgical operations used in the extraction of pure metals from their respective ores are given below.

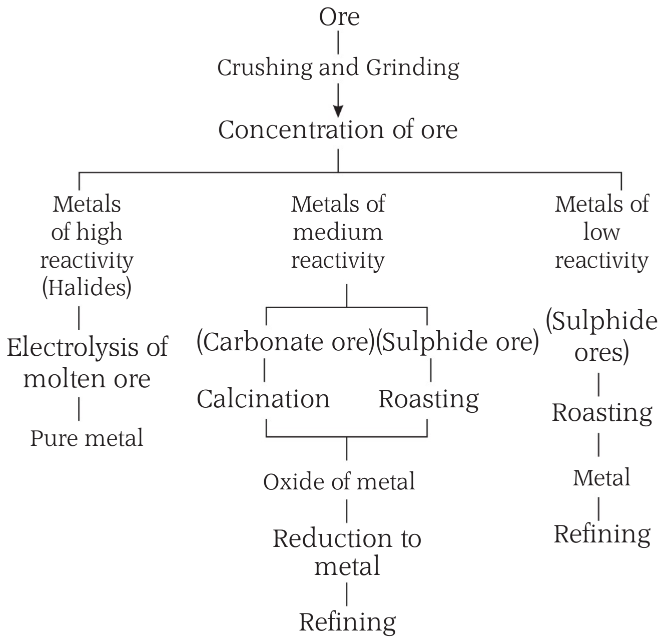


Fig. 6.1 Steps involved in the extraction of metals from ores

Crushing and Grinding of the Ore

Generally, ores occur in nature as huge lumps. They are crushed into small pieces in gyratory crushers. The crushed ore is then grinded with the help of rollers or in the stamp mill to powder form.

Concentration of the Ore

The process of gangue removal or increase in concentration of ore depends upon the nature of ore and the impurities present in it.

Some of the important methods involved are

(a) Gravity Separation or Levigation

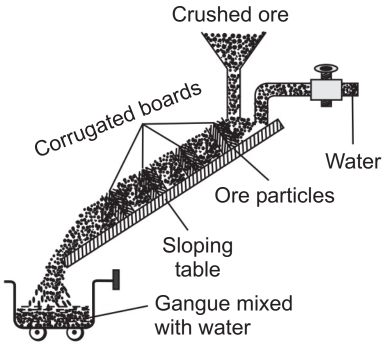


Fig. 6.2 Concentration of ore by levigation

In this method, the ore is powdered and then washed in a running stream of water. The lighter earthy material and gangue are washed away, while the heavy ore particles remain behind. The oxide ores of iron Fe_2O_3 and Fe_3O_4 are concentrated by this method. This method is also called **levigation.**

(b) Froth Floatation Process

In this process, the ore is powdered and then placed in a water tank. Now some **pine oil and potassium ethylxanthate** is added to it. A strong stream of air is passed then in the tank containing water and powdered ore. When the whole mass is agitated, froth is formed. The ore particles are preferentially wetted by the oil and come at the surface along with the froth.

Some compounds are used to stabilize the froth (*e.g.,* cresols and aniline) and are called **froth stabilizers.** The impurities are wetted by water and remain behind in the tank. The substances like pine oil, xanthates and fatty acids are called **collector**, which attach themselves by polar groups to grains of minerals which then become water repellant and thus pass on into the froth.

Activators and depressants are the compounds which activate and depress respectively the floating property of one of the components of the ore and thus, help in the separation of different minerals present in the same ore. Copper sulphate is an example of activator, while sodium and potassium cyanides are the examples of depressants.

The use of these three types of reagents can be illustrated in the separation of galena PbS which is usually associated with sphalerite ZnS and pyrites FeS_2. Floatation is carried out in presence of potassium ethyl xanthate (collector) and sodium cyanide and alkali (depressants). The latter compounds depress the floatation property of ZnS and FeS_2 particles and hence, only PbS particles go into the froth when air is blown in. After the removal of galena, the process is repeated by adding copper sulphate (activator) which activates the floating character of ZnS particles and thus, this time ZnS comes with the froth. The acidification of remaining slurry leads to the floatation of FeS_2.

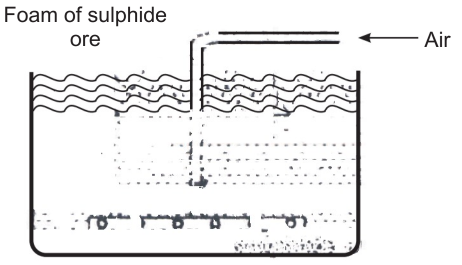


Fig. 6.3 Froth floatation process for the concentration of sulphide ores

The sulphide ores of Cu, Ag, Zn, Pb, etc., are concentrated by this process.

(c) Magnetic Separation

The process of magnetic separation depends upon the magnetic properties of the ore and the gangue. If the ore or the impurity is magnetic then this process is used to separate the magnetic substance from non-magnetic substance.

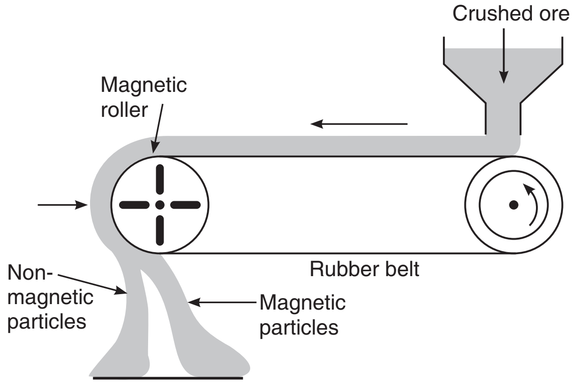


Fig. 6.4 An electromagnetic separator, used to concentrate the ore

The ore is concentrated by a magnetic separator which consists of a leather belt moving over two rollers. One of the roller is magnetic. The method is useful for separating tungsten ore particles from cassiterite (SnO_2). The process may also be employed for separating other transition metal ores like magnetite (Fe_3O_4), chromite ($FeO \cdot Cr_2O_3$) and pyrolusite (MnO_2) from unwanted gangue.

(d) Leaching

It involves the treatment of the ore with a suitable reagent so as to make it soluble while impurities remain insoluble. The ore is recovered from the solution by suitable chemical methods. Some important examples of leaching are

(i) In **Bayer's process** pure aluminium oxide is obtained from the bauxite ore by treating the powdered ore with a concentrated solution of NaOH resulting in dissolution of Al_2O_3, leaving the impurities behind as,

$$Al_2O_3(s) + 2OH^-(aq) + 3H_2O \longrightarrow 2Al(OH)_4^-(aq)$$

(ii) Similarly, the leaching method is also employed in concentrating Ag and Au ores with the help of their dissolution in NaCN or KCN or Cu with the help of H^+ or Fe scraps..

In case of gold, $O_2(g)$ oxidises free metal to Au^+, which complexes with CN^-.

$$4Au(s) + 8CN^- + O_2(g) + 2H_2O \longrightarrow 4[Au(CN)_2]^- + 4OH^-$$

The pure metal is then displaced from the solution by active metal (as Zn).

$$[2Au(CN)_2]^- + Zn \longrightarrow 2Au(s)\downarrow + [Zn(CN)_4]^{2-}$$

Conversion of Concentrated Ore to Oxide

The concentrated ore, if not an oxide, is converted into oxide because oxides can be reduced easily as compared to sulphides and other such compounds.

The concentrated ore is converted into its oxide by following two ways

(a) Roasting

The concentrated ore is heated alone or mixed with some other substance, *below its melting point in the presence of air,* resulting in oxidation of ore and impurities. This type of specialised heating of concentrated ore is called roasting. *Usually the sulphide ores undergo roasting.* In the process of roasting in general, normally the impurities like As and S are oxidised to volatile oxides like SO_2, As_2O_3 etc., and removed.

Some examples of roasting are

(i) In extraction of iron as

$$S + O_2 \longrightarrow SO_2\uparrow$$
$$4As + 3O_2 \longrightarrow 2As_2O_3\uparrow$$
$$4FeO + O_2 \longrightarrow 2Fe_2O_3$$

Here, sulphur and arsenic impurities are removed as volatile oxides due to roasting, while any ferrous oxide present is converted to ferric oxide.

(ii) Zinc blende (ZnS) is roasted to give ZnO in the extraction of Zn as

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

(iii) On roasting, the copper ore chalcopyrite ($CuFeS_2$), the impurities S and As present in it are removed as volatile SO_2 and $As_2O_3 \cdot CuFeS_2$ is converted into cuprous sulphide and ferrous sulphide as

$$S + O_2 \longrightarrow SO_2\uparrow$$
$$4As + 3O_2 \longrightarrow 2As_2O_3\uparrow$$
$$2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2$$

Some part of cuprous sulphide and ferrous sulphide is converted into Cu_2O and FeO as

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2\uparrow$$
$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2\uparrow$$

(iv) For silver ore, chloro roasting is done as

$$Ag_2S + 2NaCl \longrightarrow 2AgCl + Na_2S$$
$$AgCl + 2Hg \longrightarrow Ag-Hg + HgCl$$

(b) Calcination

The hydroxide and carbonate ores after concentration does not undergo roasting, these are subjected to calcination instead. In the process of calcination, the ore is heated below its melting point in the absence of air or in the limited supply of air. Such a heating results in conversion of these hydroxide and carbonate ores to metal oxides.

During calcination, the ore becomes porous, and volatile impurities are removed.

Some examples of calcination are given below

(i) Aluminium hydroxide is converted to alumina as,

$$2Al(OH)_3 \xrightarrow{1500^\circ C} Al_2O_3 + 3H_2O$$

(ii) Limonite (iron ore) gives anhydrous ferric oxide as,

$$Fe_2O_3 \cdot 3H_2O \xrightarrow{\Delta} Fe_2O_3 + 3H_2O$$

(iii) Siderite (iron ore) gives ferrous oxide as,

$$FeCO_3 \xrightarrow{\Delta} FeO + CO_2$$

(iv) Calamine (zinc ore) gives zinc oxide as,

$$ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$$

(v) $NaHCO_3$ gives Na_2CO_3 and $CaCO_3$ gives CaO as,

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + CO_2 + H_2O$$

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

It must be noted that calcination proceeds only with the expulsion of some small molecules like water, CO_2, SO_2, etc., without any other chemical change while during roasting definite chemical changes like oxidation, chlorination, etc., takes place. Calcination and roasting also make the mass porous so that it can easily be reduced to the metallic state in the next operation.

Calcination and roasting are carried out in various types of furnaces, most important of which is reverberatory furnace. The furnaces used in calcination and roasting employ refractory materials which resist high temperature and do not become soft.

Acidic refractories	: SiO_2 and $SiO_2 + Al_2O_3$
Basic refractories	: CaO and MgO
Neutral refractories	: Graphite, chromites, carborundum (SiC).

Refractory material should not combine with the ore or the metal and must be able to protect the furnace from high temperature.

Reduction of Oxide to Metal

Once an ore has been concentrated, it is reduced to free metals by several methods. The method used depends on the activity of the metal as measured by its standard reduction potential. The most active metals have the most negative standard reduction potential and are most difficult to reduce and the least active metals have the most positive standard reduction potential and are easiest to reduce.

(a) Smelting or Reduction by Carbon or its Oxides

Carbon (as coal, coke, charcoal, CO etc.,) reduces many metal oxides into respective metals, such as

$$\underset{\text{cassiterite}}{SnO_2} + 2C \xrightarrow{1473-1573\text{ K}} Sn + 2CO$$

$$ZnO + CO \xrightarrow{1600\text{ K}} Zn + CO_2$$

$$Fe_2O_3 + CO \xrightarrow{823\text{ K}} 2FeO + CO_2$$

$$FeO + CO \xrightarrow{1123\text{ K}} Fe + CO_2$$

Besides these, oxides of Pb, Cr, Mn, Be, etc., can also be reduced by the same process.

Some of the oxide ores like haematite (Fe_2O_3), tinstone (SnO_2) contain some infusible earthy impurities even after concentration. The impurities may be basic (*i.e.,* metallic oxides like CaO, FeO, MgO etc.) or acidic (*i.e.,* non-metallic oxides like SiO_2, P_2O_5, etc.). In order to remove acidic or basic impurities, the concentrated ore is mixed with coke and another substance, called the **flux.** The mixture is heated in the presence of air at high temperature and this heating is called **smelting.** Reactions taking place in smelting are

(i) Coke or CO reduces oxide ore to free metal, *e.g.,*

$$PbO + C \longrightarrow Pb\,(\text{molten lead}) + CO\uparrow$$

$$PbO + CO \xrightarrow{\text{High temperature}} Pb\,(\text{molten lead}) + CO_2\uparrow$$

$$Fe_2O_3(\text{haematite}) + 3CO \longrightarrow 2Fe(\text{spongy iron}) + 3CO_2\uparrow$$

$$SnO_2(\text{tinstone}) + 2C \longrightarrow Sn\,(\text{molten tin}) + 2CO\uparrow$$

(ii) The flux combines with acidic or basic impurities present in the oxide ore and forms a fusible mass, called **slag.** Thus, the impurity is removed in the form of fusible slag as

$$\text{flux} + \text{impurity} \longrightarrow \text{fusible slag}$$

The slag floats over the molten metal and can be removed from upper exit.

Depending upon the requirement, a flux may be acidic or basic. Basic flux is used to remove acidic impurities and *vice-versa*. The examples of acidic flux are SiO_2, P_2O_5, B_2O_3, etc. The examples of basic flux are CaO, MgO, etc.

In case of tin, the concentrated ore is mixed with one-fifth of its weight of powdered anthracite (carbon) and a little limestone, $CaCO_3$ and heated in a reverberatory furnace at 1200–1300°C. The ore is reduced to metallic state while silica (impurity) is removed as slag.

$$SnO_2 + 2C \longrightarrow Sn + 2CO\uparrow$$

$$CaCO_3 \xrightarrow[-CO_2]{\Delta} CaO \xrightarrow{SiO_2} \underset{\substack{\text{calcium silicate}\\ \text{(slag)}}}{CaSiO_3}$$

Excess of lime must be avoided because it would otherwise react with tin to form calcium stannate.

The molten metal collects on the bottom of the furnace. It contains 99.5% of metallic tin, called the **black tin.**

Caution Points

- (*i*) *Some ores are self-fluxing because they contain some gangue (stony matrix accompanying the ore) which is self fusible and thus, no foreign flux is required.*
- (*ii*) *Blast furnace is used in the reduction of iron oxides while reverberatory furnace is used in the reduction of tin oxide.*

(b) With Hydrogen

Hydrogen being inflammable is used as a reducing agent in very few cases, *e.g.,*

$$MO_3 + 3H_2 \longrightarrow M + 3H_2O \qquad (M = \text{Mo or W})$$

This method is not widely used, because many metals react with H_2 at elevated temperatures forming hydrides. Also there are chances of explosion of H_2 with O_2.

Sample **Problem 1** *Although carbon and hydrogen are better reducing agents but they are not used to reduce metallic oxides at high temperatures because* **[NCERT Exemplar]**

- (a) *they are non-metals*
- (b) *they are less reactive*
- (c) *they become more reactive and from carbide and hydride*
- (d) *they are costly*

Interpret (c) This is because at high temperatures, carbon and hydrogen react with metals to form carbides and hydrides respectively.

(c) Goldschmidt Aluminothermic Process

Chromium and manganese oxides are reduced through aluminothermic reduction processes or Goldschmidt aluminothermic process, *e.g.,*

$$Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$$
$$3Mn_3O_4 + 8Al \longrightarrow 4Al_2O_3 + 9Mn$$

In this process, mixture of the metallic oxide and aluminium powder, commonly known as **thermite,** is taken in a steel crucible placed in a bed of sand. A mixture of aluminium powder and barium peroxide (BaO_2) is placed over the charge in the form of a heap and magnesium wire is embedded in it. The charge is covered by a thick layer of carbon followed by a thin layer of feldspar to avoid loss of heat and to protect the mass from oxidation. The magnesium ribbon which acts as a fuse is lighted. It starts burning and hence, mixture also starts burning. Since the reaction is highly exothermic, once it starts, it goes on till all the oxide is converted into metal.

Sample **Problem 2** *In aluminothermite process, aluminium is used as*

- (a) *reducing agent* (b) *oxidising agent*
- (c) *solder* (d) *flux*

Interpret (a) The reaction occurring in aluminothermic process is

$$\underbrace{\overset{+3}{M}_2O_3 + 2Al \longrightarrow Al_2O_3 + 2\overset{0}{M}}_{\text{Reduction}}$$

Here, metal is reducing from its +2 to 0 oxidation state, so Al acts as a reducing agent.

(d) Reduction by Water Gas

It is applied for nickel oxide.

$$2NiO + CO + H_2 \longrightarrow 2Ni + CO_2 + H_2O$$

(e) With Other Metals

Na and Mg metals are used in certain cases as reducing agents, *e.g.,*

$$TiO_2 + 2Mg \longrightarrow Ti + 2MgO$$
$$TiO_2 + 4Na \longrightarrow Ti + 2Na_2O$$

(f) Auto-reduction

This process is also known as **self reduction.** This is used when no external reducing agent is required. The sulphide ores of less electropositive metals like Hg, Pb, Cu etc., are heated in air to either convert the complete ore or part of the ore into oxide or sulphate which then reacts with the remaining sulphide ore to give the metal and sulphur dioxide, *e.g.,*

(i) Extraction of Cu from copper glance

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$
$$Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2$$

(ii) Extraction of Hg from cinnabar

$$2HgS + 3O_2 \longrightarrow 2HgO + 2SO_2$$
$$2HgO \xrightarrow{\Delta} 2Hg + O_2$$

(iii) Extraction of Pb from galena

$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$$
$$2PbO + PbS \longrightarrow 3Pb + SO_2$$

Caution Point *Oxides of metals lying below* Hg (*and that of* Hg) *in electrochemical series, i.e., oxides of* Ag, Pd, Pt, Au *decompose on heating giving metal.*

(g) Displacement Method

If the temperature needed for carbon to reduce an oxide is too high for economic or practical purpose, the reduction may be affected by another highly electropositive metal. *e.g.,* Ag and Au are obtained from their complex cyanides (cyanide process) when more reactive Zn metal displaces them as

$$2M(CN)_2^- + Zn \longrightarrow Zn(CN)_4^{2-} + 2M$$

(where, M = Ag, Au)

(h) Electrolytic Method

The oxides of highly electropositive metals of group 1 and 2 cannot be reduced easily with carbon at moderate temperatures. These metals are thus, extracted by the electrolysis of their salts (generally, oxides, hydroxides or chlorides in fused state). The metal is liberated at the cathode. *e.g.,* Sodium is obtained by the electrolysis of fused NaCl or brine.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

$$Na^+ + e^- \longrightarrow Na \qquad \text{(at cathode)}$$

$$Cl^- \longrightarrow Cl + e^- \qquad \text{(at anode)}$$

$$Cl + Cl \longrightarrow Cl_2$$

In the case of NaCl (brine solution), Hg electrodes are used so that Na metal after deposition at cathode forms amalgam with Hg.

Metals other than those of s-block can also be extracted by electrolysis of fused compounds, *e.g.,* fused Al_2O_3 mixed with Na_3AlF_6 is used for the production of Al.

Caution Point *Electrolysis can be carried out in solvents other than water.* F_2 *reacts violently with* H_2O *hence, it is produced by electrolysis of* KHF_2 *in* HF.

Refining of Crude Metal

Metals extracted through any of the methods described above are usually contain some impurities.

Following methods are used to purify the metals

(a) Distillation Method

This process is used for those metals which are easily volatile. In this method, the impure metal is heated in a retort and its vapours are separately condensed in a receiver. The non-volatile impurities are left behind in the retort. This is used for the purification of Zn, Cd, Hg, etc.

(b) Liquation Method

Low melting metals can be separated by this method. In this method, the impure metal is poured on the sloping hearth of a reverberatory furnance and heated gently to a temperature slightly above the melting point of the metal. The pure molten metal runs out leaving behind the infusable matter (called dross) on the hearth. This is used for the purification of Bi, Sn, Pb, Hg, etc.

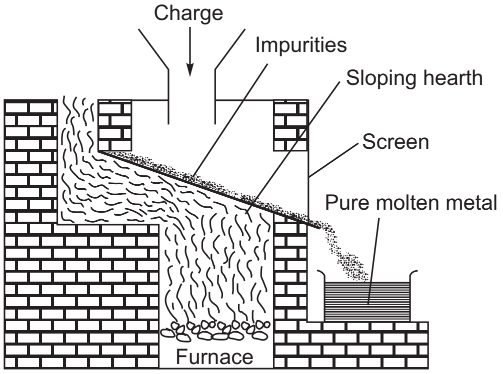


Fig. 6.5 Liquation method

(c) Electrolysis

Many of metals such as Cu, Ag, Au, Al, Pb etc., are purified by this method. Here, the cathode is made up of pure metal and anode is made up of impure metal. The electrolyte used is infact an aqueous solution of salt of the metal. Thus,

$$\text{Anode} \longrightarrow \text{impure metal}$$

$$\text{Cathode} \longrightarrow \text{pure metal}$$

$$\text{Electrolyte} \longrightarrow \text{salt of metal in aqueous solution}$$

On passing electric current, pure metal deposits on cathode. The equivalent mass of anode dissolves in the form of salt and comes in the solution. The impurities either remain dissolved in solution or settled down as anode mud around anode. The applied voltage here is such that more electropositive metals (impurity) remain as ions in the both whereas, the less electropositive metals (also impurities) remain unionised and fall down as anode mud.

(i) Electrorefining of Cu

Anode Blister copper (98%); **Cathode** : Pure copper

Electrolyte Aq. solution of $CuSO_4$ (15%) + 5% dil. H_2SO_4

The function of dil. H_2SO_4 is to check the hydrolysis of $CuSO_4$ and increases and the conductance of the solution.

(ii) Electrorefining of silver (Moebius process)

Anode Impure silver; **Cathode** : Pure silver

Electrolyte Aq. $AgNO_3$ + 1% dil. HNO_3.

(iii) Electrorefining of lead (Bett's process)

Anode Impure lead; **Cathode** : Pure lead

Electrolyte A mixture of $PbSiF_6$ and H_2SiF_6.

(d) Poling

The impure metal containing its oxides as impurity can be purified by this method. The molten impure metal is stirred with green poles of wood. The green poles of wood release the hydrocarbon gases which reduce the oxide impurities. This method is especially used in the purification of copper (old method).

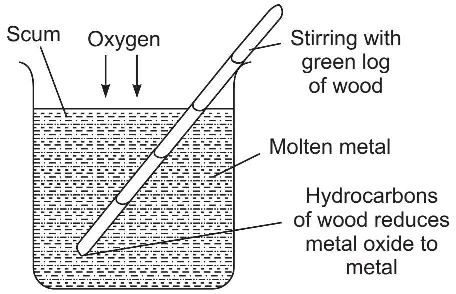


Fig. 6.6 Refining of metal by poling

(e) Zone-Refining Method

This method is employed to get the metals of very high purity. Metals like Ge, Si, B, Ga, In, etc., are purified by this method. The method is based upon the principle that an impure molten metal on gradual cooling will deposit crystals of the pure metal while impurities will be left in remaining part of molten metal. In this process, the impure metal is taken in the form of rod and a circular heater is fitted around this rod which is slowly moved along the length of the rod. As the heater moved, the molten impurities also moved along with the heater while the pure metal recrystallises without leaving its position. Lastly the end of rod where the impurities finally get concentrated is cut off, leaving the rod of comparative more pure metal. The process is repeated a number of times until the desired state of purity is reached. The method is especially useful for producing the semiconductors of very high purity.

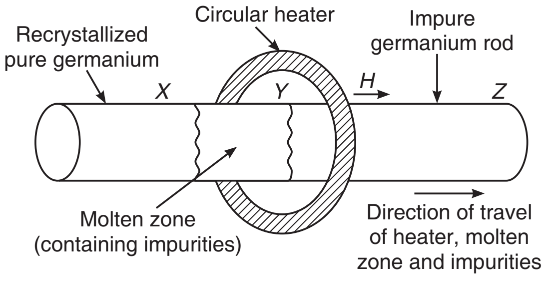


Fig. 6.7 Zone refining of germanium metal

(f) Vapour Phase Refining Method

This method is based upon the principle that the impure metal is converted into suitable volatile compound which on being heated, gets decomposed to give pure metal. Among its examples we can observe,

(i) Mond process (also called carbonyl process)
(ii) van-Arkel de-Boer's process (also called iodine refining process)

The **Mond's process** is used for the purification of Ni. It is the most important process for getting 99.9% pure Ni metal from crude Ni. The process was discovered by German chemist, **Ludvig** in 1893. In the process, the crude Ni is heated in the stream of CO to form volatile nickel carbonyl, $Ni(CO)_4$. This $Ni(CO)_4$ when heated higher, it will decomposed to give pure metal as

$$\underset{\text{impure}}{\text{Ni}} + 4\text{CO} \xrightarrow{330-350\text{ K}} \text{Ni(CO)}_4 \xrightarrow{450-470\text{ K}} \underset{\text{pure}}{\text{Ni}} + 4\text{CO}$$

In the **van-Arkel de-Boer's process,** the impure metal is heated with iodine in a sealed vessel, so that the metal forms volatile metallic iodide and impurities do not react with iodine. The metallic iodide is then decomposed when heated further at higher temperatures. The metals purified through this way are Zr (zirconium), Ti (titanium), V (vanadium), Th (thorium), etc. For example, purification of Ti through this method can be done as

$$\underset{\text{(impure)}}{\text{Ti}} + 2\text{I}_2(g) \xrightarrow{150-250^\circ\text{C}} \text{TiI}_4(g) \xrightarrow[\text{tungsten filament}]{1400^\circ\text{C}} \underset{\text{pure}}{\text{Ti}(s)} + 2\text{I}_2(g)$$

(g) Amalgamation Process

This method is used for the extraction of noble metals like Ag, Au etc., from the native ores. The finely powdered ore is brought in contact with Hg which combines with the particles of the metal present in the ore and form amalgam. The metal is recovered from the amalgam by subjecting it to distillation, where the Hg distills over, leaving behind the metal.

(h) Cupellation

This method is used when impure metal contains impurities of other metals which form volatile oxides, *e.g.,* traces of lead ore removed from silver (as volatile PbO) by this process.

(i) Chromatography

This method is used when the elements are available only in minute quantities and the impurities are not very much different in their chemical behaviour from the element to be purified.

Adsorption chromatography is generally used. In this, the impure metal is dissolved in a suitable solvent and the solution is allowed to run slowly into an adsorbent column packed with alumina (Al_2O_3). The metal and the impurities present are adsorbed at different rates. These are then eluted with suitable eluent (solvent). In this method, weakly adsorbed component is eluted first and the strongly adsorbed component is eluted afterwards.

Check Point 1

1. Impurity of FeO is removed by SiO_2 instead of CaO. Why?
2. Explain, why is chalcocite roasted but not calcined during recovery of copper?
3. Explain, why aluminium metal is frequently used as a reducing agent for the extraction of metals such as Cr, Mn etc?
4. In electrolysis, why graphite is used as anode instead of diamond?

6.4 Principles Involved in the Extraction of Metals

Extraction of metal from its ore depends upon thermodynamic as well as electrochemical principles, *which are described below*

Electrochemical Principles Involved in Extraction

The method employed for the extracting a metal from its ore depends on the nature of the metal and that of the ore and may be related to the position of the metal in the electrochemical series. In general, metals with $E° < -1.5$ V yield compounds which are very difficult to reduce and the help of electricity has usually to be taken for the isolation of such metals. On the other hand, noble metals with $E° > +0.5$ V form easily reducible compounds. In general, a metal higher up in the electrochemical series should be more difficult to reduce to metallic form. However, it must be borne in mind that this is a very general statement and cannot be strictly applied because metals are seldom extracted from aqueous solution.

Hot Spot 1

THERMODYNAMIC Principles Involved in Metallurgy

It is an important topic of the chapter for JEE Main examination. The nature of questions may vary from easy to typical and sometimes is confusing.

The free energy change (ΔG) occurring during the reduction processes help in deciding the suitable method for reduction.

For the spontaneous reduction of an oxide, halide or sulphide by an element, the essential condition is that there is a decrease in the free energy of the system (–ve ΔG).

More the negative value of ΔG, the higher is the reducing power of an element. ΔG can be given as

$$\Delta G = \Delta H - T\Delta S$$

where, ΔH = enthalpy change;

ΔG = Gibbs free energy

T = temperature;

ΔS = entropy change

For the reduction of a metal oxide with a reducing agent, the plot of $\Delta G°$ against temperature is studied, which is called **Ellingham diagram.**

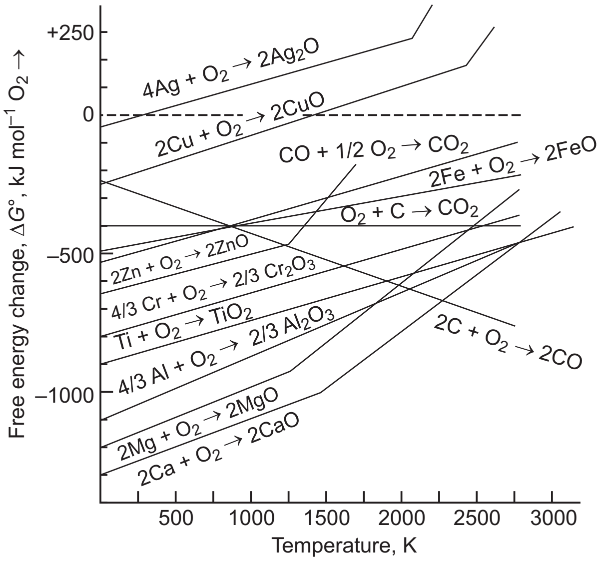


Fig. 6.8 Combined Ellingham diagram for metals and carbon

Characteristics of Ellingham Diagram

1. All the plots slope upwards since $\Delta G°$ becomes more positive when temperature increases, *i.e.,* stability of oxides decreases.
2. A metal will reduce the oxide of other metals which lie above it in Ellingham diagram, *i.e.,* the metals for which the free energy of formation (ΔG_f°) of their oxides is more negative can reduce those metal oxides which has less negative ΔG_f°.
3. The decreasing order of the negative values of ΔG_f° of metal oxides is

   Ca > Mg (below 1773 K) > Al > Ti > Cr> C > Fe > Ni > Hg > Ag

   Thus, Al reduces FeO, CrO and NiO in thermite reduction but it will not reduce MgO at temperature below 1773 K.

   Mg can reduce Al_2O_3 below 162 K but above 1023 K, Al can reduce MgO.
4. CO is more effective reducing agent below 1073 K and above 1073 K, coke is more effective reducing agent, *e.g.,* CO reduces Fe_2O_3 below 1073 K but above it, coke reduces Fe_2O_3. Coke reduces ZnO above 1270 K.

Example

It is interesting to think of the reduction of ZnO with C as involving a competition between Zn and C for O atoms. We consider following values at 1100°C for the oxidation of Zn and C.

(i) $2Zn + O_2 \longrightarrow 2ZnO; \quad \Delta G° = -360 \text{ kJ}$

(ii) $2C + O_2 \longrightarrow 2CO; \quad \Delta G° = -460 \text{ kJ}$

(i) and (ii) gives

$2Zn + 2CO \longrightarrow 2ZnO + 2C; \quad \Delta G° = +100 \text{ kJ}$

or (iii) $Zn + CO \longrightarrow ZnO + C; \quad \Delta G° = +50 \text{ kJ mol}^{-1}$

(iv) $ZnO + C \longrightarrow Zn + CO; \quad \Delta G° = -50 \text{ kJ mol}^{-1}$

For reaction (iii), in which Zn reduces CO, $\Delta G°$ is positive indicating that this reduction is non-spontaneous (in forward direction), but for the reaction (iv) with negative value of $\Delta G°$ in which C reduces ZnO is spontaneous (in forward direction).

Why must we carry out the reduction of ZnO with C at 1100°C? From an energy stand point it would certainly be more economical to carry it out at a lower temperature. The following graphical representation (Ellingham diagram) is useful tool to help answer such questions. The lines ($2C + O_2 \longrightarrow 2CO$) and ($2Zn + O_2 \longrightarrow 2ZnO$) cross at about 950°C. At about this temperature, Zn and C have equal affinities for O atoms. $\Delta G°$ for reaction (iv) is zero. Above this temperature $\Delta G°$ is negative, and below this temperature $\Delta G°$ is positive. To make reaction (iv) go essentially to completion we need a temperature somewhat in excess of 950°C.

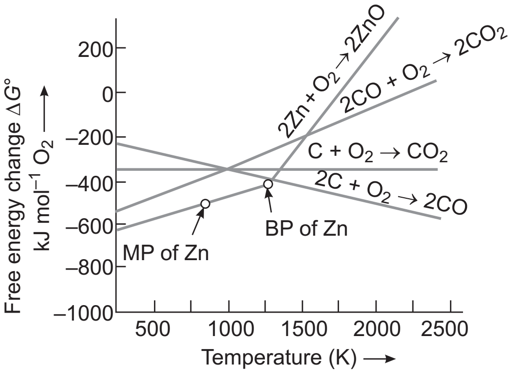


Fig. 6.9 Ellingham diagram for carbon, carbon monoxide and zinc systems

Sample Problem 3 *The value of* $\Delta_f G°$ *for formation of* Cr_2O_3 *is –540 kJ/mol and that of* Al_2O_3 *is –827 kJ/mol. The correct statement from the following is*

(*a*) Cr *have more affinity towards oxygen as compared to* Al
(*b*) Al *have more affinity towards oxygen as compared to* Cr
(*c*) *Affinity towards oxygen depends upon temperature.*
(*d*) *Both (b) and (c)*

Interpret (*b*) The two thermochemical equations may be written as

(i) $\frac{4}{3}\text{Cr}(s) + O_2(g) \longrightarrow \frac{2}{3}Cr_2O_3(s); \quad \Delta_f G° = -540 \text{ kJ}$

(ii) $\frac{4}{3}\text{Al}(s) + O_2(g) \longrightarrow \frac{2}{3}Al_2O_3(s); \quad \Delta_f G° = -827 \text{ kJ}$

Subtracting Eq. (i) from Eq. (ii), we get

$$\frac{2}{3}Cr_2O_3(s) + \frac{4}{3}\text{Al}(s) \longrightarrow \frac{2}{3}Al_2O_3(s) + \frac{4}{3}\text{Cr}(s); \; \Delta_f G° = -287 \text{ kJ}$$

As $\Delta_f G°$ comes out to be negative, the reaction is feasible, *i.e.,* Al can be used for the reduction of Cr_2O_3 or Al have more affinity towards oxygen as compared to Cr.

Sample Problem 4 *The reaction,*

$$Cr_2O_3(s) + 2\text{Al}(s) \longrightarrow Al_2O_3 + 2\text{Cr}; \quad (\Delta G° = -421 \text{kJ})$$

is thermodynamically feasible as is apparent from the Gibbs energy value, but the reaction does not occur at room temperature because **[NCERT]**

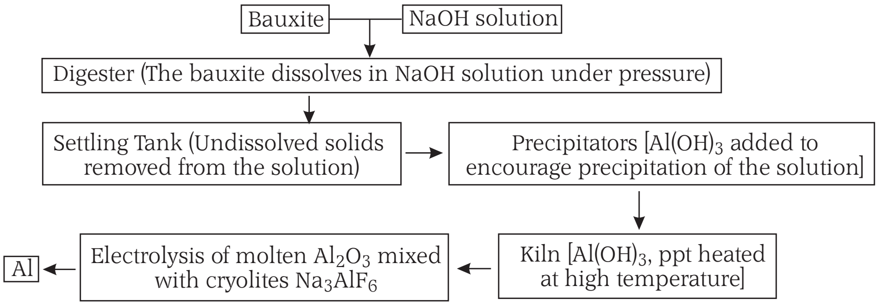
(*a*) *the reaction is reversible at low temperature*
(*b*) *the reactants are solids*
(*c*) *the products are solids*
(*d*) Cr *has more affinity towards oxygen as compared to* Al

Interpret (*b*) The reactants are solids so they cannot react in the present state. When the temperature is elevated, reactants melt and the reaction proceeds. Therefore, a higher temperature than room temperature is required.

6.5 Extraction Schemes of Some Metals

Aluminium

Its chief ore is **bauxite** ($Al_2O_3 \cdot 2H_2O$). *The outline of its extraction from its ore is shown below*



Cryolite improves the electrical conductivity of the cell as Al_2O_3 is poor conductor. This also serves as an added impurity and lower the melting point of the mixture to about 950°C. Al of 99.6 to 99.8% purity is obtained. Probable net reactions are

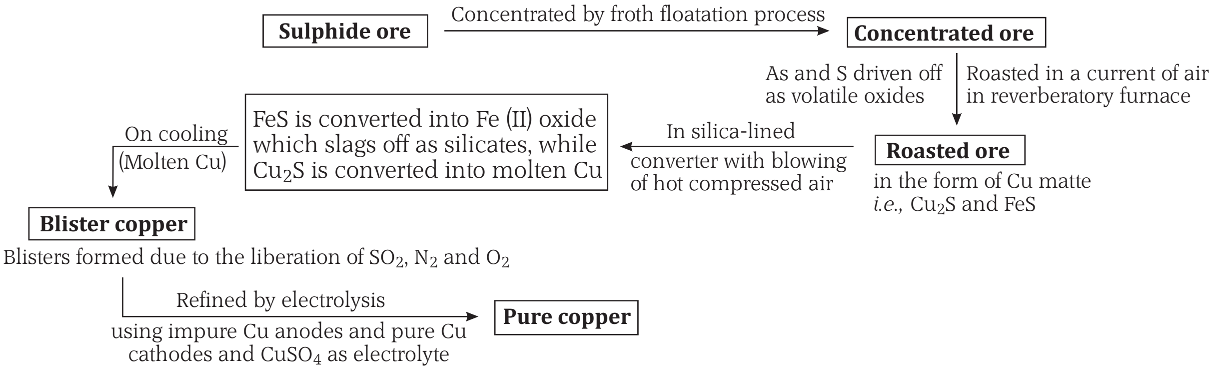
Oxidation at anode $\quad C + 2O^{2-} \longrightarrow CO_2 + 4e^-] \times 3$

Reduction at cathode $\quad Al^{3+} + 3e^- \longrightarrow Al] \times 4$

$$3C + 4Al^{3+} + 6O^{2-} \longrightarrow 4Al + 3CO_2$$

Copper

It does not occur abundantly in nature. Its chief ore are **copper pyrites** ($CuFeS_2$), **malachite** ($CuCO_3 \cdot Cu(OH)_2$), **cuperite** (Cu_2O), **copper glance** (Cu_2S). *The outline of its extraction from its ore looks like*



Low grade copper can be extracted by hydrometallurgical process (wet process) as

Step I Leaching with H_2SO_4 converts salts into sulphates :

$$CuCO_3 + H_2SO_4 \xrightarrow{\Delta} CuSO_4 + H_2O + CO_2$$

$$Cu(OH)_2 + H_2SO_4 \xrightarrow{\Delta} CuSO_4 + 2H_2O$$

$$CuFeS_2 + 2H_2SO_4 \xrightarrow{\Delta} CuSO_4 + FeSO_4 + 2H_2S$$

***Step II* Electrochemical Displacement** Fe is above Cu in electrochemical series hence if Fe scrap is added to $CuSO_4$ solution, Cu is displaced :

$$CuSO_4 + Fe \longrightarrow FeSO_4 + Cu\downarrow$$

Sample **Problem 5** *How is leaching carried out in case of low grade copper ores?* **[NCERT]**

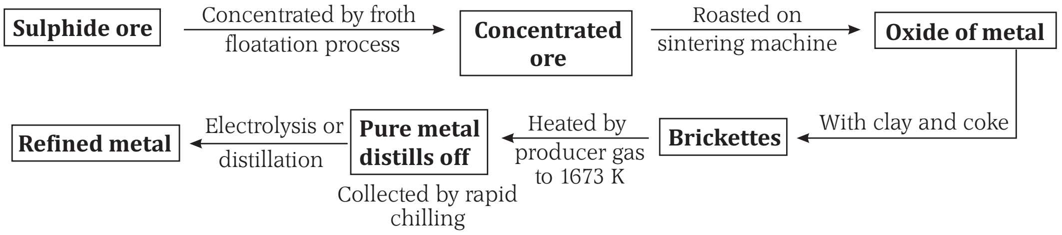
- (a) *By treating copper ore with heat*
- (b) *By treating copper ore with scrap iron*
- (c) *By treating copper ore with* H_2
- (d) *Both* (b) *and* (c)

Interpret (b) In case of low grade ores of copper, hydrometallurgy is used for extraction purposes. Leaching is done by using acid or bacteria. The solution containing Cu^{2+} is treated with scrap iron or H_2.

$$Cu^{2+}(aq) + H_2(g) \longrightarrow Cu(s) + 2H^+(aq)$$

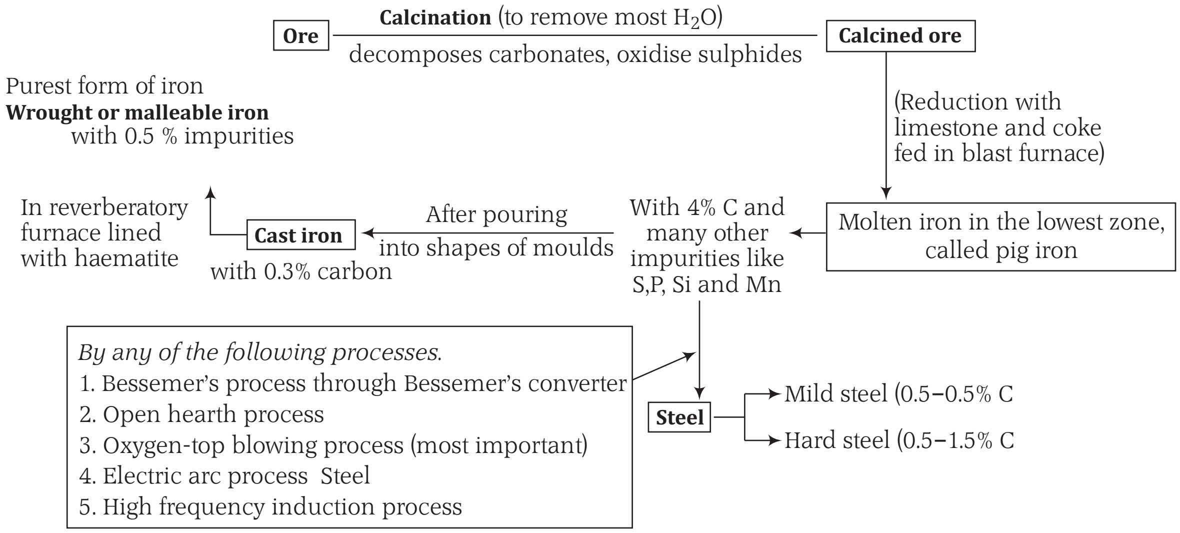
Zinc

Its chief ore is **zinc blende** (ZnS) and other ores are **calamine** ($ZnCO_3$), z**incite** (ZnO), **willemite** (Zn_2SiO_4) etc. *The outline of its extraction looks like*



Iron

Iron is the second most abundant metal after Al in the earth's crust. Its most important ores are **haematite** (Fe_2O_3), **magnetite** (Fe_3O_4), **siderite** ($FeCO_3$) and **iron pyrites** (FeS_2). *The outline of its extraction from its ore looks like*



Reactions Occurring in Blast Furnace

Formation of reducing agents, principally CO(*g*) and H_2(g):

$$2C + O_2 \longrightarrow 2CO \qquad (1700^\circ C)$$

$$C + CO_2 \longrightarrow 2CO \qquad (> 1000^\circ C)$$

$$C + H_2O \longrightarrow CO + H_2 \qquad (> 600^\circ C)$$

Reduction of iron oxide :

$$3CO + Fe_2O_3 \longrightarrow 2Fe + 3CO_2 \qquad (900^\circ C)$$

$$3H_2 + Fe_2O_3 \longrightarrow 2Fe + 3H_2O \qquad (900^\circ C)$$

Slag formation to remove impurities from ore :

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2 \qquad (800-900^\circ C)$$

$$CaO + SiO_2 \longrightarrow CaSiO_3(l) \qquad (1200^\circ C)$$

$$3CaO + P_2O_5 \longrightarrow Ca_3(PO_4)_2(l) \qquad (1200^\circ C)$$

Impurity formation in iron

$$MnO + C \longrightarrow Mn + CO \qquad (1400^\circ C)$$

$$SiO_2 + 2C \longrightarrow Si + 2CO \qquad (1400^\circ C)$$

$$P_2O_5 + 5C \longrightarrow 2P + 5CO \qquad (1400^\circ C)$$

Iron obtained from a blast furnace is called pig iron. It contains about 95% Fe, 4% C and varying quantities of other impurities. Cast iron can be obtained by pouring pig iron directly into molds of the desired shape. Cast iron is very hard and brittle and can be used where it will not be subjected to mechanical or thermal shock.

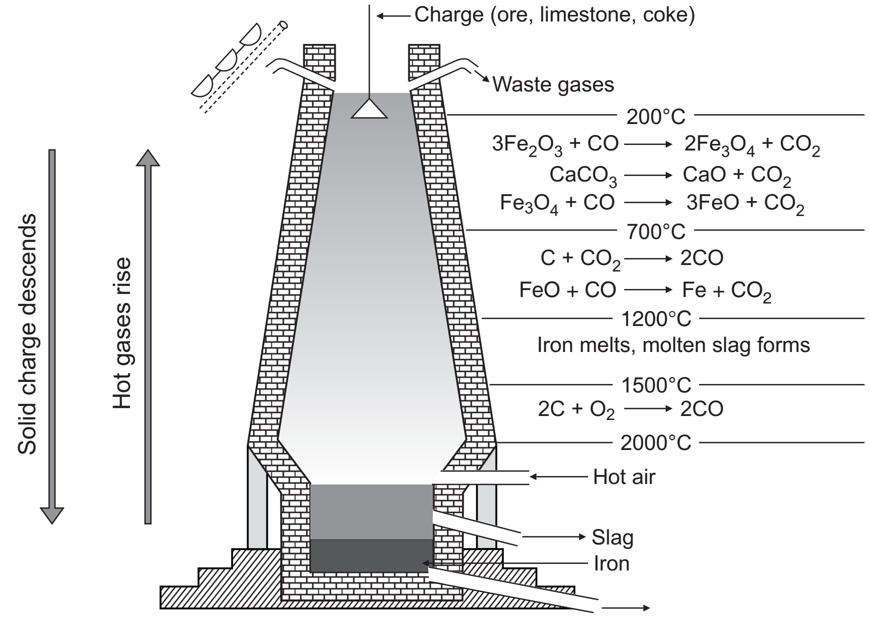
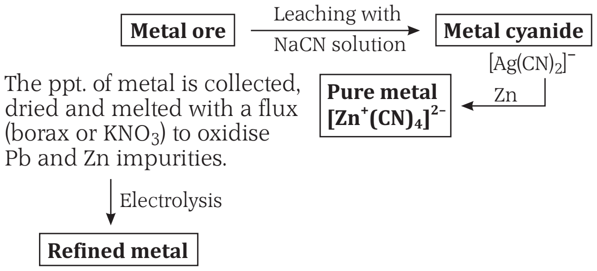


Fig. 6.10 Reduction process of iron oxide in blast furnace

Caution Point *Heating the steel to appropriate temperature for a short time and then cooling it rapidly in order to give it the desired mechanical properties is called tempering. In this way, the ratio of carbon present as graphite and as cementite can be varied within rather wider limits.*

Silver

It occurs as **argentite** or **silver glance** (Ag_2S), **pyrargyrite** or **ruby silver** (Ag_3SbS_3), **proustite** (Ag_3AsS_3) and **horn silver** (AgCl). The most important method of extraction is cyanide process in which



Desilverisation of Lead

When lead-silver alloy is poor in silver (such as argentiferrous lead or galena), desilverisation of lead is affected by **Parke's process.** *It depends upon the fact that:*

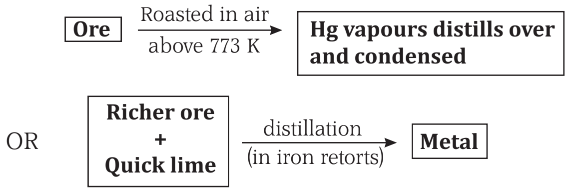
(i) When zinc is added to a melted alloy of silver and lead, zinc takes away silver from the alloy and itself forms an alloy with silver and not with lead.
(ii) Alloy of zinc and silver melts at a higher temperature than lead.
(iii) The alloy of silver and zinc is lighter than lead and forms two separate layers.
(iv) On distillation of silver and zinc alloy, zinc separates.

Pattinson's Process

It depends upon the fact that the alloy of lead and silver containing less than 1.8 per cent of silver, melts at a lower temperature than pure lead. If this type of alloy is melted, and the melted alloy is allowed to cool, lead first separates and repeating the process, one becomes richer in silver. Further recovery is done by cupellation process.

Mercury

It is found as $1 \times 10^{-5}\%$ of earth crust and its most important ore is **cinnabar** (HgS).



It can be purified by dropping slowly through dil. HNO_3. The metallic impurities displace Hg from nitrate and go into the solution. Further purification is carried out by distillation under reduced pressure.

Check Point 2

1. Give an example in which water gas is used in the extraction of metal?
2. In place of copper, zinc is used for the recovery of silver from the complex $[Ag(CN)_2]^-$. Why?
3. In the electrolysis of aluminium, some cryolite is added. Explain, why?
4. Why lime stone is used in blast furnace?

WORKED OUT Examples

Example 1 *Lead is extracted from galena* (PbS), *either by following ways.*

(*I*) $PbS \xrightarrow[-SO_2]{\text{Roasted in air}} PbO \xrightarrow[-CO_2]{\text{Heated with C}} Pb$

(*II*) $PbS \xrightarrow[-SO_2]{\text{Roasted in air}} PbO \xrightarrow{\text{Heated with PbS}} Pb + SO_2$

Auto-reduction process is

(a) *I*	(*b*) *II*
(c) *Both* (a) *and* (*b*)	(*d*) *None of these*

Solution (*b*) In auto-reduction, no external reducing agent is required. In such a reduction reaction, the product formed acts as a reducing agent and reduces the oxide to metal. Thus, only reaction II is called auto-reduction.

$$2PbS + 3O_2 \xrightarrow{\text{Roasted in air}} 2PbO + 2SO_2$$

$$\underset{\substack{\text{product (acts as}\\\text{reducing agent)}}}{2PbO} + PbS \longrightarrow 3Pb + SO_2$$

Example 2 *The chemical process in the production of steel from haematite ore involves*

(a) *reduction*
(*b*) *oxidation*
(*c*) *reduction followed by oxidation*
(*d*) *oxidation followed by reduction*

Solution (*d*) In haematite, some FeO is also present alongwith Fe_2O_3. Thus, first of all this FeO is oxidised to Fe_2O_3 and after that the Fe_2O_3 gets reduced to Fe_3O_4 and then FeO and finally to Fe. Hence, in this process, first oxidation occurs and after that reduction takes place.

Example 3 *Select the incorrect reduction process.*

(a) $2[Ag(CN)_2]^- + Zn \longrightarrow [Zn(CN)_4]^{2-} + 2Ag$

(*b*) $CuO + H_2 \longrightarrow Cu + H_2O$

(*c*) $ZnO + H_2 \longrightarrow Zn + H_2O$

(*d*) $MgO + C \longrightarrow Mg + CO$

Solution (*c*) It is not possible for a less reactive element to reduce a more reactive element. Zn is moderately reactive metal and is more reactive as compared to hydrogen. Thus, hydrogen has no ability to reduce Zn^{2+} to Zn. Cu being less reactive is reduced by hydrogen.

Example 4 *Which of the following process involves smelting?*

(*a*) $Al_2O_3 \cdot 2H_2O \xrightarrow{\Delta} Al_2O_3 + 2H_2O$

(*b*) $Fe_2O_3 + 3C \xrightarrow{\Delta} 2Fe + 3CO$

(*c*) $ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$

(*d*) $2PbS + 3O_2 \xrightarrow{\Delta} 2PbO + 2SO_2$

Solution (*b*) When concentrated ore is mixed with coke and flux and heated in the presence of air at high temperature, impurities get removed. This process is called smelting. Actually, it is a reduction process, in which oxide is reduced to metal. Therefore, following process will involve smelting.

$$Fe_2O_3 + 3C \xrightarrow{\Delta} 2Fe + 3CO$$

Example 5 *Match the method of concentration of the ore in Column I with the ore in Column II and select the correct alternate.*

Column I	*Column II*
i. *Magnetic separation*	(*A*) $Al_2(SiO_3)_3$
ii. *Gravity separation*	(*B*) Ag_2S
iii. *Froth floatation*	(C) $FeCr_2O_4$

	(i)	(ii)	(iii)
(a)	*A*	*B*	*C*
(*b*)	*C*	*B*	*A*
(*c*)	*B*	*A*	*C*
(*d*)	*C*	*A*	*B*

Solution (*d*) (i) Magnetic separation method is used when either ore or impurity is magnetic in nature, e.g., $FeCr_2O_4$.

(ii) Gravity separation is used when ore is heavy and impurities are lighter e.g., $Al_2(SiO_3)_3$.

(iii) Froth floatation is generally used for sulphide ores e.g., Ag_2S.

Example 6 *Consider* $\Delta G_f^\circ(CuO) = -129.7\ kJ\ mol^{-1}$, $\Delta G_f^\circ(H_2O) = -237.2\ kJ\ mol^{-1}$ *and* $\Delta G_f^\circ(CO) = -137.2\ kJ\ mol^{-1}$. *The better reducing agent for the reduction of* CuO *is*

(*a*) *hydrogen*	(*b*) CO
(*c*) C	(*d*) *All can be used*

Solution (*a*) (I) $CuO + C \longrightarrow Cu + CO$

$$\Delta G^\circ = \Delta G_f^\circ(CO) - \Delta G_f^\circ(CuO)$$
$$= -137.2 + 129.7$$
$$= -7.5 \text{ kJ mol}^{-1}$$

(II) $CuO + H_2 \longrightarrow Cu + H_2O$

$$\Delta G^\circ = \Delta G_f^\circ(H_2O) - \Delta G_f^\circ(CuO)$$
$$= -237.2 + 129.7$$
$$= -107.5 \text{ kJ mol}^{-1}$$

More negative value of ΔG° for reaction (II) indicates that H_2 is better reducing agent.

Example 7 *In which of the following isolations no reducing agent is required?*

(*a*) *Iron from haematite*
(*b*) *Aluminium from bauxite*
(*c*) *Zinc from zinc blende*
(*d*) *Mercury from cinnabar*

Solution (*d*) In case of auto-reduction, no reducing agent is required

(a) $\underset{\text{haematite}}{Fe_2O_3} + \underset{\text{reducing agent}}{3CO} \longrightarrow 2Fe + 3CO_2$

(b) $\underset{\text{bauxite}}{Al_2O_3} + \underset{\text{reducing agent}}{3C} + N_2 \longrightarrow 2AlN + 3CO\uparrow$

$$AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$$
$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$$
$$\xrightarrow{\text{electrolysis}} Al$$

(c) $\underset{\text{zinc blende}}{2ZnS} + 3O_2 \longrightarrow 2ZnO + 2SO_2$

$ZnO + \underset{\text{reducing agent}}{C} \longrightarrow Zn + CO$

(d) $\underset{\text{cinnabar}}{2HgS} + 3O_2 \longrightarrow 2HgO + 2SO_2$

$$\underset{\text{product}}{2HgO} \xrightarrow{\Delta} 2Hg + O_2$$

Example 8 *Of the following reduction processes*

(*I*) $PbO + C \longrightarrow Pb$
(*II*) $ZnO + C \longrightarrow Zn$
(*III*) $Fe_2O_3 + C \longrightarrow FeO$
(*IV*) $Ca_3(PO_4)_2 + C \longrightarrow P$

correct processes are

(*a*) *I, II*	(*b*) *I, II, IV*
(*c*) *II, III*	(*d*) *All of these*

Solution (*b*) Except III, all the reduction processes are correct. Fe_2O_3 (haematite ore) is reduced into Fe, instead of FeO.

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

Start Practice for JEE Main

Round I (Topically Divided Problems)

Occurrence of Metals

1. Metal occur in the native form because of their
(a) high electronegativity (b) high reactivity
(c) low reactivity (d) low density

2. Which of the following metal is sometimes found native in nature?
(a) Mg (b) Cu
(c) Al (d) Fe

3. All ores are minerals, while all minerals are not ores because
(a) minerals are complex compounds
(b) the minerals are obtained from mines
(c) the metal cannot be extracted economically from all the minerals
(d) All of the above are correct

4. A number of elements are available in earth's crust but most abundant elements are **[NCERT Exemplar]**
(a) Al and Fe (b) Al and Cu
(c) Fe and Cu (d) Cu and Ag

5. Formula of magnetite is
(a) Fe_3O_4 (b) Fe_2O_3
(c) FeS_2 (d) $FeCO_3$

6. Which is not a mineral of aluminium?
(a) Corundum (b) Anhydrite
(c) Diaspore (d) Bauxite

7. An important ore of iron is
(a) pyrites (b) malachite
(c) haematite (d) siderite

8. Which of the following is a carbonate ore?
(a) Pyrolusite (b) Diaspore
(c) Cassiterite (d) Malachite

9. Metal which can be extracted from all the three dolomite, magnesite and carnallite is
(a) Na (b) K
(c) Mg (d) Ca

10. Ore pitch blende is the main source of
(a) Ra (b) Th
(c) Mg (d) Ce

Steps Involved in the Extraction of Metals

11. The ore that can be concentrated by magnetic separation method is **[NCERT]**
(a) magnetite (b) haematite
(c) siderite (d) All of these

12. Froth floatation process for the concentration of the ores is an illustration of the practical application of
(a) adsorption (b) sedimentation
(c) coagulation (d) absorption

13. Which of the following ore is not concentrated by froth floatation process?
(a) Pyrolusite (b) Pentlandite
(c) Zinc blende (d) Copper pyrites

14. How do we separate two sulphide ores by froth floatation method?
(a) by adding pine oil
(b) by adding sodium cyanide
(c) by adding foaming agent
(d) by passing air

15. Copper pyrites is concentrated by
(a) gravity method
(b) froth floatation process
(c) electromagnetic method
(d) All of the above

16. Cassiterite is concentrated by
(a) liquation
(b) floatation
(c) electromagnetic separation
(d) levigation

17. Froth floatation method is successful in separating impurities from ores because
- (a) the pure ore is soluble in water containing additives like pine oil, cresylic acid etc
- (b) the pure ore is lighter than water containing additives like pine oil, cresylic acid, etc
- (c) the impurities are soluble in water containing additives like pine oil, cresylic acid, etc
- (d) the pure ore is not easily wetted by water as by pine oil, cresylic acid, etc

18. The method of concentrating the ore which makes use of the difference in density between ore and impurities is called
- (a) leaching
- (b) liquation
- (c) levigation
- (d) magnetic separation

19. Bauxite ore is concentrated by
- (a) froth floatation
- (b) electromagnetic separation
- (c) chemical separation
- (d) hydraulic separation

20. Extraction of gold and silver involves leaching the metal with CN^- ion. The metal is recovered by …… . **[NCERT** Exemplar**]**
- (a) displacement of metal by some other metal from the complex ion
- (b) roasting of metal complex
- (c) calcination followed by roasting
- (d) thermal decomposition of metal complex

21. The reaction $2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$ in the metallurgical process of zinc is called
- (a) roasting
- (b) smelting
- (c) cupellation
- (d) calcination

22. In blast furnace, iron oxide is reduced by
- (a) silica
- (b) carbon
- (c) limestone
- (d) CO

23. In the metallurgy of iron, when $CaCO_3$ is added to blast furnace, calcium ion appears as
- (a) slag
- (b) gangue
- (c) CaO
- (d) metallic Ca

24. Which statement is correct?
- (a) Slags are carefully choosen to combine with the slag present in the ore to produce easily fusible gangue to carry away the impurities
- (b) Gangues are carefully choosen to combine with the slag present in the ore to produce easily fusible flux to carry away the impurities
- (c) Gangues are carefully choosen to combine with flux present in the ore to produce easily fusible slag to carry away the impurities
- (d) Fluxes are carefully choosen to combine with the gangue present in the ore to produce easily fusible slag to carry away the impurities

25. In metallurgy, flux is a substance used to convert
- (a) soluble impurities to insoluble impurities
- (b) infusible impurities to fusible material
- (c) fusible impurities to infusible impurities
- (d) mineral into silicate

26. In the extraction of copper from its sulphide ore, the metal is formed by the reduction of Cu_2O with **[NCERT** Exemplar**]**
- (a) FeS
- (b) CO
- (c) Cu_2S
- (d) SO_2

27. Which of the following reactions is an example of auto-reduction? **[NCERT** Exemplar**]**
- (a) $Fe_3O_4 + 4CO \longrightarrow 3Fe + 4CO_2$
- (b) $Cu_2O + C \longrightarrow 2Cu + CO$
- (c) $Cu^{2+}(aq) + Fe(s) \longrightarrow Cu(s) + Fe^{2+}(aq)$
- (d) $Cu_2O + \frac{1}{2}Cu_2S \longrightarrow 3Cu + \frac{1}{2}SO_2$

28. When copper ore is mixed with silica in a reverberatory furnace, copper matte is produced. The copper matte contains …… . **[NCERT** Exemplar**]**
- (a) sulphides of copper (III) and iron (II)
- (b) sulphides of copper (II) and iron (III)
- (c) sulphides of copper (I) and iron (II)
- (d) sulphides of copper (I) and iron (III)

29. Why copper matte is put in silica lined converted? **[NCERT]**
- (a) To oxidise it
- (b) To reduce it
- (c) to convert its impurities into fusible mass
- (d) to convert its impurities into infusible mass

30. The slag obtained during the extraction of copper from copper pyrites is composed of
- (a) Cu_2S
- (b) SiO_2
- (c) $CuSiO_3$
- (d) $FeSiO_3$

31. The electrolytic method of reduction is employed for the preparation of metals that
- (a) are strongly electropositive
- (b) are weakly electropositive
- (c) are moderately electropositive
- (d) from oxides

32. Which metal is extracted by electrolytic reduction method?
- (a) Cu
- (b) Al
- (c) Ag
- (d) Fe

33. Electrolytic reduction of alumina to aluminium by Hall-Heroult process is carried out
(a) in the presence of NaCl
(b) in the presence of fluorite
(c) in the presence of cryolite which forms a melt with lower melting point
(d) in the presence of cryolite which forms a melt with high melting point

34. In the metallurgy of aluminium …… . **[NCERT Exemplar]**
(a) Al^{3+} is oxidised to $Al(s)$.
(b) graphite anode is oxidised to carbon monoxide and carbon dioxide.
(c) oxidation state of oxygen changes in the reaction at anode.
(d) oxidation state of oxygen changes in the overall reaction involved in the process.

35. What is the role of graphite rod in the electrometallurgy of aluminium? **[NCERT]**
(a) It acts as anode
(b) It acts as cathode
(c) It acts as oxidising agent
(d) Both (a) and (c)

36. Brine is electrolysed by using inert electrodes. The reaction at anode is …… . **[NCERT Exemplar]**
(a) $Cl^-(aq) \longrightarrow \frac{1}{2}Cl_2(g) + e^-$; $E^\ominus_{cell} = 1.36$ V
(b) $2H_2O(l) \longrightarrow O_2(g) + 4H^+ + 4e^-$; $E^\ominus_{cell} = 1.23$ V
(c) $Na^+(aq) + e^- \longrightarrow Na(s)$; $E^\ominus_{cell} = 2.71$ V
(d) $H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g)$; $E^\ominus_{cell} = 0.00$ V

37. Purest form of iron is
(a) pig iron (b) wrought iron
(c) cast iron (d) steel

38. Zone refining is based on the principle that …… . **[NCERT Exemplar]**
(a) impurities of low boiling metals can be separated by distillation.
(b) impurities are more soluble in molten metal than in solid metal.
(c) different components of a mixture are differently adsorbed on an adsorbent.
(d) vapours of volatile compound can be decomposed in pure metal.

39. Electrolytic refining is used to purify which of the following metals? **[NCERT Exemplar]**
(a) Cu and Zn (b) Ge and Si
(c) Zr and Ti (d) Zn and Hg

40. In order to refine blister copper, it is melted in a furnace and is stirred with green logs of wood. The purpose is
(a) to expel the dissolved gases in blister copper
(b) to bring the impurities to surface and oxidize them
(c) to increase the carbon content of copper
(d) to reduce the metallic oxide impurities with hydrocarbon gases liberated from the wood

41. Which method is used to refine Zr and Ti? **[NCERT Exemplar]**
(a) Mond's process (b) Cyanide process
(c) van Arkel method (d) Lavigation

42. What should be the considerations during the extraction of metals by electrochemical method? **[NCERT Exemplar]**
(a) Reactivity of metal obtained
(b) Selectivity of metal obtained
(c) Suitability of electrodes
(d) Both (a) and (c)

43. Mond's process is used for the purification of
(a) Ni (b) Ti
(c) Zr (d) Hg

44. Refractory materials are generally used in furnaces because
(a) they can withstand high temperature
(b) they are chemically inert
(c) they do not require replacement
(d) they possess great structural strength

45. In the modern blast furnaces, the charge consists of a mixture of
(a) iron pyrites + bituminous coal
(b) hydrated iron oxides + dolomite + coke
(c) calcined iron oxides + limestone + coke
(d) calcined iron oxides + lime + anthracite coal

46. In blast furnace, the highest temperature is in
(a) fusion zone (b) reduction zone
(c) combustion zone (d) slag zone

47. In the equation,

$$4M + 8CN^- + 2H_2O + O_2 \longrightarrow 4[M(CN)_2]^- + 4OH^-,$$

identify the metal M.
(a) Au (b) Fe
(c) Zn (d) Cu

Miscellaneous

48. Thermite is a mixture of
(a) Fe powder and Al_2O_3 (b) Al powder and Fe_2O_3
(c) Cu powder and Fe_2O_3 (d) Zn powder and Cr_2O_3

49. Which statement is incorrect?
(a) Galena is an ore of Pb
(b) Electrostatic separation is used for lead sulphide
(c) Ore is heated strongly, above its melting point in roasting
(d) Silica acts as acidic flux

50. Match Column I with Column II and select the correct answer using the codes given below the list.

	Column I		Column II
1.	Ti	A.	Bauxite
2.	Si	B.	Cerussite
3.	Al	C.	van-Arkel method
4.	Pb	D.	Zone refining

Codes
(a) 1–B, 2–A, 3–C, 4–D (b) 1–B, 2–C, 3–A, 4–B
(c) 1–C, 2–A, 3–B, 4–D (d) 1–C, 2–D, 3–A, 4–B

Round II (Mixed Bag)

Only One Correct Option

1. Load stone is an ore of
(a) iron (b) lead
(c) silicon (d) tin

2. One of the following metals forms a volatile compound and this property is taken advantage for its extraction. This metal is
(a) cobalt (b) iron
(c) tungsten (d) nickel

3. Wolframite ore is separated from tin stone ore by the process, called
(a) calcination
(b) electromagnetic separation
(c) roasting
(d) smelting

4. 'Lapis-Lazuli' is a blue coloured precious stone. It is mineral of the class
(a) sodium alumino silicate
(b) basic copper carbonate
(c) zinc cobalt
(d) Prussian blue

5. When a metal is to be extracted from its ore, if the gangue associated with the ore is silica, then
(a) a basic flux is needed
(b) an acidic flux is needed
(c) both basic and acidic flux are needed
(d) neither of them is needed

6. An ore of tin containing $FeCrO_4$ is concentrated by
(a) electrostatic method (b) gravity separation
(c) magnetic separation (d) froth floatation

7. Gallium arsenide is purified by
(a) van-Arkel method (b) zone refining method
(c) electrolytic method (d) liquation

8. Pb and Sn are extracted from their chief ore by
(a) electrolysis and self reduction
(b) self reduction and electrolysis
(c) carbon reduction and self reduction
(d) self reduction and carbon reduction

9. Native silver metal forms a water soluble complex with a dilute aqueous solution of NaCN in the presence of
(a) nitrogen (b) oxygen
(c) carbon dioxide (d) argon

10. Which of the following statement is incorrect?
(a) Silver glance mainly contains silver sulphide
(b) Zinc blende mainly contains zinc chloride
(c) Gold is found in native state
(d) Copper pyrites also contains Fe_2S_3

11. Among the following statements, the incorrect one is
(a) calamine and siderite are carbonates
(b) malachite and azurite are ores of copper
(c) argentite and cuprite are oxides
(d) zinc blende and pyrites are sulphides

12. Bauxite ore is made up of $Al_2O_3 + SiO_2 + TiO_2 + Fe_2O_3$. This ore is treated with conc NaOH solution at 500 K and 35 bar pressure for few hours and filtered when hot. In the filtrate, the species present are
(a) $NaAl(OH)_4$ only
(b) $Na_2Ti(OH)_6$ only
(c) $NaAl(OH)_4$ and Na_2SiO_3 both
(d) Na_2SiO_3 only

13. Among the following groups of oxides, the group containing oxides that cannot be reduced by carbon to give the respective metals is
(a) Cu_2O, K_2O (b) PbO, Fe_3O_4
(c) Fe_2O_3, ZnO (d) CaO, K_2O

14. Match items of Column I with the items of Column II and assign the correct codes.

	Column I		Column II
(A)	Cyanide process	(1)	Ultrapure Ge
(B)	Froth floatation process	(2)	Dressing of ZnS
(C)	Electrolytic reduction	(3)	Extraction of Al
(D)	Zone refining	(4)	Extraction of Au
		(5)	Purification of Ni

Codes

	A	B	C	D
(a)	4	2	3	1
(b)	2	3	1	5
(c)	1	2	3	4
(d)	3	4	5	1

15. Match the items of Column I with the items of Column II and assign the correct code.

	Column I		Column II
(A)	Pendulum	(1)	Chrome steel
(B)	Malachite	(2)	Nickel steel
(C)	Calamine	(3)	Na_3AlF_6
(D)	Cryolite	(4)	$CuCO_3, Cu(OH)_2$
		(5)	$ZnCO_3$

Codes

	A	B	C	D
(a)	1	2	3	4
(b)	2	4	5	3
(c)	2	3	4	5
(d)	4	5	3	2

More than One Correct Option

16. Which of the following statements are correct? **[NCERT Exemplar]**

(a) A depressant prevents certain type of particles to come to the froth

(b) Copper matte contains Cu_2S and ZnS

(c) The solidified copper obtained from reverberatory furnace has blistered appearance due to the evolution of SO_2 during the extraction

(d) Zinc can be extracted by self-reduction

17. Which of the following statements is correct about the role of substances added in the froth floatation process? **[NCERT Exemplar]**

(a) Collectors enhance the non-wettability of the mineral particles

(b) Collectors enhance the wettability of gangue particles

(c) By using depressants in the process two sulphide ores can be separated

(d) Froth stabilisers decrease wettability of gangue

18. In the froth floatation process, zinc sulphide and lead sulphide can be separated by …… . **[NCERT Exemplar]**

(a) using collectors

(b) adjusting the proportion of oil to water

(c) using depressant

(d) using froth stabilisers

19. Which of the following reactions occur during calcination? **[NCERT Exemplar]**

(a) $CaCO_3 \longrightarrow CaO + CO_2$

(b) $2FeS_2 + \frac{11}{2}O_2 \longrightarrow Fe_2O_3 + 4SO_2$

(c) $Al_2O_3 \cdot xH_2O \longrightarrow Al_2O_3 + xH_2O$

(d) $ZnS + \frac{3}{2}O_2 \longrightarrow ZnO + SO_2$

20. Which of the following options are correct? **[NCERT Exemplar]**

(a) Cast iron is obtained by remelting pig iron with scrap iron and coke using hot air blast

(b) In extraction of silver, silver is extracted as cationic complex

(c) Nickel is purified by zone refining

(d) Zr and Ti are purified by van Arkel method

Assertion and Reason

Directions (Q. Nos. 21 to 26) *Each of these questions contains two statements : Statement* I (*Assertion*) *and Statement* II (*Reason*). *Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes* (*a*), (*b*), (*c*), (*d*) *given below :*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I.

(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.

(c) Statement I is true; Statement II is false.

(d) Statement I is false; Statement II is true.

21. **Statement I** In the Hoop's process of purification of aluminium, the fused materials remains in three diffferent layers. These layers remain intact even in electrolytic reduction.

Statement II All the layers have different densities.

22. **Statement I** Sulphide ores are concentrated by froth floatation method.

Statement II Cresols stabilise the froth in froth floatation method. **[NCERT Exemplar]**

23. **Statement I** Hydrometallurgy involves dissolving the ore in a suitable reagent followed by precipitation by a more electropositive metal.

Statement II Copper is extracted by hydrometallurgy.
[NCERT Exemplar]

24. **Statement I** Zirconium can be purified by van Arkel method.

Statement II ZrI_4 is volatile and decomposes at 1800K. **[NCERT Exemplar]**

25. **Statement I** Alkaline earth metals are not easy to produce by chemical reduction.

Statement II Their aqueous solutions cannot be used for displacing one metal by another.

26. **Statement I** The reduction of a metal oxide is easier if the metal formed is in liquid state at the temperature of reduction.

Statement II The value of entropy change of the reduction process is more on positive side when the metal formed is in liquid state.

Comprehension Based Questions

Directions (Q. Nos. 27 to 29) Metallurgy is the process of extraction of metals from the substances in which these are found in nature. It involves a series of processes like ore dressing, conversion of concentrated ore to oxide, reduction and refining of metal.

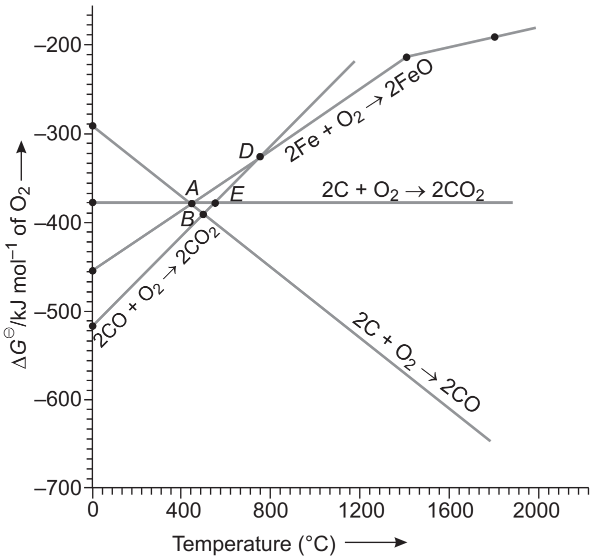
In one of the refining processes, the molten impure metal is stirred with green logs of wood. These wood release some gases by which the impurities are reduced and thus, removed.

27. The metal which is purified by the method discussed above is
- (a) sodium
- (b) copper
- (c) iron
- (d) manganese

28. The gas release during the process to remove the impurities is
- (a) CO
- (b) H_2
- (c) CH_4
- (d) CO_2

29. This process is used for metals which
- (a) are less volatile
- (b) are less fusible
- (c) contains infusible impurities
- (d) contains oxides as impurity

Directions (Q. Nos. 30 to 33)



30. Choose the correct option of temperature at which carbon reduces FeO to iron and produces CO.
[NCERT Exemplar]
- (a) Below temperature at point A.
- (b) Approximately at the temperature corresponding to point A.
- (c) Above temperature at point A but below temperature at point D.
- (d) Above temperature at point A.

31. Below point 'A' FeO can …… .
- (a) be reduced by carbon monoxide only.
- (b) be reduced by both carbon monoxide and carbon.
- (c) be reduced by carbon only.
- (d) not be reduced by both carbon and carbon monoxide.

32. For the reduction of FeO at the temperature corresponding to point D, which of the following statements is correct?
- (a) ΔG value for the overall reduction reaction with carbon monoxide is zero.
- (b) ΔG value for the overall reduction reaction with a mixture of 1 mole carbon and 1 mole oxygen is positive.
- (c) ΔG value for the overall reduction reaction with a mixture of 2 moles carbon and 1 mole oxygen will be positive.
- (d) ΔG value for the overall reduction reaction with carbon monoxide is negative.

33. At the temperature corresponding to which of the points in figure, FeO will be reduced to Fe by coupling the reaction $2FeO \longrightarrow 2Fe + O_2$ with all of the following reactions?

(i) $C + O_2 \longrightarrow CO_2$ (ii) $2C + O_2 \longrightarrow 2CO$ and (iii) $2CO + O_2 \longrightarrow 2CO_2$

(a) Point *A* (b) Point *B*
(c) Point *D* (d) Point *E*

Previous Years' Questions

34. Which of the following factors is of **no significance** for roasting sulphide ores to the oxides and not subjecting the sulphide ores to carbon reduction directly **[AIEEE 2008]**

(a) Metal sulphides are thermodynamically more stable than CS_2
(b) CO_2 is thermodynamically more stable than CS_2
(c) Metal sulphides are less stable than the corresponding oxides
(d) CO_2 is more volatile than CS_2

35. During the process of electrolytic refining of copper, some metals present as impurity settle as 'anode mud'. These are **[AIEEE 2005]**

(a) Fe and Ni (b) Ag and Au
(c) Pb and Zn (d) Se and Ag

36. Which one of the following ores is best concentrated by froth-floatation method ? **[AIEEE 2004]**

(a) Magnetite (b) Cassiterite
(c) Galena (d) Malachite

37. Aluminium is extracted by the electrolysis of **[AIEEE 2002]**

(a) alumina
(b) bauxite
(c) molten cryolite
(d) alumina mixed with molten cryolite

38. Cyanide process is used for the extraction of **[AIEEE 2002]**

(a) barium (b) silver (c) boron (d) zinc

39. Refining of impure copper with zinc impurity is to be done by electrolysis using electrodes as **[AIEEE 2002]**

	Cathode	**Anode**
(a)	pure copper	pure zinc
(b)	pure zinc	pure copper
(c)	pure copper	impure copper
(d)	pure zinc	impure zinc

Answers

Round I

1. (c)	**2.** (b)	**3.** (c)	**4.** (a)	**5.** (a)	**6.** (b)	**7.** (c)	**8.** (d)	**9.** (c)	**10.** (a)
11. (d)	**12.** (a)	**13.** (a)	**14.** (b)	**15.** (b)	**16.** (c)	**17.** (d)	**18.** (c)	**19.** (c)	**20.** (a)
21. (a)	**22.** (d)	**23.** (a)	**24.** (d)	**25.** (b)	**26.** (c)	**27.** (d)	**28.** (c)	**29.** (c)	**30.** (d)
31. (a)	**32.** (b)	**33.** (c)	**34.** (b)	**35.** (a)	**36.** (a)	**37.** (b)	**38.** (b)	**39.** (a)	**40.** (d)
41. (c)	**42.** (d)	**43.** (a)	**44.** (a)	**45.** (c)	**46.** (c)	**47.** (a)	**48.** (b)	**49.** (c)	**50.** (d)

Round II

1. (a)	**2.** (d)	**3.** (b)	**4.** (a)	**5.** (a)	**6.** (c)	**7.** (b)	**8.** (d)	**9.** (b)	**10.** (b)
11. (c)	**12.** (c)	**13.** (d)	**14.** (a)	**15.** (b)	**16.** (a,c)	**17.** (a,c)	**18.** (b,c)	**19.** (a,c)	**20.** (a,d)
21. (a)	**22.** (b)	**23.** (b)	**24.** (a)	**25.** (b)	**26.** (a)	**27.** (b)	**28.** (c)	**29.** (d)	**30.** (d)
31. (a)	**32.** (a)	**33.** (b,d)	**34.** (c)	**35.** (b)	**36.** (c)	**37.** (d)	**38.** (b)	**39.** (c)	

the Guidance

Round I

1. Less reactive metals are found in native state (free state).

2. Copper is found in native as well as in combined state.

3. Metals cannot be extracted economically from all the minerals that is why all minerals are not ores.

6. Bauxite ($Al_2O_3 \cdot 2H_2O$)
Corundum (Al_2O_3)
Diaspore ($Al_2O_3 \cdot H_2O$)

8. Pyrolusite — MnO_2
Malachite — $CuCO_3 \cdot Cu(OH)_2$
Diaspore — $Al_2O_3 \cdot H_2O$
Cassiterite — SnO_2

9.

Dolomite	$MgCO_3 \cdot CaCO_3$
Magnesite	$MgCO_3$
Carnallite	$KCl \cdot MgCl_2 \cdot 6H_2O$

10. Ore pitch blende is main source of radium.

11. Magnetic ores (iron ores) are generally separated by this method. Magnetite (Fe_3O_4), haematite (Fe_2O_3), siderite ($FeCO_3$) are such ores.

12. The adsorption phenomenon is involved in the froth floatation process.

13. Pyrolusite (MnO_2) is not a sulphide ore, so it is not concentrated by froth floatation process.

14. Two sulphide ores can be separated by adjusting the proportion of oil and water or by using depressants, *e.g.*, If an ore contains ZnS and PbS both, a depressant NaCN is added during froth floatation. It forms a complex with ZnS and prevents it from coming into froth. PbS comes into the froth and thus, separated.

17. In froth floatation method, the pure ore is not easily wetted by water but wetted by pine oil, so it is successfully separated from impurities.

18. Levigation (gravity separation) is based on the difference in the specific gravities of the gangue particles and the ore particles.

19. Bauxite ore is concentrated by chemical separation or leaching. In this, powdered ore is treated with a suitable reagent which can dissolve the ore but not the impurities.

20. Extraction of gold and silver involves leaching the metals with CN^- ion. The metal is recovered by displacement of metal by some other metals from the complex ion.

23. In the metallurgy of iron, when $CaCO_3$ is added to blast furnace, it removes impurities from ore and forms slag.

$$CaCO_3 \longrightarrow CaO + CO_2 \quad (1070\text{–}1170\text{ K})$$
$$CaO + SiO_2 \longrightarrow CaSiO_3 \quad (1470\text{ K})$$
$$3CaO + P_2O_5 \longrightarrow Ca_3(PO_4)_2$$

24. Flux is a substance with combine with gangue that present in the roasted or calcined ore to form fusible product, called slag.

25. Flux is mixed with concentrated ore which is not soluble in molten metal. It converts the infusible impurities to fusible material.

26. In the extraction of copper (Cu) from its sulphide ore, the metal is formed by the reduction of Cu_2O with Cu_2S (cuprous sulphide).

27. Auto-reduction is also known as self reduction. This is used when no external reducing agent is required. The sulphide ores of less electropositive metal like Hg, Pb, Cu etc., are heated in air to convert a part of the ore into oxide or sulphide which then reacts with the remaining sulphide ore to give the metal and sulphur dioxide, *e.g.*,

$$Cu_2O + \frac{1}{2}Cu_2S \longrightarrow 3Cu + \frac{1}{2}SO_2$$

28. Copper matte is produced when copper ore is mixed with silica in reverberatory furnace. The copper matte contains sulphide of copper (I) and iron (II).

29. In copper matte iron sulphide, FeS is present as impurity which in the presence of oxygen converts into iron oxide, a basic impurity. Silica (SiO_2) is an acidic flux.

Copper matte mainly contains Cu_2S and FeS. For removing the gangue FeS, silica present in the lining of the Bessemer's converter acts as a flux and forms slag (iron silicate) on reaction with FeO.

$$\underset{\text{gangue}}{2FeS} + 3O_2 \longrightarrow 2FeO + 2SO_2$$
$$\underset{\text{gangue}}{FeO} + \underset{\text{flux}}{SiO_2} \longrightarrow \underset{\text{slag}}{FeSiO_3}$$

30. The slag obtained during the extraction of copper from copper pyrites is of $FeSiO_3$. It is carried out in smelting.

$$FeO + SiO_2 \longrightarrow \underset{\text{slag}}{FeSiO_3}$$

31. In electrolytic reduction, the oxides of highly electropositive metals are reduced at very high temperature.

32. Metals like, Na, K, Mg, Ca, Al etc., are reduced by electrolytic reduction.

34. In the metallurgy of aluminium (Al) graphite anode is oxidised to carbon monoxide (CO) and carbon dioxide (CO_2).

35. Graphite rods act as anode during the electrolytic reduction of alumina (Hall-Heroult process). At anode, O_2 gas is produced which reacts with the carbon of anode (rods) to produce CO_2 gas, so these graphite rods are consumed slowly and need to be replaced from time to time.

$$Al_2O_3 \rightleftharpoons 2Al^{3+} + 3O^{2-}$$

At cathode $\quad Al^{3+} + 3e^- \longrightarrow Al$

At anode $\quad 3O^{2-} \longrightarrow 3[O] + 6e^-] \times 2$

or $\quad 3[O] + 3[O] \longrightarrow 3O_2$

$\quad C(s) + O_2(g) \longrightarrow CO_2(g)$

36. Brine is electrolysed by using inert electrodes. And at anode the reaction is

$$Cl^-(aq) \longrightarrow \frac{1}{2}Cl_2(g) + e^-; \qquad E^{\ominus}_{cell} = 1.36\text{ V}$$

As anode is always the site of oxidation.

37. Wrought or malleable iron is the purest form of iron.

38. Zone refining method is employed to get the metals of very high purity. Metals like Ge, Si, B, Ga, In etc., are purified by this method. This method is based on the principle that impurities are more soluble in molten metal than in solid metal.

39. Electrolytic refining is used to purify several metals such as Cu, Zn, Ag, Au, Pb, Al, etc.

40. $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$

$$3Cu_2O + \underset{\text{from green logs of wood}}{CH_4} \longrightarrow 6Cu + 2H_2O + CO$$

41. Zr and Ti are refined by van Arkel method. It involves 2 steps :

(a) **Formation of iodide**; *e.g.*, zirconium

$$Zr + 2I_2 \longrightarrow ZrI_4$$

(b) **Decomposition of iodide**

$$ZrI_4 \xrightarrow{1800\text{ K}} \underset{\text{pure}}{Zn} + 2I_2$$

42. (1) Reactivity of metal produced.

(2) Suitability of electrodes.

Above two considerations are taken into account during extraction of metals by electrochemical method.

43. Mond's process is used for the purification of Ni.

$$Ni + 4CO \xrightarrow{\text{Heat}} [Ni(CO)_4] \xrightarrow{\text{Decompose}} Ni + 4CO$$

44. Refractory materials are the substances which can withstand very high temperature without melting or becoming salt.

46.

Combustion zone	1800 K
Fusion zone	1600 K
Slag zone	1300 K
Reduction zone	800 K

47. This reaction is used for the extraction of gold from its ores.

$$4Au + 8CN^- + 2H_2O + O_2 \longrightarrow 4[Au(CN)_2]^- + 4OH^-$$

48. Thermite is a mixture of Al and Fe_2O_3 in 1 : 3 ratio.

49. Roasting is the process in which the ore is heated strongly below its melting point in the presence of air.

50. Ti — van Arkel method

Si — Zone refining method

Al — Bauxite (Al_2O_3)

Pb — Cerussite ($PbCO_3$)

Round II

1. Load stone (magnetite, Fe_3O_4) is an ore of iron.

2. Mond's process for refining of Ni is an example of vapour phase refining.

3. Wolframite ore [$FeWO_4$] is present in tin stone as impurities and it has same mass per unit volume as that of tin stone. So, it is separated by electromagnetic separator because wolframite is magnetic in nature, hence it gets attracted by magnet while tin stone does not.

4. Lapis lazuli is the sodium aluminosilicate, present in earth rocks as blue stone.

5. $$\underset{\text{acidic impurity}}{SiO_2} + \underset{\text{basic flux}}{CaO} \longrightarrow \underset{\text{slag}}{CaSiO_3}$$

6. Electromagnetic separation is used when either the ore or the impurities associated with it, are magnetic in nature.

7. Gallium arsenide is purified by zone refining method.

8. PbO and $PbSO_4$ get reduced by PbS itself which is already present in mixture. Because the reduction takes place by mixture itself, hence the process is known as self reduction.

$$2PbO + PbS \xrightarrow{\Delta} 3Pb + SO_2\uparrow$$

$$PbSO_4 + PbS \xrightarrow{\Delta} 2Pb + 2SO_2\uparrow$$

SnO_2 is reduced by C.

9. A water soluble complex of silver with a dilute aqueous solution of NaCN is sodium argentocyanide. In the cyanide process, the native form is crushed and treated with 0.1–0.2% solution of NaCN and aerated.

$$4Ag + 8NaCN + 2H_2O + O_2 \longrightarrow 4Na[Ag(CN)_2] + 4NaOH$$

Argentocyanide is soluble. Further metal is recovered from the complex by reduction with zinc.

10. Zinc blende is ZnS, not $ZnCl_2$.

11. Cuprite (Cu_2O) is oxide but argentite (Ag_2S) is not oxide.

12. In bauxite ore, only Al_2O_3 and SiO_2 react with conc NaOH and forms sodium metaaluminate and silicate respectively. Aluminate further dissolves in water.

$$Al_2O_3 + 2H_2O + 2NaOH \xrightarrow[35\text{ bar}]{500\text{ K}} 2NaAlO_2 + 3H_2O$$

$$NaAlO_2 + 2H_2O \longrightarrow 2NaAl(OH)_4$$

13. CaO, K_2O cannot be reduced by carbon reduction method.

14. Noble metals like Ag and Au are concentrated (or extracted) by cyanide process.

Froth floatation process is used to concentrate sulphide ore like ZnS. Ore concentration is also known as ore dressing.

Electrolytic reduction is applied in case of highly reactive metals like Al, Na, etc.

Ultrapure metals like Ge, Si, etc., are purified by zone refining.

15. Nickel steel is related with pendulum, $CuCO_3 \cdot Cu(OH)_2$ is malachite, $ZnCO_3$ is calamine and Na_3AlF_6 is cryolite.

16. The solidified copper obtained from reverberatory furnace has blistered appearance due to evolution of sulphur dioxide (SO_2) during the extraction. A depressant prevents, certain type of particles to come to the froth.

17. In the froth floatation process collector enhance the non-wettability of the mineral particles. In this process, depressant helps in separating two different sulphide ores.

18. In the froth floatation process, zinc sulphide (ZnS) and lead sulphide (PbS) can be separated by the using depressant and adjusting the proportion of oil to water.

19. Calcination involves heating of the ore below its melting point in the absence of air or in limited supply. Oxygen containing ores like oxide, hydroxides and carbonates are calcined. Thus, the following reactions occurs during calcination.

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

$$Al_2O_3 \cdot xH_2O \xrightarrow{\Delta} Al_2O_3 + xH_2O$$

20. Zr (zirconium), Ti (titanium), V (vanadium), Th (thorium) etc., are purified by van-Arkel method.

Cast iron is obtained by remelting pig iron with scrap iron and coke using hot air blast.

Nickel is purified by Mond's process and silver is extracted as anionic complex.

21. Upper most layer of pure molten aluminium, middle layer of molten fluorides of Na^+, Ba^{2+} and Al^{3+} and lower layer of molten impure aluminium have different densities.

22. Sulphide ores of Cu, Ag, Zn, Pd, etc. are concentrated by froth floatation method as they form froth with froathing agent. The cresols stabilise the froth in froth floatation method.

23. Hydrometallurgy involves dissolving the ore in a suitable reagent and this process is followed by precipitation by a more electropositive metal. Copper (Cu) is extracted by hydrometallurgy.

24. The van-Arkel method is used for the purification of zirconium (Zr).

ZrI_4 when heated higher, it will decomposed to give pure metal as

$$\underset{\text{(impure)}}{Zr} + 2I_2(g) \xrightarrow{\Delta} ZrI_4 \xrightarrow{1800\text{ K}} \underset{\text{(pure)}}{Zr} + 2I_2(g)$$

25. Alkaline earth metals are strong reducing agents so they can't be produced by reduction method. Aqueous solutions of alkaline earth metals can't be used for displacing one metal by another.

26. Degree of randomness increases on changing the phase from solid to liquid or from liquid to gas.

27. The discussion is about copper metal which is refined by poling, *i.e.,* by stirring impure metal with green logs of wood.

28. During this process, methane, CH_4 gas (hydrocarbon gases) is obtained which reduces copper oxide to copper.

29. This method is applicable for metals having their oxide as impurity.

30. Above temperature at point *A* carbon (C) reduces FeO to iron (Fe) and is also produced carbon monoxide (CO).

31. FeO can be reduced by carbon monoxide only at below point *A*.

32. ΔG value for the overall reduction reaction with carbon monoxide (CO) is zero for the reduction of FeO at the temperature corresponding to point *D*.

33. The temperature at the point *B* and point *E*, reduce FeO to Fe (iron) by coupling the reaction $2FeO \longrightarrow 2Fe + O_2$ with all of the following reactions.

(i) $C + O_2 \longrightarrow CO_2$

(ii) $2C + O_2 \longrightarrow 2CO$

(iii) $2CO + O_2 \longrightarrow 2CO_2$

34. $2MS + C \longrightarrow 2M + CS_2; \quad \Delta G_1 = \text{positive}$

$2MO + C \longrightarrow 2M + CO_2; \quad \Delta G_2 = \text{negative}$

The value of ΔG for the formation of CO_2 is negative, *i.e.*, it is thermodynamically more stable than CS_2. Also metal sulphides are thermodynamically more stable than CS_2. Metal sulphides are more stable than the corresponding oxides, so they are roasted to convert into less stable oxides.

35. During electrolysis, noble metals (inert metals) like Ag, Au and Pt are not affected and separate as anode mud from the impure anode.

36. Froth floatation is used to concentrate sulphide ores [Galena (PbS)].

37. Aluminium is extracted by electrolysis of a fused mixture of alumina (2-8%), synthetic cryolite Na_3AlF_6 (80-85%), AlF_3 and fluorspar. This makes alumina good conductor and lowers the fusion temperature also.

38. Cyanide process or Mac Arthur-Forest cyanide process

$$2Ag_2S + 8NaCN + O_2 + 2H_2O \longrightarrow 4Na[Ag(CN)_2] + 4NaOH + 2S$$

Soluble silver complex is filtered and treated with zinc dust and silver gets precipitated.

$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag\downarrow$$

39. For purification, impure copper gets oxidised (deelectronation) falling into solution with mud, that's why impure at anode.

7 *p*-Block Elements-II

JEE Main MILESTONE

- Group15 Elements
- Nitrogen (N)
- Phosphorus
- Group16 Elements
- Ozone (O_3)
- Sulphur
- Group17 Elements
- Compounds of Elements of Group 17
- Group 18 Elements
- Compounds of Elements of Group 18

VA (15) Group Elements and Their Compounds

7.1 Group15 Elements

Group VA contains 5 elements, namely, **nitrogen** (N), **phosphorus** (P), **arsenic** (As), **antimony** (Sb) and **bismuth** (Bi). These elements are collectively called **pnicogens** (taken from Greek word '*pniomigs*' meaning suffocating) and their compounds are called **pniconides.**

Elements of group 15, 16, 17 *and* 18 *are included in p-block II. These have general configuration* $ns^2 np^{3-6}$*. The similarity among these elements is that most of these are non-metals. All of these elements are of great importance and found use in our daily life.*

Occurrence

Nitrogen constitutes about 78% (by volume) of atmosphere, and is therefore, the most common gas. Phosphorus is the only element that does not occur in free state. It is usually found as phosphate. Nitrogen in combined state, is found as nitrates or in proteins and amino acids. The rest elements occur as sulphides or oxides. P is the eleventh most abundant element in the earth's crust.

General and Physical Properties

Elements of this group exhibit a regular trend in general and physical properties. *These properties along with their trend along the group are described below.*

(a) Electronic Configuration

The electronic configuration of various elements of this family are as

Table 7.1 **Electronic Configuration of VA Group Elements**

S.N.	Element	Atomic number	Electronic configuration
1.	Nitrogen, N	7	[He] $2s^2p^3$
2.	Phosphorus, P	15	[Ne] $3s^2p^3$
3.	Arsenic, As	33	[Ar] $3d^{10}\ 4s^2p^3$
4.	Antimony, Sb	51	[Kr] $4d^{10}\ 5s^2p^3$
5.	Bismuth, Bi	83	[Xe] $4f^{14}5d^{10}6s^2p^3$

It is clear from the electronic configuration that their *p*-orbitals of valence shell are half-filled. This is a stable configuration in accordance with Hund's rule. Thus, these elements, having exactly half-filled orbitals, are fairly stable and not so reactive (*e.g.*, nitrogen behaves as almost inert element).

(b) Atomic Volumes and Radii

Atomic volumes and atomic radii increases down the group, however **arsenic shows exceptionally low value of atomic volume.**

(c) Physical State

A gradual transition in physical state is seen among the elements under ordinary conditions, *i.e.,* nitrogen is a gas which can be converted into a liquid at very low temperature; phosphorus though a solid but can pass readily into vapour state. Arsenic, antimony and bismuth are infact solids of varying boiling and melting points.

(d) Ionisation Energy

The first ionisation energy of N is very high and the values for succeeding elements decreases symmetrically as seen in *s*-block elements.

(e) Metallic Character

It increases down the group as, nitrogen and phosphorus are distinctly **non-metals,** succeeding two members are **amphoteric** in nature *i.e.,* As and Sb have metallic as well as non-metallic character while, the last element, Bi is a **metal.**

(f) Electronegativity

It decreases down the group as we move from N to Bi indicating a gradual change from non-metallic to metallic character. These elements are more electronegative as compared to the elements of 14 group.

(g) Melting and Boiling Points

These elements do not show a regular trend of melting and boiling points. In this group, the melting point first increases from N to As and afterwards decreases. While boiling point increases from N to Sb and then decreases. But Bi has less boiling point as compared to Sb. We can write these order as

$$\text{N} < \text{P} < \text{As} > \text{Sb} > \text{Bi} \quad \text{(melting point)}$$
$$\text{N} < \text{P} < \text{As} < \text{Sb} > \text{Bi} \quad \text{(boiling point)}$$

(h) Oxidation State

The normal oxidation states of these elements are +5 and +3, out of which +3 stabilises on moving down the group due to inert pair effect. Nitrogen show all oxidation states from +5 to −3 as +5 in N_2O_5, +4 in N_2O_4, + 3 in N_2O_3, +2 in NO, +1 in N_2O, 0 in N_2, −1 in NH_2OH, −2 in N_2H_4 and −3 in NH_3. Nitrogen even shows oxidation state of $-\frac{1}{3}$ in hydrazoic acid, N_3H. Phosphorus show three oxidation states +3, +4 and +5 while, rest of the elements show only +5 and +3 oxidation states.

Nitrogen, however, have least tendency to form compounds in + 5 oxidation state due to the fact that it does not have vacant *d*-orbitals.

All the elements in their tripositive state (+3 oxidation state) have the tendency to donate one **electron pair.** Nitrogen shows this tendency to maximum extent. All elements (except N) also show the tendency to accept electron pair. Nitrogen does not show such a property due to absence of vacant *d*-orbital in it.

The above described properties are summarised in the table given below

Table 7.2 **Physical Properties of Group 15 Elements**

Property	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
At. no.	7	15	33	51	83
At. mass (amu)	14.007	30.970	74.922	121.750	208.980
Density in solid state (g cm^{-3})	1.03	1.82	5.73	6.62	9.78
Atomic volume (cm^3)	17.3	17.0	13.1	18.4	21.3
Atomic radius (Å)	0.75	1.06	1.19	1.38	1.46
Ionic radius of trivalent ion (Å)	1.71	2.12	2.22	2.45	1.20
IE (kJ mol^{-1})	1402	1012	946	840	703

Property	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
Oxidation state	–3, – 2, – 1, 0 +1, +2, +3, +4, +5	–3, + 3, +4, +5	–3, +3, +5	–3, + 3, +5	+3, + 5
Electronegativity	3.0	2.1	2.0	1.8	1.7
MP (°C)	–210	44.1 (white phosphorus)	817 (at 36 atm)	630.5	271.3
BP (°C)	–195.8	280	615 (sublimes)	1587	1564
Heat of fusion (kJ mol^{-1})	0.36	0.63	27.7	19.9	10.9

(i) Nature of Compounds

Since, it is not easy from energy considerations to gain three electrons to achieve stable configuration, the formation of trinegative (A^{3-}) ion is rare. Only N has the capability to form such a type of ion due to its small size. However, covalent compounds of nitrogen are more common. The electronegativities of other elements are so low that they would generally form covalent bonds even with highly electropositive elements. Bi compounds, although covalent, do give ions in polar solvents like water.

(j) Catenation

All the elements of this group show property of catenation *i.e.,* self linkage to a very smaller extent (in comparison with carbon). The catenation in stable nitrogen compounds is restricted generally to two or three nitrogen atoms as, *eg,* in N_2H_4, N_3^- etc. The P atom has maximum tendency to catenate amongst group 15th elements, which can be explained on the basis of P—P bond energy (200.8 kJ/mol) which is more closer to C—C bond energy (353.9 kJ/mol) in comparison to N—N or As—As bond energies (163.1 and 146.1 kJ/mol respectively).

(k) Molecular State

Nitrogen has the tendency to form $p\pi$-$p\pi$ bonds with other atoms of similar type (N) or different type, *e.g.,* carbon. Stable nitrogen compounds contain maximum two or three nitrogen atoms but unstable compounds containing up to 8 nitrogen atoms in a chain have also been synthesized.

Thus, nitrogen usually exists as discrete diatomic gaseous molecule ($N\equiv N$). Other members, however, do not have a tendency of $p\pi$ - $p\pi$ bonding, but have empty d-orbitals, thus, they exist as discrete tetra atomic molecules like P_4, As_4, Sb_4 in which, the atoms are linked together by single bonds.

(l) Allotropy

All the elements of group 15 *(except* Bi*) show allotropy as*

1. N exists in two solid forms namely α-**nitrogen** with cubic crystalline structure and β-**nitrogen** with hexagonal crystalline structure. The transition temperature is −238.5°C. It also has one gaseous allotropic form.
2. Phosphorus exists in a number of allotropic forms, *e.g.,* white phosphorus, red phosphorus, scarlet phosphorus, metallic or α-black phosphorus, β-black phosphorus, violet phosphorus etc.
3. As exists as **grey, yellow** and **black** arsenic.
4. Similarly, Sb exists as **metallic,** α- or **yellow** and **black** or β-**antimony**.

Chemical Properties

Elements of this group form compounds mainly covalent compounds with other elements.

Properties of these compounds are described below.

(a) Hydrides

These elements form AH_3 type hydrides *e.g.,* **ammonia** (NH_3), **phosphine** (PH_3), **arsine** (AsH_3), **stibine** (SbH_3) and **bismuthine** (BiH_3). These hydrides are prepared from binary metal compounds, *e.g.,* Mg_3N_2, Ca_3P_2, Zn_3As_2, Mg_3Sb_2, Mg_3Bi_2 etc., as

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$

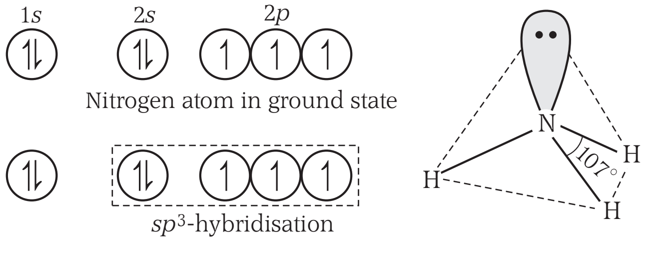
$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$

$$Zn_3As_2 + 6HCl \longrightarrow 3ZnCl_2 + 2AsH_3$$

These can also be prepared by the reduction of trihalides of these elements with $LiAlH_4$ as

$$MCl_3 + 3LiAlH_4 \longrightarrow MH_3 + 3LiCl + 3AlH_3$$

The hydrides have pyramidal structure with sp^3-hybridisation as shown below



Pyramidal structure of NH_3 molecule formed by sp^3-hybridisation of N orbitals

The physical properties of these hydrides are summarised in the following table

Table 7.3 **Comparative Study of the Properties of Hydrides**

S. No.	Property	NH_3	PH_3	AsH_3	SbH_3	BiH_3
1.	Thermal stability	Highly stable	Not so decomposes at 400°C	Unstable 230°	Unstable at room temperature	Unstable, having half-life 20 min
2.	Reducing character	Not good	Moderate	Good	Strong	Strong
3.	Basic character	Base	Weak base	Neutral	Neutral	Feebly acidic
4.	Reactions (i) with metal salt solutions	Precipitate as hydroxides, *e.g.*, $Fe(OH)_3$	Precipitate as phosphides, *e.g.*, Ag_3P	Precipitate as arsenides, *e.g.*, Ag_3As	Precipitate as antimonides *e.g.*, Ag_3Sb (unstable)	No such reaction
	(ii) complexes	Stable, *e.g.*, $[Cu(NH_3)_4]^{2+}$	No stable complexes	No stable complexes	No stable complexes	No stable complexes
5.	Structure	Pyramidal	Pyramidal	Pyramidal	Pyramidal	
6.	Bond angle	–107.3°	–93.5°	–91.8°	–91.3°	–90°
7.	Melting point	–78°C	–132°C	–119°C	–88°C	—
8.	Boiling point	–34.5°C	–87.5°C	–62.4°C	–18.4°C	+ 16.8°C
9.	Bond length	1.02	1.42	1.52	1.71	—
10.	H–bonding	Present	Not present	Not present	Not present	Not present
11.	Heat of formation	–46.1	–9.6	66.4	145.1	277.8

The above physical properties can be explained as

1. The decrease in thermal stability can also be explained by increase in size of central atom. Due to such increase, the tendency to form stable covalent bond with comparatively small H atom decreases i.e., strength of *M*—H bond decreases resulting to decreased thermal stability.
2. The increase in reducing behaviour can be explained on the basis of decrease in thermal stability. Thus, while NH_3, being stable is not a good reducing agent, other hydrides being less stable are good reducing agents.
3. The variation in bond angles may be explained on the basis of the size and electronegativity of central atom. On moving down the group, the size of central atom increases and electronegativity decreases. So, the location of bond pairs of electrons shifts more and more away from the central atom as we go from NH_3 to SbH_3. Due to such a shifting, the repulsion between bond pair of electrons decreases owing to which bond angle also decreases.
4. The boiling point of these hydrides follows the trend

$$PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$$

The abnormally high boiling point of NH_3 is attributed to presence of intermolecular H–bonding in NH_3.

(b) Halides

They form trihalides of AX_3 type and pentahalides of AX_5 type.

The important characteristics of these trihalides are as follows

1. These trihalides are mostly covalent and their ionic character increases down the group *i.e.*, trihalides of Bi are ionic in nature.
2. These halides have **pyramidal structure** and sp^3-hybridisation.
3. The halides particularly the chlorides, are readily hydrolysed but the products of hydrolysis differ in different cases *e.g.*, if trihalides are **completely hydrolysed**

$$\left\{\begin{array}{l} PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl \\ NCl_3 + 3H_2O \longrightarrow NH_3 + 3HClO \\ 2AsCl_3 + 3H_2O \longrightarrow As_2O_3 + 6HCl \end{array}\right.$$

If partially hydrolysed,

$$\left\{\begin{array}{l} SbCl_3 + H_2O \longrightarrow SbOCl + 2HCl \\ BiCl_3 + H_2O \longrightarrow BiOCl + 2HCl \end{array}\right.$$

The ease of hydrolysis of trihalides (for same halogens) is

$$NCl_3 > PCl_3 > AsCl_3 > SbCl_3 > BiCl_3$$

NF_3 and PF_3 do not undergo hydrolysis.

4. The trihalides of P, As and Sb, especially fluorides and chlorides, are **Lewis acids** *e.g.,*

$$PF_3 + F_2 \longrightarrow PF_5$$
$$SbF_3 + 2F^- \longrightarrow [SbF_5]^{2-}$$
$$SbCl_3 + 2Cl^- \longrightarrow [SbCl_5]^{2-}$$

5. The order of basic character of trihalides of nitrogen is

$$NI_3 > NBr_3 > NCl_3 > NF_3$$

Except NF_3, all other trihalides of nitrogen are unstable and decompose with explosive violence.

6. The P—*X*—P bond angle decreases while acid strength increases as the electronegativity of halogen increases,

i.e., Bond angle $\propto$ electronegativity of halogen.

$$\propto \frac{1}{\text{acid strength}}$$

P, As and Sb have the ability to form pentahalides but Bi and N (due to the absence of vacant *d*-orbital) do not form them. The pentahalides of P (except PCl_5) are not stable due to inert pair effect. PCl_5 itself is not very stable and decomposes to PCl_3 and Cl_2.

The other properties of pentahalides are as follows

1. These pentahalides have sp^3d-hybridisation and **trigonal bipyramidal** structure.
2. They are thermally less stable than the trihalides.
3. PCl_5 is molecular in gaseous phase but exists as, $[PCl_4]^+[PCl_6]^-$ in crystalline state, Similarly, PBr_5 and PI_5 also exist in ionic forms as, $[PBr_4]^+[Br]^-$ and $[PI_4]^+[I]^-$ respectively in solid state.

In addition to trihalides and pentahalides, some other halides are also known, *e.g.,* N_2F_4, N_2F_2, N_3F etc. Besides this, several mixed halides of nitrogen are also known *e.g.,* NCl_2F, $NClF_2$, $NBrF_2$, NF_2H, NF_2H, NCl_2H etc. However, these are unstable and difficult to isolate. P also forms P_2Br_4 and several mixed halides like PCl_4F, $PClF_4$, PCl_2F_3 etc. As and Sb also form mixed halides like AsF_2Cl, $AsFCl_2$, $AsClBr_2$, $AsCl_2Br$, $SbCl_4F$ etc.

(c) Oxides

All elements form oxides of type R_2O_3 and R_2O_5. Besides N, P, Sb and Bi also form dioxides of formula RO_2. N show all oxidation states from +1 to +5 in its oxides as :

Table 7.4 **Different Oxides of V Group Elements**

S. No.	Oxidation state	N	P	As	Sb	Bi
1.	+1	N_2O	—	—	—	—
2.	+2	NO	—	—	—	—
3.	+3	N_2O_3	P_4O_6	As_2O_3	Sb_2O_3	Bi_2O_3
4.	+4	N_2O_4	P_4O_8	—	—	—
5.	+5	N_2O_5	P_4O_{10}	As_2O_5	Sb_2O_5	Bi_2O_5

The trioxides of nitrogen, phosphorus and arsenic are acidic; the trioxide of Sb is **amphoteric** while that of Bi is **basic** in nature.

This is because down the group, metallic character increases, and metal oxides are more basic than the non-metal oxides.

However, the pentoxides are acidic in all the cases but acidic nature decreases down the group. All the penta-oxides (except P_2O_5) can readily loose oxygen to form lower oxides, thus they act as **strong oxidising agents.** The stability of pentaoxides follows the order

$$P_2O_5 > As_2O_5 > Sb_2O_5 > N_2O_5 > Bi_2O_5$$

The ability of nitrogen to form $p\pi$-$p\pi$ bonds depicts in the structure of its oxides.

(d) Oxyacids

All elements (except Bi) of this group form oxyacids.

Anomalous Behaviour of Nitrogen

Nitrogen, because of its small size, high electronegativity, high ionisation energy, non-availability of *d*-orbital and capacity of $p\pi$-$p\pi$ multiple bond formation shows properties that are quite different from the other members of the group.

These properties are as follows

1. Nitrogen is a gas while other members are found in solid state.
2. Nitrogen exists in diatomic form while other elements like phosphorus, arsenic and antimony exist as tetra-atomic molecules (P_4, As_4, Sb_4).
3. Nitrogen forms trinegative ion, *i.e.,* N^{3-} while other members do not form.
4. Nitrogen is chemically inert under ordinary conditions due to high bond dissociation energy, while other members are quite reactive because of the presence of single bond in their molecules.
5. Nitrogen does not show pentacovalency due to non-availability of *d*-orbitals while it is shown by all other elements.

6. The hydride of nitrogen (NH_3) is highly basic in nature while the hydrides of other elements are slightly basic. Moreover, only hydrides of nitrogen shows H-bonding while those of other members do not.
7. Nitrogen forms oxides of five types (*i.e.,* N_2O, NO, N_2O_3, N_2O_4 and N_2O_5) while other members of the family form oxides of only two types (*i.e.*, tri and pentaoxides).
8. Except NF_3, other halides of nitrogen *i.e.,* NCl_3, NBr_3 and NI_3 are unstable while the halides of other elements are fairly stable.
9. Nitrogen does not form complexes due to the non-availability of *d*-orbitals while other members have a tendency of complex formation, *e.g.,* $[PCl_6]^-$, $[AsCl_6]^-$ etc.

Sample **Problem 1** *Which of the following is the strongest reducing agent amongst all the hydrides of group15 elements?*

[**NCERT** Exemplar]

(*a*) NH_3 (*b*) BiH_3 (*c*) PH_3 (*d*) AsH_3

Interpret (*b*) Reducing agents have a tendency to lose hydrogen atom and lesser the bond dissociation enthalpy of *E*—H bond, more is the reducing character of hydrides.

Among the 15 group elements, the size of Bi atom is largest and hence, the Bi—H bond length is largest or Bi—H bond dissociation energy is lowest. That's why Bi—H bond dissociates more readily than the other hydrides of the group, and hence, BiH_3 is the strongest reducing agent.

7.2 Nitrogen (N)

N is fairly widely distributed in nature both in free as well as in combined state. In combined state it occurs only as nitrates *e.g.,* $NaNO_3$ (chile salt petre), KNO_3 (salt petre). Coal containing compounds of nitrogen yield NH_3 on distillation which is an important compound. N is also an essential constituent of all living cells as the protein part which contains about 16% of nitrogen.

Its some compounds are discussed below

Dinitrogen (N_2)

It is the molecular form of elemental nitrogen and chemically inert.

Methods of Preparation

1. In laboratory, dinitrogen is obtained by heating ammonium nitrite or ammonium dichromate.

$$NH_4Cl(aq) + NaNO_2(aq) \longrightarrow N_2(g) + 2H_2O(l) + NaCl(aq)$$

$$(NH_4)_2Cr_2O_7 \xrightarrow{\text{Heat}} N_2 + 4H_2O + Cr_2O_3$$

2. Pure nitrogen in small amounts can be obtained be heating sodium or barium azides.

$$Ba(N_3)_2 \xrightarrow{\Delta} Ba + 3N_2$$

3. On commercial scale, nitrogen is invariably obtained by liquifying air and then carrying out its fractional evaporation. It having a lower boiling point (77.2 K) boils of more readily than less volatile oxygen (boiling point 90.04 K).

Physical Properties

The important physical properties of nitrogen are as

1. Nitrogen is a colourless, tasteless, odourless gas which does not support combustion and is non-poisonous. However, animals die in its atmosphere for want of oxygen.
2. It is sparingly soluble in water.
3. Liquid nitrogen is colourless and boils at 195.8°C.
4. On rapid evaporation, it changes to an ice like solid melting at 209.9°C.
5. Naturally occurring nitrogen consists of two isotopes N^{14} and N^{15}. N^{15} is often used as an isotopic tracer.

Chemical Properties

N_2 is an inert diatomic gas with the structure

$$\ddot{N}\equiv\ddot{N}$$

The heat of dissociation of N_2 is extremely large (945 kJ) that's why even at 3000°C, there is no appreciable dissociation. This speakes for a very strong N≡N bond which is principally responsible for the inactivity of free nitrogen.

However, nitrogen shows the following chemical reactions

1. N_2 combines readily with **highly electropositive metals** (first group elements) even at room temperature and form ionic nitrides with N^{3-} ion. These nitrides are crystalline compounds with high melting points.
2. N_2 combines with less electropositive elements like Mg, Ca, Sr, Ba etc., at red heat; with B and Al at bright red heat and with Si at white heat, to form corresponding nitrides as :

$$3Mg + N_2 \longrightarrow Mg_3N_2$$

$$2Al + N_2 \longrightarrow 2AlN$$

$$3Si + 2N_2 \longrightarrow Si_3N_4$$

Out of these nitrides, the nitrides of group 2nd elements are generally ionic, while those of group 3rd and 4th are covalent in nature.

The nitrides formed with transitional metals like Fe, Mn, Mo, W are true interstitial compounds with N_2 atoms occupying the interstices in the metal structure. These nitrides are extremely hard with high melting point, metallic lustre and metallic conductivity.

3. N_2 combines with H_2 to give NH_3 (Haber's process) as :

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad (\Delta H = -92 \text{ kJ})$$

The reaction is carried out in the presence of finely divided Fe with a little Mo, at 100-1000 atm pressure and 400-550°C.

4. N_2 combines **with** O_2 to give NO as

$$N_2 + O_2 \rightleftharpoons 2NO \qquad (\Delta H = +180.7 \text{ kJ})$$

The reaction is highly endothermic and takes place at elevated temperatures (about 3000°C), but even at such a high temperature, the yield is 5% maximum.

5. When N_2 combines with $CaCl_2$, the product is calcium cynamide, $CaCN_2$(CaNCN) as

$$CaC_2 + N_2 \longrightarrow CaNCN + C$$

(The reaction takes place at 1000°C in the current of N_2.)

Active Nitrogen

When we pass electric discharge in the atmosphere of nitrogen at low pressure, **active nitrogen** is produced. The process of formation of active nitrogen is accompanied by a yellow glow which persists for several hours and indicates slow release of energy in the process. This nitrogen gets deactivated on collision with the walls of vessels. This process is accompanied with the release of energy and accounts for the yellow glow. As the name implies, it is highly reactive chemically and reacts with liquid Hg, Na vapours, As, P etc, giving their nitrides.

The exact nature of active nitrogen has not been fully understood but it is suggested that it contains some nitrogen in atomic state which is responsible for its high reactivity.

Uses

Nitrogen is used

(i) for filling electric lamps.
(ii) to dilute the action of oxygen in air.
(iii) to provide inert atmosphere in certain metallurgical operations and in the packets of foodstuffs.
(iv) for the manufacture of certain chemicals like NH_3. HNO_3, calcium cyanamide and other nitrogen compound.

Sample **Problem 2** *On heating ammonium dichromate and barium azide separately we get* [**NCERT** Exemplar]

(a) N_2 *in both cases*
(b) N_2 *with ammonium dichromate and* NO *with barium azide*
(c) N_2O *with ammonium dichromate and* N_2 *with barium azide*
(d) N_2O *with ammonium dichromate and* NO_2 *with barium azide*

Interpret (*a*) $\underset{\text{ammonium dichromate}}{(NH_4)_2Cr_2O_7} \xrightarrow{\Delta} Cr_2O_3 \downarrow + N_2 \uparrow + 3H_2O$

$$\underset{\text{barium azide}}{Ba(N_3)_2} \xrightarrow{\Delta} Ba + 3N_2$$

Ammonia

It was first isolated by Priestley (in 1774).

Methods of Preparation

Following methods are employed to prepare NH_3

1. NH_3 is prepared on industrial scale by **Haber's process** which involves the direct combination of N_2 and H_2 according to the equation :

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad (\Delta H = -92.0 \text{ kJ})$$

The reaction is reversible, exothermic and proceeds with a tremendous decrease in volume. Thus, it requires **low temperature** and **high pressure** for a better yield of ammonia (according to Le-Chatelier's principle) alongwith highly porous finely divided iron containing small amount of promotors (Mo or oxides of K and Al).

2. It can also be prepared by decomposing ammonium salts with caustic alkalies or lime. In laboratory, it is prepared by heating with slaked lime.

$$2NH_4Cl + CaO \longrightarrow CaCl_2 + H_2O + 2NH_3$$

Ammonia obtained, cannot be dried over concentrated sulphuric acid, calcium chloride or phosphorus pentoxide as the gas reacts with these substances. However, quicklime can be used.

3. It is also prepared by the hydrolysis of calcium cyanamide with superheated steam at 450 K.

$$CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3$$

Physical Properties

NH_3 is a colourless, pungent smelling gas, lighter than air and highly soluble in water. Because of hydrogen bonding, ammonia has a higher boiling point (−33.4°C) than the expected value. Its high solubility in water is also due to the hydrogen bonding between NH_3 and H_2O. Its aqueous solution is basic in nature.

$$NH_3 + H_2O \rightleftharpoons NH_4OH$$

Chemical Properties

Its important chemical properties are as follows

1. Ammonia burns in oxygen with a greenish-yellow flame as

$$4NH_3 + 3O_2 \longrightarrow 2N_2 + 6H_2O$$

2. When electric spark is passed over a mixture of NH_3 and O_2, it gets exploded and if the temperature is 500°C and Pt guaze is present as catalyst, the following reaction occurs

$$4NH_3 + 5O_2 \xrightarrow[\text{electric spark, Pt gauze}]{500°C} 4NO + 6H_2O$$

3. It acts as reducing agent and reduces metallic oxides like CuO and PbO to metals and itself gets oxidised to N_2, *e.g.,*

$$3CuO + 2NH_3 \longrightarrow 3Cu + 3H_2O + N_2$$

4. With calcium, it forms calcium hydride and nitrogen.
5. It reacts with conc. HCl and produces white fumes of the ammonium chloride.

$$NH_3 + HCl \longrightarrow NH_4Cl$$

6. When heated with alkali metals and barium, amides are obtained.

$$2Na + 2NH_3 \longrightarrow 2NaNH_2 + H_2$$

7. With chlorine, it forms NH_4Cl and nitrogen gas.

$$\underset{\text{excess}}{8NH_3} + 3Cl_2 \longrightarrow N_2 + 6NH_4Cl$$

However, if chlorine is in excess, the following reaction occurs

$$NH_3 + \underset{\text{excess}}{3Cl_2} \longrightarrow \underset{\text{explosive}}{NCl_3} + 3HCl$$

8. Aqueous ammonia contains uncombined ammonia (46.2%), hydrated ammonia ($H_3N...HOH$, 52.4%) and relatively few (1.4%) NH_4^+ and OH^- ions. It precipitate many metallic hydroxides from their salt solutions. In some cases, the precipitated hydroxides dissolve in excess ammonia and form complex amines.

$$CuSO_4 + 2NH_4OH \longrightarrow Cu(OH)_2 \downarrow + (NH_4)_2SO_4$$
$$Cu(OH)_2 + 4NH_3 \longrightarrow [Cu(NH_3)_4](OH)_2$$

9. It gives yellow-brown colour or precipitate with Nessler's reagent (*i.e.,* alkaline K_2HgI_4)

$$\underbrace{2K_2HgI_4 + 3KOH}_{\text{(Nessler's reagent)}} + NH_3 \longrightarrow \underset{\substack{\text{(iodide of Millon's base)}\\ \text{(yellow-brown)}}}{H_2NHgOHgI} + 7KI + 2H_2O$$

10. It gives yellow precipitate of ammonium chloroplatinate with chloro-platinic acid.

$$2NH_4Cl + H_2PtCl_6 \rightleftharpoons (NH_4)_2PtCl_6 + 2HCl$$

Liquid ammonia is an excellent ionising solvent. It ionises as

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

In it, alkali metals and to a lesser extent Ca, Sr and Ba dissolve and deep blue solutions are obtained. These deep blue solutions are excellent reducing agents and are electrical conductor due to the presence of solvated electrons.

Uses

Ammonia is used for the following purposes

1. It is used for the manufacture of other reagents like HNO_3 (Ostwald's process), $NaHCO_3$ (Solvay process), $(NH_4)_2SO_4$, etc.
2. It is used as a cleansing agent for removing greese.
3. It is used as a refrigerant.
4. It is also used for the synthesis of urea, an excellent fertilizer.

Structure of Ammonia

Ammonia is covalent molecule, in which three H-atoms are linked to N by single covalent bonds.

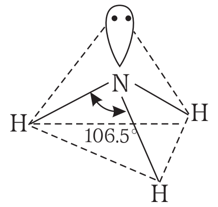


Fig. 7.1 Pyramidal structure of NH_3

Sample Problem 3 *When ammonia reacts with a solution of Cu^{2+}, colour of solution becomes* **[NCERT Exemplar]**

(*a*) *orange red*
(*b*) *deep green*
(*c*) *deep blue*
(*d*) *greenish yellow*

Interpret (*c*) When ammonia (in aqueous solution as ammonium hydroxide) reacts with a solution of Cu^{2+}, a deep blue solution is obtained due to the formation of tetraamine copper (II) ion.

$$Cu^{2+}(aq) + 4NH_4OH(aq) \xrightarrow{\Delta} \underset{\substack{\text{tetraamine copper}\\ \text{(II) ion}\\ \text{(deep blue solution)}}}{[Cu(NH_3)_4]^{2+}} + 4H_2O$$

Nitric Acid, HNO_3

It is the hydrate of N_2O_5.

Methods of Preparation

Following methods can be employed to prepare nitric acid.

1. In the **laboratory,** it is prepared by heating $NaNO_3$ or KNO_3 with conc. H_2SO_4. Reddish brown vapours of HNO_3 so produced, are condensed in a water-cooled receiver.

$$NaNO_3 + H_2SO_4(\text{conc.}) \longrightarrow NaHSO_4 + HNO_3$$

The acid thus produced is yellow in colour due to the presence of NO_2 formed by the decomposition of HNO_3.

$$4HNO_3 \xrightarrow{\Delta} 4NO_2 + 2H_2O + O_2$$

The acid is purified by redistillation and by passing a current of dry air or CO_2 through the warm acid.

2. **On a large scale,** the acid is generally prepared by **Ostwald's process** which consists of the following steps

   ***Step* 1** $NH_3(N = -3)$ obtained by Haber's process is oxidised to NO (N = +2) by atmospheric O_2 (free from dust) in the presence of platinum-guaze catalyst electrically heated at 750 – 900°C

   $$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O \ (\Delta H = -90.0 \text{ kJ})$$

   Since, the reaction is exothermic, heat generated in the reaction maintains the temperature for the catalyst.

   ***Step* 2** NO produced as above is oxidised by atmospheric O_2 to NO_2 which is cooled to about 50°C and then absorbed in water (in the presence of air) to give HNO_3.

   $$2NO + O_2 \longrightarrow 2NO_2$$
   $$4NO_2 + O_2 + 2H_2O \longrightarrow 4HNO_3$$

   (The usual concentrated nitric acid contains 98% HNO_3 and its specific gravity = 1.5).

Physical Properties

The important physical properties of HNO_3 *are as*

1. Pure HNO_3 is colourless fuming liquid of specific gravity 1.56 (at 0°C). It boils at 86°C and freezes to a colourless solid having melting point – 41.3°C. It is soluble in water in all proportions.
2. It is highly corrosive in nature and causes painful blisters when it comes in contact with skin.
3. HNO_3 is colourless but often gradually turns yellow. This is because HNO_3, when exposed to light, undergoes decomposition to form NO_2 which gets dissolved in HNO_3 and gives it yellow colour.

   $$4HNO_3 \longrightarrow 4NO_2 + O_2 + 2H_2O$$

   The yellow colour of the acid can be removed by warming it to 60 – 80° C and bubbling dry air through it.

Chemical Properties

HNO_3 is a strong acid and also a very strong oxidising agent. *Its important chemical reactions are as follows*

1. At room temperature, the pure acid undergoes dissociation to give N_2O_4 and O_2.

   $$HNO_3 \longrightarrow N_2O_5 + H_2O$$
   $$N_2O_5 \rightleftharpoons N_2O_4 + \frac{1}{2}O_2$$

   On heating, HNO_3 decomposes to give O_2 and brown fumes of NO_2.

   $$4HNO_3 \longrightarrow 4NO_2 + O_2 + 2H_2O$$

2. HNO_3 being a very strong monobasic acid, reacts with basic oxides, carbonates, bicarbonates, sulphites and hydroxides, forming corresponding nitrates. *e.g.*,

   $$CaO + 2HNO_3 \longrightarrow Ca(NO_3)_2 + H_2O$$
   $$Na_2CO_3 + 2HNO_3 \longrightarrow 2NaNO_3 + H_2O + CO_2$$

3. Being a strong acid, HNO_3 is completely ionised in water as :

   $$HNO_3 \longrightarrow H^+ + NO_3^-$$

4. HNO_3 is a very strong oxidising agent, since it can easily give nascent oxygen both in the conc. and dil. forms.

   $$2HNO_3 \longrightarrow H_2O + 2NO_2 + O$$

   In these reactions, HNO_3 is reduced to NO_2, O_2, NH_4NO_3 (or NH_4^+ ions), N_2O, NO, N_2 or NH_2OH depending on the nature of the substance to be oxidised, concentration of HNO_3 and the temperature employed.

Non-metals and metalloids (*e.g.,* C, Sn, P, As, Pb, S and I) are oxidised to their corresponding highest oxy-acids while, the metals like Mg, Mn, Zn, Fe, Sn, Pb, Cu, Ag and Hg are oxidised to their corresponding nitrates.

Some examples of such type of reactions (*i.e., the reactions in which* HNO_3 *acts as an oxidising agent*) *are given below*

I. **HNO_3 oxidises non-metals and metalloids to their oxyacids as**

(i) P is oxidised to H_3PO_4.

$$P + 5HNO_3 \longrightarrow H_3PO_4 + 5NO_2 + H_2O$$

This reaction takes place through the following steps :

$$2P + \underset{(\text{from } HNO_3)}{5O} \longrightarrow P_2O_5$$
$$P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4$$
$$\overline{\underline{2P + 5O + 3H_2O \longrightarrow 2H_3PO_4}}$$

(ii) Carbon is oxidised to H_2CO_3.

$$C + 4HNO_3 \longrightarrow H_2CO_3 + 4NO_2 + H_2O$$

(iii) Tin is oxidised to metastannic acid, H_2SnO_3 (by conc. HNO_3)

$$Sn + 4HNO_3 \longrightarrow H_2SnO_3 + 4NO_2 + H_2O$$

(iv) P, As and Sb are oxidised to H_3PO_4 (phosphoric acid), H_3AsO_4 (arsenic acid) and H_3SbO_4 (antimonic acid) respectively

$$M + 5HNO_3 \longrightarrow H_3MO_4 + 5NO_2 + H_2O$$
$$(M = \text{P, As, Sb})$$

(v) Sulphur is oxidised to H_2SO_4.

$$S + \underset{(\text{conc. and hot})}{6HNO_3} \longrightarrow H_2SO_4 + 6NO_2 + 2H_2O$$

(vi) Iodine is oxidised to iodic acid, HIO_3.

$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

II. **It converts reactive metals** (present above hydrogen in electrochemical series) to metal nitrates and itself gets reduced to H_2 (in case of Mg and Mn) or to NH_4NO_3, NO_2 , NO and NO_2 (with other metals). Actually in later case following two steps are involved.

***Step* 1** The metal (M) on being treated with HNO_3 is converted into metallic nitrate and nascent hydrogen is produced

$$M + 2HNO_3 \longrightarrow M(NO_3)_2 + 2H$$

***Step* 2** Nascent hydrogen, produced as above, reduces HNO_3 to NH_4NO_3 (or NH_4^+ ion), N_2O, NO or NO_2

$$2HNO_3 + 8H \longrightarrow NH_4NO_3 + 3H_2O$$
$$2HNO_3 + 8H \longrightarrow N_2O + 5H_2O$$
$$HNO_3 + H \longrightarrow NO_2 + H_2O$$
$$HNO_3 + 3H \longrightarrow NO + 2H_2O$$

Some important examples of such reactions are as follows

Zinc

(i) Zn reacts with very dil. HNO_3 (6%) and is oxidised to $Zn(NO_3)_2$. Here, HNO_3 is reduced to NH_4NO_3 as :

$$4Zn + \underset{\text{(very dilute)}}{10HNO_3} \longrightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

(ii) Zn reacts with cold and dil. HNO_3 (20%) and is oxidised to $Zn(NO_3)_2$. Here, HNO_3 is reduced to N_2O as

$$4Zn + \underset{\substack{\text{(cold and}\\\text{dilute)}}}{10HNO_3} \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$$

(iii) Zn reacts with cold and conc. HNO_3 (70%) and is oxidised to $Zn(NO_3)_2$. Here, HNO_3 is reduced to NO_2 as

$$Zn + \underset{\text{(cold and conc.)}}{4HNO_3} \longrightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$$

(iv) If Zn reacts with cold and moderately conc HNO_3 (50%), NO is evolved and $Zn(NO_3)_2$ is formed

$$3Zn + 8HNO_3 \longrightarrow 3Zn(NO_3)_2 + 4H_2O + 2NO$$

Iron

(i) Fe reacts with very dil. HNO_3 and is oxidised to $Fe(NO_3)_2$. Here, HNO_3 is reduced to NH_4NO_3 as

$$4Fe + \underset{\text{(very dilute)}}{10HNO_3} \longrightarrow 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O$$

(ii) Fe is oxidised to $Fe(NO_3)_2$ by dil HNO_3 and HNO_3 is reduced to N_2O as

$$4Fe + \underset{\text{(dilute)}}{10HNO_3} \longrightarrow 4Fe(NO_3)_2 + N_2O + 5H_2O$$

(iii) Fe reacts with cold and conc. HNO_3 and is oxidised to $Fe(NO_3)_3$. Here, HNO_3 is reduced to NO_2 as

$$Fe + \underset{\text{(cold and conc.)}}{6HNO_3} \longrightarrow Fe(NO_3)_3 + 3NO_2 + 3H_2O$$

(iv) With hot and conc. HNO_3, Fe is oxidised to $Fe(NO_3)_3$ and HNO_3 is reduced to NO as

$$Fe + \underset{\text{(hot and conc.)}}{4HNO_3} \longrightarrow Fe(NO_3)_3 + 2H_2O + NO$$

Highly conc. HNO_3 renders iron passive (inert).

III. **HNO_3 also oxidises less reactive metals** (present below hydrogen in the electrochemical series) Examples of such metals are Cu, Ag and Hg. These metals when treated with HNO_3 are oxidised to their corresponding nitrates and HNO_3 is reduced to NO_2, NO, NO_2 or N_2 depending on the nature of the metal, concentration of the acid and temperature employed. Thus,

$$M + 2HNO_3 \longrightarrow M(NO_3)_2 + N_2O, NO, NO_2 \text{ or } N_2 + H_2O$$
(M = Cu, Ag, Hg)

These reactions, infact, involve the following two steps

(i) Since, Cu, Ag and Hg lie below hydrogen in the electrochemical series, they are not able to liberate hydrogen from HNO_3 as Zn, Fe, Sn and Pb can do. In case of these metals HNO_3 acts as an oxidising agent, *i.e.*, HNO_3 gives nascent oxygen and is itself reduced to N_2O, NO, NO_2 or N_2.

$$2HNO_3 \longrightarrow N_2O + H_2O + 4O$$
$$2HNO_3 \longrightarrow 2NO + H_2O + 3O$$
$$2HNO_3 \longrightarrow 2NO_2 + H_2O + O$$
$$2HNO_3 \longrightarrow N_2 + H_2O + 5O$$

(ii) Nascent oxygen obtained as above, oxidises the metal to its oxide which on reaction with HNO_3, gives metallic nitrate.

$$M + O \longrightarrow MO \text{ (metallic oxide)}$$
$$MO + 2HNO_3 \longrightarrow M(NO_3)_2 + H_2O$$

Some important examples of such reactions are

Copper

(i) With cold and dil HNO_3 evolves N_2O as

$$\underset{\text{(cold and dil)}}{10HNO_3} + 4Cu \longrightarrow N_2O + 5H_2O + 4Cu(NO_3)_2$$

(ii) With cold and moderately conc. HNO_3 evolves NO as

$$3Cu + \underset{\substack{\text{(cold and}\\\text{moderately conc)}}}{8HNO_3} \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

(iii) With cold and conc. HNO_3 evolves NO_2 as

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

(iv) With hot and conc. HNO_3 evolves N_2 as

$$12HNO_3 + 5Cu \longrightarrow N_2 + 6H_2O + 5Cu(NO_3)_2$$

Silver

(i) With dil HNO_3, $AgNO_3$ is obtained and NO is evolved as

$$3Ag + \underset{\text{(dilute)}}{4HNO_3} \longrightarrow 3AgNO_3 + NO + 2H_2O$$

(ii) With conc. HNO_3, NO_2 is evolved as

$$Ag + \underset{\text{(conc.)}}{2HNO_3} \longrightarrow AgNO_3 + NO_2 + H_2O$$

Mercury

(i) With dil HNO_3, $Hg_2(NO_3)_2$ is formed and NO is evolved as

$$6Hg + \underset{\text{(dilute)}}{8HNO_3} \longrightarrow \underset{\text{mercurous nitrate}}{3Hg_2(NO_3)_2} + 2NO + 4H_2O$$

(ii) With conc. HNO_3, mercuric nitrate, $Hg(NO_3)_2$ is obtained and NO_2 is evolved as :

$$Hg + \underset{\text{(conc.)}}{4HNO_3} \longrightarrow Hg(NO_3)_2 + 2NO_2 + 2H_2O$$

IV. **HNO_3** (Both dil. and conc. can also oxidise many compounds) In these reactions, dil. HNO_3 reduced to NO while conc. HNO_3 is reduced to NO_2. When HNO_3 oxidises $SnCl_2$ in presence of HCl, it is reduced to NH_2OH. Thus,

$$\underset{\text{(dil.)}}{2HNO_3} \longrightarrow H_2O + 2NO + 3O$$

$$\underset{\text{(conc.)}}{2HNO_3} \longrightarrow H_2O + 2NO_2 + O$$

$$HNO_3 + 6H \longrightarrow 2H_2O + NH_2OH$$

Some important examples of such reactions with HNO_3 *are as follows.*

(i) **I_2 is liberated from KI solution** ($I^- \longrightarrow I_2^0$)

$$\underset{\text{(dil.)}}{8HNO_3} + 6KI \longrightarrow 2NO + 4H_2O + 6KNO_3 + 3I_2$$

(ii) **CuS is oxidised to sulphur** ($S^{2-} \longrightarrow S$)

$$\underset{\text{(dil.)}}{8HNO_3} + 3CuS \longrightarrow 2NO + 4H_2O + 3S + 3Cu(NO_3)_2$$

(iii) **H_2S is oxidised to sulphur** (by both dil. and conc. HNO_3 ($S^{2-} \longrightarrow S$)

$$\underset{\text{(dil.)}}{2HNO_3} + 3H_2S \longrightarrow 2NO + 4H_2O + 3S$$

$$\underset{\text{(conc.)}}{2HNO_3} + H_2S \longrightarrow 2NO_2 + S + 2H_2O$$

(iv) **FeS is oxidised to $FeSO_4$** ($S^{2-} \longrightarrow SO_4^{2-}$)

$$FeS + \underset{\text{(conc)}}{8HNO_3} \longrightarrow FeSO_4 + 8NO_2 + 4H_2O$$

(v) **SO_2 is oxidised to H_2SO_4** (by both dil. and conc. HNO_3)

($SO_2 \longrightarrow SO_4^{2-}$)

$$SO_2 + \underset{\text{(conc.)}}{2HNO_3} \longrightarrow H_2SO_4 + 2NO_2$$

$$\underset{\text{(dil.)}}{2HNO_3} + 2H_2O + 3SO_2 \longrightarrow 2NO + 3H_2SO_4$$

(vi) **Solution of $FeSO_4$ is oxidised to $Fe_2(SO_4)_3$** (by both dil. and conc. HNO_3) in the presence of H_2SO_4 ($Fe^{2+} \longrightarrow Fe^{3+}$)

$$\underset{\substack{\text{green}\\\text{solution}}}{6FeSO_4} + 3H_2SO_4 + \underset{\text{dil.}}{2HNO_3} \longrightarrow \underset{\substack{\text{yellow}\\\text{solution}}}{3Fe_2(SO_4)_3} + 2NO + 4H_2O$$

$$2FeSO_4 + \underset{\text{conc.}}{2HNO_3} + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2NO_2 + 2H_2O$$

(vii) **HBr and HI are oxidised to Br_2 and I_2 respectively** ($Br^- \longrightarrow Br_2$, $I^- \longrightarrow I_2$)

$$\underset{\text{(dil.)}}{2HNO_3} + 6HX \longrightarrow 2NO + 4H_2O + 3X_2$$

$$\underset{\text{(conc.)}}{2HNO_3} + 2HX \longrightarrow X_2 + 2NO_2 + 2H_2O$$

(viii) **As_2O_3 is oxidised to** H_3AsO_4 ($As^{3+} \longrightarrow AsO_4^{3-}$)

$$2HNO_3 + As_2O_3 + H_2O \longrightarrow 4NO_2 + 2H_3AsO_4$$

(ix) **Cane-sugar** (sucrose), **$C_{12}H_{22}O_{11}$ is oxidised to oxalic acid, $H_2C_2O_4$ by conc. HNO_3**

$$\underset{\text{(conc.)}}{36HNO_3} + C_{12}H_{22}O_{11} \longrightarrow 23H_2O + 36NO_2 + 6H_2C_2O_4$$

(x) **Toluene** ($C_6H_5CH_3$) **is oxidised to benzoic acid** (C_6H_5COOH) **by dil. HNO_3**

$$\underset{\text{(dil)}}{2HNO_3} + C_6H_5CH_3 \longrightarrow 2NO + 2H_2O + C_6H_5COOH$$

(xi) **$SnCl_2$ is oxidised to $SnCl_4$ in presence of HCl** ($Sn^{2+} \longrightarrow Sn^{4+}$)

$$3SnCl_2 + 6HCl + HNO_3 \longrightarrow 2H_2O + 3SnCl_4 + NH_2OH$$

V. Metals like Cr, Ni, Al, Fe become passive (inert) when treated with conc HNO_3, *e.g.*, Fe displaces Cu from $CuSO_4$ solution but this property of Fe is lost when it is dipped in slightly conc HNO_3. This is because, a thin oxide (iron oxide) layer is deposited over the metal surface, when it is treated with conc HNO_3. This layer makes the iron passive or inert.

VI. When 1 part of conc. HNO_3 is mixed with 3 parts of conc. HCl, we get **aqua-regia.** *Aqua-regia produces nascent chlorine* (Cl) *along with nitrosyl chloride* (NOCl) *as*

$$HNO_3 + 3HCl \longrightarrow NOCl + 2H_2O + 2Cl$$

Due to production of nascent chlorine, aqua-regia is very active, *e.g.,* Au and Pt (noble metals) which are not acted upon by HNO_3 get dissolved in aqua-regia due to the formation of soluble complexes namely $H[AuCl_4]$ and $H_2[PtCl_6]$ respectively. *e.g.,*

$$2Au + 3HNO_3 + 11HCl \longrightarrow H[AuCl_4] + 2NOCl + 6H_2O$$

VII. Conc. HNO_3 attacks many aromatic organic compounds (*e.g.*, C_6H_6, $C_6H_5CH_3$, C_6H_5OH etc.) in the presence of conc. H_2SO_4 and substitutes one or more H-atoms in these organic compounds by nitro group, producing nitro compounds (nitration). Here, H_2SO_4 absorbs water liberated in the reaction and also produces nitronium ion (NO_2^+) by reacting with HNO_3. This NO_2^+ ion makes the nitration of aromatic compounds. *e.g.*,

$$HNO_3 + C_6H_6 \xrightarrow{H_2SO_4} \underset{\text{nitrobenzene}}{C_6H_5NO_2} + H_2O$$

VIII. With protein, HNO_3 gives yellow coloured xanthoprotein. The acid produces yellow stain on skin and wood, since the skin and wood both contain protein.

Uses

Nitric acid is used

1. as a laboratory reagent and making aqua-regia.
2. as strong oxidising agent.
3. to clean noble metals such as Au, Ag, Pt.
4. to make explosive materials such as TNT, picric acid, gun cotton etc.
5. in making of colour, perfume, artificial fibre etc.
6. for the manufacture of fertilizers.

Sample **Problem 4** *Which of the following products will be obtained when copper metal is reacted with* HNO_3? [**NCERT**]

(*a*) NO *and* N_2O_5 (*b*) NO_2 *and* N_2O_5
(*c*) NO *and* NO_2 (*d*) HNO_2 *and* N_2

Interpret (*c*) The products of the reaction of copper with HNO_3 depends upon the concentration of HNO_3 used.

(i) Copper metal reacts with dilute HNO_3 to form nitrogen (II) oxide (NO).

$$3Cu + 8HNO_3(\text{dilute}) \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

(ii) Copper metal reacts with conc. HNO_3 to form nitrogen (IV) oxide or nitrogen dioxide (NO_2).

$$Cu + 4HNO_3(\text{conc.}) \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

Sample **Problem 5** *In the preparation of* HNO_3, *we get* NO *gas by catalytic oxidation of ammonia. The moles of* NO *produced by the oxidation of two moles of* NH_3 *will be* [**NCERT Exemplar**]

(*a*) 2 (*b*) 3 (*c*) 4 (*d*) 6

Interpret (*c*) In the preparation of nitric acid by Ostwald's process, ammonia is oxidised to NO by atmospheric O_2 in the presence of platinum-guaze catalyst.

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$$

or
$$2NH_3 + \frac{5}{2}O_2 \longrightarrow 2NO + 3H_2O$$

Oxides of Nitrogen

Nitrogen forms Several Oxides

The preparation and properties of these oxides can be summarised as

Table 7.5 **Preparation and Properties of Various Oxides of Nitrogen**

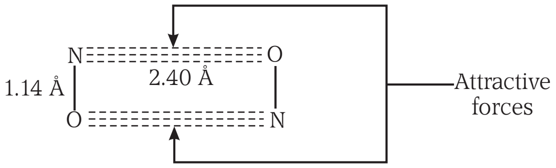
Formula	Name	Preparation	Properties
N_2O	Nitrous oxide or laughing gas	$NH_4NO_3 \rightarrow N_2O + 2H_2O$	Colourless gas, rather unreactive.
NO	Nitrogen monoxide (Nitric oxide)	$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$	Colourless gas, reactive, paramagnetic.
NO_2	Nitrogen dioxide	$Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$	Brown gas, reactive, paramagnetic.
N_2O_3	Dinitrogen trioxide or nitrous anhydride	$NO + NO_2 \rightarrow N_2O_3$	Dark blue in the liquid or solid state, unstable in the gas phase.
N_2O_4	Dinitrogen tetroxide (mixed anhydride of N_2O and NO)	$2NO_2 \rightleftharpoons N_2O_4$	Colourless, exists in equilibrium with NO_2 both in the gaseous and liquid state.
N_2O_5	Dinitrogen pentoxide	$2HNO_3 + P_2O_5 \rightarrow 2HPO_3 + N_2O_5$	Unstable as gas; in the solid state exists as $[NO_2]^+[NO_3]^-$.

Some other Properties of Oxides of Nitrogen

1. N_2O (nitrous oxide) is a colourless gas, fairly soluble in cold water but practically insoluble in hot water, easily liquifiable at room temperature by applying pressure (critical temperature 35°C). It has a faint odour. When inhaled in moderate quantities, it produces hysterical laughter (that's why called **laughing gas**). Its higher quantity doses may make a person unconcious. Chemically, it is relatively inert and does not reacts with halogens, alkali metals and even ozone at room temperature. However, it decomposes to N_2 and O_2 at 600°C and form metal azides with molten alkali metals as

$$NaNH_2 + N_2O \xrightarrow{200°C} NaN_3 + H_2O$$

2. **NO** (nitric oxide) is an odd electron molecule, because of the presence of an unpaired electron. It undergoes partial dimerisation in liquid state and exists as a dimer in solid state as



It readily reacts with oxygen to give brown fumes of NO_2 as

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

3. **NO_2** (nitrogen dioxide) is also an odd electron molecule and in gaseous phase, exists in equilibrium with dimer N_2O_4 which is colourless *i.e.*,

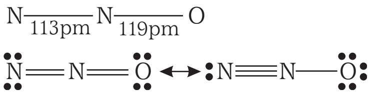
$$\underset{\substack{\text{brown}\\\text{(paramagnetic)}}}{2NO_2(g)} \qquad \underset{\substack{\text{colourless}\\\text{(diamagnetic)}}}{N_2O_4(g)}$$

4. **N_2O_5** (dinitrogen pentaoxides) is the strongest acid among all the pentoxides and a very strong oxidising agent.

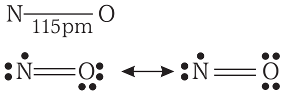
Structure of Oxides of Nitrogen

The molecular and Lewis dot resonance structures of oxides of nitrogen are shown as

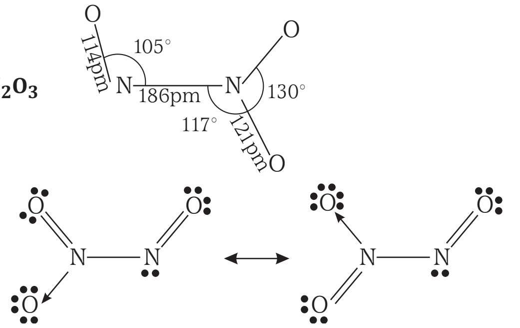
(i) **N_2O**



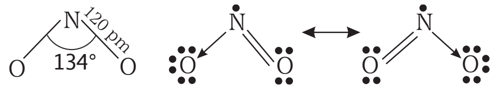
(ii) **NO**



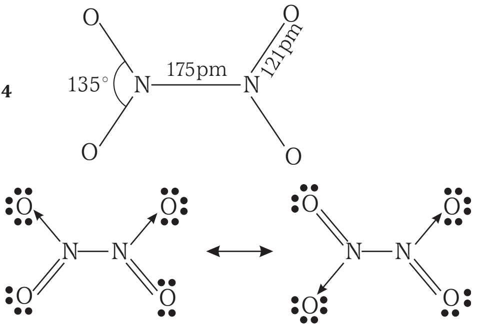
(iii) **N_2O_3**



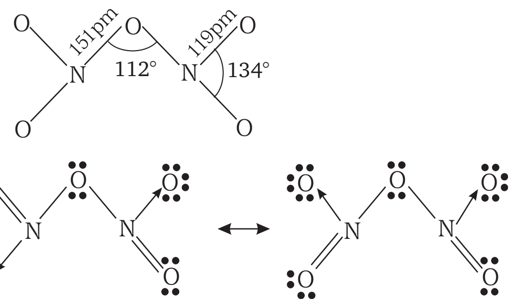
(iv) **NO_2**



(v) **N_2O_4**



(vi) **N_2O_5**



Sample **Problem 6** *Nitric acid forms an oxide of nitrogn on reaction with P_4O_{10}. How many resonating structures of the oxide of nitrogen will be formed?* **[NCERT Exemplar]**

(*a*) 2

(*b*) 3

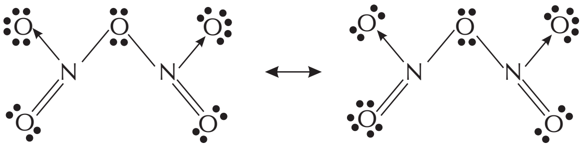
(*c*) 4

(*d*) 5

Interpret (*a*) P_4O_{10} being a dehydrating agent, removes a molecule of water and forms anhydride of HNO_3.

$$4HNO_3 + P_4O_{10} \longrightarrow 4HPO_3 + 2N_2O_5$$

Resonation structures of N_2O_5 are



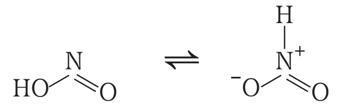
Oxyacids of Nitrogen

Nitrogen forms following oxyacids

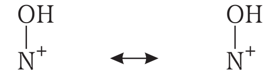
(i) Hyponitrous acid, $H_2N_2O_2$
(ii) Nitrous acid, HNO_2
(iii) Nitric acid, HNO_3
(iv) Pernitrous acid, HOONO
(v) Pernitric acid, $HOONO_2$

Out of these, the most important one is nitric acid.

The structure of some oxyacids of nitrogen are



(nitrous acid)



(nitric acid)

7.3 Phosphorus

It is the most reactive element in this group and found in the combined state as phosphates in the rocks and in the soil. It is an essential constituent of teeth, bones, blood and nervous tissues. its important minerals are phosphorite $[Ca_3(PO_4)_2]$, chlorapatite $[3Ca_3(PO_4)_2 . CaCl_2]$, Fluorapatite or apatite $[3Ca_3(PO_4)_2 . CaF_2]$. Ist yellow form is always kept under water.

MethodS of Preparation

Following methods are employed to prepare phosphorus.

(a) **Retort Process**

$$\underset{\text{phosphorite}}{Ca_3(PO_4)_2} + 3H_2SO_4 \longrightarrow \underset{\text{orthophosphoric acid}}{2H_3PO_4} + 3CaSO_4$$

$$H_3PO_4 \longrightarrow \underset{\text{methaphosphoric acid}}{HPO_3} + H_2O$$

$$4HPO_3 + 10C \longrightarrow P_4 + 10CO + 2H_2O$$

(b) **Electrothermal Process**

Phosphorus is obtained from direct reduction of mineral phosphorite by carbon in presence of silica.

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \xrightarrow{1400\text{-}1500°C} 6CaSiO_3 + P_4 + 10CO$$

(c) **From Bone Ash**

It is manufactured by heating bone ash or phosphorite with sand (SiO_2) and coke (C) in an electric furnance as

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \longrightarrow 6CaSiO_3 + 10CO + P_4$$

Allotropes of Phosphorus

Phosphorus exists in following allotropic forms, which are inter convertible.

1. **White P** is a waxy transluscent solid, readily soluble in CS_2. Below 800°C, its vapour density corresponds to formula P_4 while above 800°C it dissociates to P_2. It melts at 44.1°C and boils at 280°C. Its ignition temperature is very low. When exposed to air, it undergoes oxidation which gradually raises its temperature and ultimately, it catches fire when temperature exceeds 30°C. That's why, **it is always kept in water.** Being extremely poisonous, it proves fatal if taken internally. P glows in dark on account of its slow oxidation (phosphorescence). It is readily soluble in turpentine oil and ether. Its structure in P_4 form can be seen as

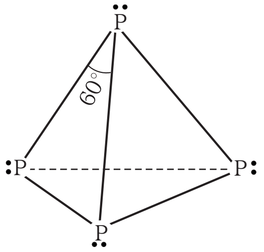


Fig. 7.2 Tetrahedral phosphorus molecule

2. **Red P** is violet red powder consisting of some crystals and some amorphous variety. It differs from white variety as it is more stable under ordinary conditions, does not ignite spontaneously in air

$$\text{Red P} \xrightarrow[\text{heating}]{\text{Sublimes on}} \text{vapours} \xrightarrow{\text{Condensed}} \text{white P}$$

Red P has an iron-grey lusture and does not show phosphorescence. It is insoluble in CS_2 and other organic solvents.

Red P does not melt at a definite temperature, its density is also variable. Because of this reason, it is not regarded as the definite allotrope of phosphorus. It is thought to be a solid solution of scarlet P in metallic (α-black) phosphorus. The exact nature of red P is however, uncertain.

3. **Metallic or α-black P** is a very stable allotrope of P and does not oxidise in air unless heated very strongly. It does not conduct electricity.

4. β-**black P** is the only form of phosphorus whose structure is definitely known. It is crystalline in nature and consists of corrugated sheets. Here, each P atom is covalently bonded to other three neighbouring atoms as shown in figure below

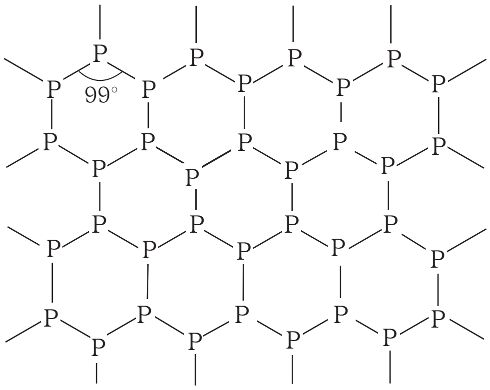


Fig. 7.3 Layer structure of β-black phosphorus

The atoms within a layer are more strongly bound than the atoms in adjacent layers. This gives rise to flaky crystals which resemble those of graphite. Its melting point is 587°C and specific gravity is 2.69. It does not burn in air even up to 400°C. It is good conductor of electricity just like graphite.

5. **Scarlet P** resembles the red variety in its physical properties and white P in its chemical properties. It has the property of only slow oxidation in air.
6. **Violet phosphorus** is crystalline in nature.

Chemical Properties of Phosphorus

White P is more reactive than other varieties and exhibits the following reactions

1. It burns in air forming its trioxide and pentoxide.
2. White P combines with hot solutions of KOH or NaOH giving phosphene.

$$P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$$

However, red P does not react with dilute alkalies. Thus, this property is helpful in separating red P with white P.

3. P forms trihalides and pentahalides with halogens, white P reacts more vigorously than red P.
4. P combines to S with explosive violence forming a number of sulphides *e.g.*, P_2S_3, P_2S_5, P_4S_3 and P_4S_7 etc.
5. P combines with metals to form phosphides as

$$6Mg + P_4 \longrightarrow 2Mg_3P_2$$
$$6Ca + P_4 \longrightarrow 2Ca_3P_2$$

(Na and K react vigorously with a white flash).

6. Since, white P can be easily oxidised, it acts as strong reducing agent. It reduces HNO_3 to nitrogen dioxide and H_2SO_4 to SO_2. It also reduces solutions of Cu, Ag and Au salts to the corresponding metals *e.g.*,

$$P_4 + 8CuSO_4 + 14H_2O \longrightarrow 8Cu + 8H_2SO_4 + 2H_3PO_4 + 2H_3PO_3$$

Uses

1. Red phosphorus is used in match industry.
2. Radioactive phosphorus is used in the treatment of leukemia and other blood disorders.
3. Yellow phosphhorus and zinc phosphide are used as a rat poison.

Sample Problem 7 *White phosphorus reacts with chlorine and the product hydrolyses in the presence of water. Calculate the mass of* HCl *obtained by the hydrolysis of the product formed by the reaction of 62 g of white phosphorus with chlorine in the presence of water.* [**NCERT** Exemplar]

(*a*) 0.219 g
(*b*) 2.19 g
(*c*) 21.9 g
(*d*) 219.0 g

Interpret (*d*) Equations for the reactions

$$\begin{array}{rcl} P_4 + 6Cl_2 & \longrightarrow & 4PCl_3 \\ PCl_3 + 3H_2O & \longrightarrow & H_3PO_3 + 3HCl \times 4 \\ \hline \underset{1\text{ mol}}{P_4} + 6Cl_2 + 12H_2O & \longrightarrow & 4H_3PO_3 + \underset{12\text{ mol}}{12HCl} \end{array}$$

$31 \times 4 = 124$ g $\qquad 12 \times 36.5 = 438.0$ g

$\because$ 124 g of white phosphorus produces HCl = 438 g

$\therefore$ 62 g of white phosphorus will produces

$$HCl = \frac{438}{124} \times 62 = 219.0 \text{ g HCl}$$

Phosphine (PH_3)

It is discovered by **Gembre** in 1783.

Methods of Preparation

Following methods are used to prepare PH_3 *(phosphine)*

1. PH_3 is generally prepared by boiling white P with a concentrated solution of NaOH in inert atmosphere of CO_2, oil gas or hydrogen as

$$P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$$

It is necessary to exclude air from the apparatus because, although pure PH_3 will not burn unless ignited, it is often accompanied with P_2H_4 and H_2 which are spontaneously flammable.

$$2P + 2NaOH + 2H_2O \longrightarrow 2NaH_2PO_2 + H_2\uparrow$$
$$6P + NaOH + 4H_2O \longrightarrow 4NaH_2PO_2 + P_2H_4$$

Because of this reaction, phosphine is used in making **Holme's signals.**

(Pure phosphine is obtained by using alcoholic KOH in place of aqueous NaOH solution).

2. It can also be obtained by heating phosphorus acid.

$$4H_3PO_3 \longrightarrow 3H_3PO_4 + PH_3$$

3. Treatment of phosphonium iodide with 30% KOH solution also gives phosphine.

$$PH_4I + KOH \longrightarrow KI + H_2O + PH_3$$

The evolved gas is passed through HCl (which decomposes P_2H_4) and then through NaOH (where HI is absorbed).

4. It is also obtained by the hydrolysis of Ca_3P_2 with water or dilute HCl.

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$

Physical Properties

It is colourless, highly reactive and extremely toxic gas with a slight smell of garlic or rotten fish. It liquefies at −89°C and solidifies at −134°C. It is highly poisonous in nature.

Chemical Properties

Important chemical properties exhibited by phosphine are as follows

1. PH_3, unlike NH_3, is not very soluble in water. Its aqueous solution is neutral. It is more soluble in non-polar solvent like CS_2 and other organic solvents.
2. When heated out of contact of air to 440°C or when electric sparks are passed, phosphine decomposes and gives red phosphorus and hydrogen gas as

$$4PH_3 \longrightarrow P_4 + 6H_2$$

A pure sample of phosphine is not spontaneously inflammmable. It burns in air or oxygen when heated at 150°C.

$$2PH_3 + 4O_2 \xrightarrow{\Delta} P_2O_5 + 3H_2O$$

However, white smoke (vortex rings) is formed, if PH_3 comes in contact with air. This is because of the formation of vortex ring of P_2O_5 due to impurity of P_2H_4 (diphosphine).

3. In contact with nitric acid, phosphine begins to burn.

$$2PH_3 + 16HNO_3 \longrightarrow P_2O_5 + 16NO_2 + 11H_2O$$

4. It forms addition compounds with anhydrous $AlCl_3$ and $SnCl_4$.

$$AlCl_3 + 2PH_3 \longrightarrow AlCl_3 \cdot 2PH_3$$
$$SnCl_4 + 2PH_3 \longrightarrow SnCl_4 \cdot 2PH_3$$

5. Phsophine gives a black precipitate of cupric phosphide, when passed through $CuSO_4$ solution.

$$3CuSO_4 + 2PH_3 \longrightarrow Cu_3P_2 + 3H_2SO_4$$

It also gives a similar reaction with silver nitrate solution.

$$3AgNO_3 + PH_3 \longrightarrow Ag_3P + 3HNO_3$$

6. The mixture of PH_3 and N_2O or PH_3 and NO explodes in the presence of electric spark.

$$PH_3 + 4NO_2 \longrightarrow H_3PO_4 + 4N_2$$

7. PH_3 is a better reducing agent than NH_3 and reduces
   (i) Ag^+ to Ag metal as

$$6Ag^+ + PH_3 + 3H_2O \longrightarrow H_3PO_3 + 6Ag\downarrow + 6H^+$$

   (ii) Cu^{2+} to Cu metal as

$$4Cu^{2+} + PH_3 + 4H_2O \longrightarrow H_3PO_4 + 4Cu\downarrow + 8H^+$$

8. In liquid NH_3, phosphine dissolves to give $NH_4^+PH_2^-$.

$$\underset{\text{base}}{NH_3} + \underset{\text{acid}}{PH_3} \longrightarrow NH_4^+PH_2^-$$

Structure of Phosphine

In phosphine, three H atoms are attached with P atom through covalent bonds and P has one lone pair of electrons, thus, its structure is pyramidal like NH_3.

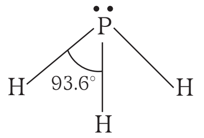


Fig. 7.4 Structure of PH_3

Uses

PH_3 is used

1. For making smoke screens.
2. For making metallic phosphides.
3. For making **Holme's signals.** For this a mixture of calcium carbide, CaC_2 and calcium phosphide, Ca_3P_2 is placed in metallic containers. Two holes are made and the container is thrown into the sea. Water enters in the container and produces acetylene and phosphine. The gaseous mixture catches fire spontaneously because of the presence of P_2H_4. The acetylene gives a bright luminous flame which serves as a signal to the approaching ship.

Sample **Problem 8** *On heating with concentrated* NaOH *solution in an inert atmosphere of* CO_2*, white phosphorus gives a gas. Which of the following statement is incorrect about the gas?* [**NCERT** Exemplar]

(a) *It is highly poisonous and has smell like rotten fish.*
(b) *Its solution in water decomposes in the presence of light.*
(c) *It is more basic than* NH_3.
(d) *It is less basic than* NH_3.

Interpret (c) White phosphorus combines with a concentrated solution of NaOH in inert atmosphere of CO_2, to yield a highly poisonous gas, phosphine. It has rotten fish like smell.

$$P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3\uparrow$$

Its aqueous solution is neutral, so it is not more basic than NH_3.

Phosphorus Trichloride

Its formula is PCl_3.

Method of Preparation

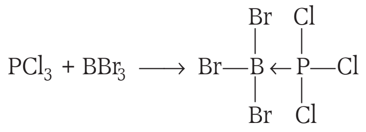
It is obtained when dry Cl_2 is passed over red or white phosphorus heated gently in a retort over a water bath.

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$

Physical and Chemical Properties

Important properties of PCl_3 *are as*

1. It is a low boiling liquid (b.p. 74°C) with a pungent odour and fumes in moist air.
2. It violently hydrolysed by water as
$$PCl_3 + 3H_2O \longrightarrow 3HCl + H_3PO_3$$
3. It reacts with chlorine and sulphur chloride as
$$PCl_3 + Cl_2 \longrightarrow PCl_5$$
$$3PCl_3 + SCl_2 \longrightarrow PCl_5 + 2PSCl_3$$
4. It reacts with oxygen and SO_3 as
$$2PCl_3 + O_2 \longrightarrow 2POCl_3$$
$$3PCl_3 + SO_3 \longrightarrow POCl_3 + SO_2$$
5. It gives many substitution reactions as
$$PCl_3 + 3AgCN \longrightarrow P(CN)_3 + 3AgCl$$
$$PCl_3 \xrightarrow{PF_3} PCl_2F + PClF_3$$
6. It forms adduct with BBr_3 as

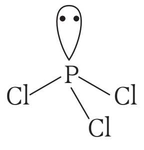


$$PCl_3 + BBr_3 \longrightarrow Br{-}\underset{\displaystyle Br}{\overset{\displaystyle Br}{B}} \leftarrow \underset{\displaystyle Cl}{\overset{\displaystyle Cl}{P}}{-}Cl$$

7. It acts as reducing agent and reduces SO_2Cl_2 and SO_3 to SO_2 and itself gets oxidised to PCl_5 or $POCl_3$. It also reduces $SOCl_2$ and SO_2Cl_2 as :
$$PCl_3 + SO_2Cl_2 \longrightarrow PCl_5 + SO_2$$
$$3PCl_3 + SOCl_2 \longrightarrow POCl_3 + PSCl_3 + PCl_5$$
8. It reacts with finely divided metals when hot as
$$12Ag + 4PCl_3 \longrightarrow 12AgCl + P_4$$
9. It reacts with concentrated H_2SO_4 forming chloro-sulphonic acid as
$$4H_2SO_4 + 2PCl_3 \longrightarrow \underset{\text{chloro-sulphonic acid}}{2HSO_3Cl} + P_2O_5 + 2SO_2 + 4HCl + H_2O$$
10. It reacts with organic compounds containing hydroxyl group.
$$\underset{\text{ethyl alcohol}}{3C_2H_5OH} + PCl_3 \longrightarrow \underset{\text{ethyl chloride}}{3C_2H_5Cl} + H_3PO_3$$
$$\underset{\text{acetic acid}}{3CH_3COOH} + PCl_3 \longrightarrow \underset{\text{acetyl chloride}}{3CH_3COCl} + H_3PO_3$$

Structure of PCl_3

Its structure is similar to ammonia, *i.e.*, it has pyramidal geometry.



Phosphorus Pentachloride

Its formula is PCl_5.

Method of Preparation

It is prepared either by passing dry Cl_2 gas (in excess) over PCl_3 or by the action of SO_2Cl_2 on P_4 or PCl_3..
$$PCl_3 + Cl_2 \longrightarrow PCl_5$$
$$P_4 + 10SO_2Cl_2 \longrightarrow 4PCl_5 + 10SO_2$$

Physical and Chemical Properties

Important properties of PCl_5 *are as follows*

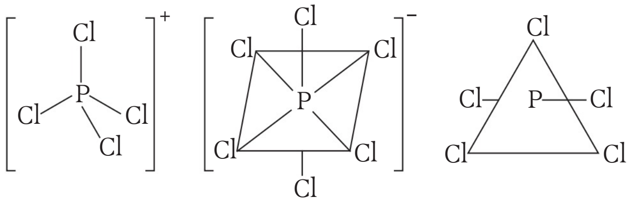
1. It is yellowish white crystalline compound with a sharp odour, m.p. −45°C (under pressure) and sublimation temperature 160°C.
2. It have the ability to dissociate as
$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$
3. It is violently hydrolysed by water as
$$PCl_5 + H_2O \xrightarrow{\text{Insufficient water}} POCl_3 + 2HCl$$
$$PCl_5 + 4H_2O \xrightarrow{\text{Excess of water}} H_3PO_4 + 5HCl$$
4. It reacts with compounds containing —OH group as
$$CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$$
$$H_2SO_4 + PCl_5 \longrightarrow \underset{\text{sulphuryl chloride}}{SO_2Cl_2} + 2POCl_3 + HCl$$
5. It reacts with P_4O_{10} as
$$6PCl_5 + P_4O_{10} \longrightarrow 10POCl_3$$
6. It reacts with ammonium chloride as
$$nPCl_5 + nNH_4Cl \xrightarrow{150°C} (NPCl_2)_n + 4nHCl$$
7. It reacts with Cl^- acceptors as
$$PCl_5 + BCl_3 \longrightarrow [PCl_4]^+[BCl_4]^-$$
8. With hydrogen it forms PCl_3 as
$$PCl_5 + H_2 \longrightarrow PCl_3 + 2HCl$$
9. It reacts with KF as
$$PCl_5 + 6KF \longrightarrow KPF_6 + 5KCl$$

Uses

It is used as chlorinating agent in organic chemistry.

Structure of PCl_5

X-ray studies have revealed that solid PCl_5 consists of ionic lattices, *i.e.*, tetrahedral $[PCl_4]^+$ cations and octahedral $[PCl_6]^-$ anions. In vapour state, it has trigonal bipyramidal shape in which P has gone sp^3d hybridisation.



(a) $[PCl_4]^+$ (b) $[PCl_6]^-$ (c) PCl_5 in vapour state

Fig.7.5 Structure of PCl_5 in solid and vapour phase

Sample **Problem 9** *Hydrolytic reaction of* PCl_5 *in heavy water produces.* **[NCERT]**

(a) D_3PO_4 (b) $POCl_3$

(c) *Both* (a) *and* (b) (d) *None of these*

Interpret (a) Here reactions are same as those with water (H_2O). PCl_5 shows following hydrolytic reactions with heavy water (D_2O).

Step I $PCl_5 + D_2O \longrightarrow POCl_3 + 2DCl$

Step II $POCl_3 + 3D_2O \longrightarrow D_3PO_4 + 3DCl$

Overall reaction $PCl_5 + 4D_2O \longrightarrow \underset{\text{deuterio phosphoric acid}}{D_3PO_4} + \underset{\text{deuterium chloride}}{5DCl}$

Oxides of Phosphorus

Phosphorus trioxide exists as a dimer and is formulated as P_4O_6.

Methods of Preparation

When white P is burn in the limited supply of air both P_4O_6 and P_4O_{10} are formed. The vapour of the mixture of oxides are passed through a condensor in which water at 50−60°C is circulated, P_4O_{10} being solid at 60°C separates out easily.

P_4O_{10} is obtained by burning P in a free supply of air or oxygen. The pentoxide formed is purified further by sublimation at 360°C.

Properties and Uses of Oxides of Phosphorus

Among the various pentoxides, P_2O_5 has the strongest affinity for water. It can extract water from several inorganic and organic compounds, thus acts as a strong **dehydrating agent.** It dehydrates H_2SO_4 to SO_3, HNO_3 to N_2O_5, **cellulose** to **carbon** and **amides** to **nitriles.**

Based upon the tetrahedral structure of phosphorus molecule, the tetrahedral structure of P_4O_6 is

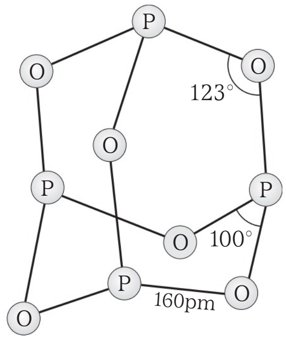


Fig. 7.6 Structure of P_4O_6

This structure has been confirmed by X-ray diffraction data.The oxides As_4O_6, Sb_4O_6 also have tetrahedral structures.

The structure assigned to P_4O_{10} molecule is

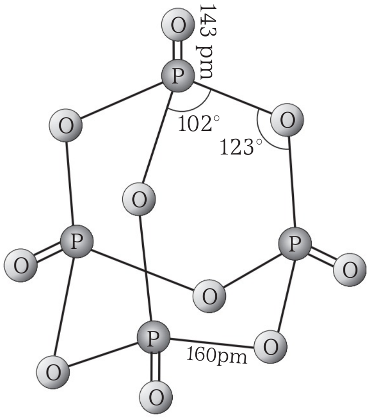


Fig. 7.7 Structure of P_4O_{10}

Hot Spot 1

OXYACIDS of Phosphorus

It is an important topic for JEE Main examination. Questions based upon this topic are generally based upon their basicity and preparation method.

The oxyacids of phosphorus can be grouped into following three series

1. Phosphorous acid series which contains following acids :

- (i) Hypophosphorous acid, H_3PO_2
- (ii) Phosphorous acid, or *ortho*phosphorous acid, H_3PO_3
- (iii) Pyrophosphorous acid, $H_4P_2O_2$
- (iv) *Meta*phosphorous acid, HPO_2

2. Phosphoric acid series, which contains

- (i) Hypophosphoric acid, $H_4P_2O_6$

3. Polyphosphoric acid series with general formula $H_{n-2}\ P_nO_{3n+1}$

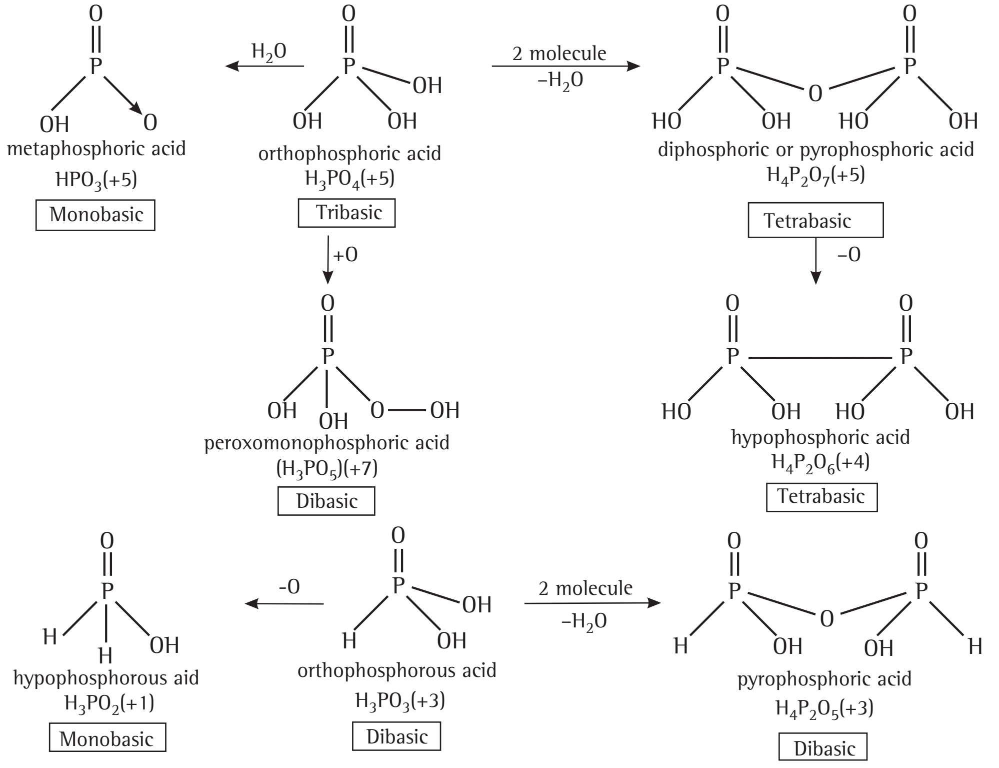
- (i) Diphosphoric acid or pyrophosphoric acid, $H_4P_2O_7$
- (ii) Triphosphoric acid, $H_5P_3O_{10}$
- (iii) Tetraphosphoric acid, $H_6P_4O_{13}$
- (iv) Metaphosphoric acid, HPO_3
- (v) Orthophosphoric acid, H_3PO_4

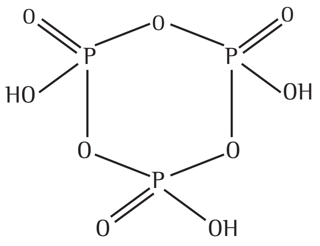
4. Peroxyphosphoric acid series, which contains

- (i) Peroxymonophosphoric acid, H_3PO_5
- (ii) Peroxydiphosphoric acid, $H_4P_2O_8$

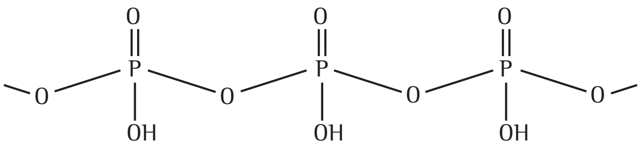
Structure

The structures of some main oxyacids of phosphorus can be summarised as





cyclometaphosphoric acid $(HPO_3)_3$



polymeta phosphoric acid (HPO_3)

The strength and solubility of the oxyacids follow the order,

$$HNO_3 > H_3PO_4 > H_3AsO_4 > H_3SbO_4$$

Some important facts related to oxyacids of phosphorus are

(i) H_3PO_3 is a strong reducing agent but weaker as compared to H_3PO_2.

(ii) $4H_3PO_3 \xrightarrow[-PH_3]{475\text{ K}} 3H_3PO_4 \xrightarrow{520\text{ K}} H_4P_2O_7 \xrightarrow{>520\text{ K}} HPO_3$

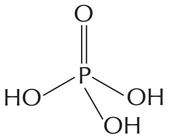
(iii) Aqueous solutions of both pyrophosphoric acid, $H_4P_2O_7$ as well as metaphosphoric acid (HPO_3) on heating give orthophosphoric acid.

Sample Problem 10 *What is the basicity of* H_3PO_4? **[NCERT]**

(a) 1 (b) 2
(c) 3 (d) 4

Interpret (c) Basicity is the number of replaceable H atoms. Only those hydrogen atoms of H_3PO_4 are replaceable which are present as OH, so draw the structure of H_3PO_4 to find the number of P—OH bonds.

The structure of H_3PO_4 is as



From the structure it is clear that it has 3 P—OH bonds which can produce three H^+ ions per molecule of H_3PO_4 in aqueous solution. Hence, basicity is three.

$$\underset{\text{Orthophosphoric acid}}{H_3PO_4} \overset{H_2O}{\rightleftharpoons} 3H^+ + PO_4^{3-}$$

Sample Problem 11 *On reaction with* Cl_2, *phosphorus forms two types of halides 'A' and 'B'. Halide 'A' is yellowish white powder but halide 'B' is colourless oily liquid. Which of the following is/are their hydrolysis products?* **[NCERT Exemplar]**

(I) H_3PO_2 (II) H_3PO_3
(III) H_3PO_4 (IV) H_3PO_4
(a) I *and* II (b) II *and* III (c) III *and* IV (d) I *and* IV

Interpret (a) *'A'* is PCl_5 and *'B'* is PCl_3.

$$P_4 + 10Cl_2 \longrightarrow 4PCl_5$$
$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$

When *'A'* and *'B'* are hydrolysed

(a) $\underset{\substack{[A]\\ \text{phosphorus}\\ \text{pentachloride}}}{PCl_5} + 4H_2O \longrightarrow \underset{\substack{\text{phosphoric}\\ \text{acid}}}{H_3PO_4} + 5HCl$

(b) $\underset{\substack{[B]\\ \text{phosphorus}\\ \text{trichloride}}}{PCl_5} + 3H_2O \longrightarrow \underset{\substack{\text{phosphrous}\\ \text{acid}}}{H_3PO_3} + 3HCl$

Check Point 1

1. Why does nitrogen not form NCl_5?
2. Why is yellow phosphorus kept under water?
3. Why are vortex rings formed if PH_3 comes in contact with air?
4. While showing oxidising properties, HNO_3 itself gets reduced to different products. Explain.
5. How is orthophosphoric acid related to pyrophosphoric acid?

VIA(16) Group Elements and Their Compounds

7.4 Group 16 Elements

This group contains 5 elements *i.e.*, **oxygen, sulphur, selenium, tellurium** and **polonium** and called **oxygen family**. The first four members are non-metals and collectively known as **chalcogens** (meaning ore forming) as metal ores normally occur in the form of oxides, sulphides etc.

Occurrence

There are three naturally occurring isotopes of oxygen *i.e.*, ${}_8O^{16}$ (99.762%), ${}_8O^{17}$ (0.038%) and ${}_8O^{18}$ (0.200%). Oxygen is most abundant element on earth and constitutes 50% by weight of earth crust. Water contains 88.8% oxygen by weight. Dioxygen (O_2) makes up about 23.2% by weight of atmosphere.

Sulphur occurs in the earth crust to the extent of 0.05% mostly as metal sulphides and sulphates. It also occur (in elemental form) in large underground beds. Se and Te are less abundant than S (0.05 ppm-Se, 0.002 ppm-Te), polonium is radioactive. It occurs in nature in radium minerals such as pitch blend to the extent of 5×10^{-9} %. It is known since, 1898.

General and Physical Properties

Elements of group 16 *shows following trends in their general and physical properties.*

(a) Electronic Configuration

General electronic configuration for the elements of this group is ns^2np^4. (where, $n = 2, 3, 4, 5, \ldots$)

(b) Atomic Volume and Atomic Radii

Both atomic volume and atomic radii increase on moving down the group.

(c) Physical State

Oxygen is a gas while, all other elements exists in solid state.

(d) Ionisation Energy

On moving down the group, the ionisation energy decreases. These elements, however, have lower ionisation energy than the corresponding elements of group 15.

(e) Electronegativity

These elements are more electronegative as compared to the corresponding elements of group 15, and there is seen a steep drop in electronegativity as the atomic size increases. Oxygen is the second most electronegative element of the periodic table and hence, its all compounds (except with fluorine) are called oxides.

(f) Electron Affinity

Electron affinity of these elements also decreases as the atomic size increases. However, electron affinity of O is lesser as compared to S. This is because of the small size and high charge density of O atom.

(g) Nature of Bonding

Oxygen can form ionic as well as covalent compounds but other elements because of their low electronegativity form mainly covalent compounds. Compounds of oxygen with highly electropositive metals like Li, Mg etc., are ionic while with less electropositive metals and non-metals are covalent.

(h) Oxidation State

Oxygen, being highly electronegative, exhibit +2, −2 and −1 oxidation states while other elements show +2, +4 and +6 oxidation states. On moving down the group, the stability of +4 oxidation state increases while that of +6 state decreases due to inert pair effect.

(i) Metallic Character

The first four elements are non-metals but non-metallic character is stronger in oxygen and sulphur. Po is distinctly a metal but it is radioactive and only short lived.

(j) Melting and Boiling Points

On moving down the group, the magnitude of van der Waals' interatomic forces increases and thus, the melting and boiling point increase regularly.

The above physical properties can be summarised in the following table

Table 7.6 **Physical Properties of 16 Group Elements**

Property	Oxygen	Sulphur	Selenium	Tellurium	Polonium
Atomic number	8	16	34	52	84
Atomic mass (amu)	15.999	32.064	78.96	127.60	210
Density in solid state (g cm^{-3})	1.14	2.07	4.79	6.23	9.2
Atomic radius (Å)	0.73	1.09	1.16	1.35	—
Ionic radius (Å) of divalent ion	1.40	1.84	1.98	2.21	—
Atomic volume (cc)	14.0	15.5	16.5	20.5	22.7
Ionisation energy (kJ mol^{-1})	1313.7	999.4	940.9	869.5	813.5
Oxidation states	−2, −1, +2	−2, +2, +4, +6	−2, +2, +4, +6	−2, +2, +4, +6	+2, +4
Electronegativity	3.5	2.5	2.4	2.1	2.0
Melting point (°C)	−218.8	114.0	217.0	449.5	254.0
Boiling point (°C)	−183.0	444.6	685.0	989.8	962
Heat of fusion (kJ mol^{-1})	0.22	1.42	5.3	17.7	11.0
Heat of atomisation (kJ mol^{-1})	250	280	207	197	145

(k) Molecular State

Oxygen exists as O_2 (diatomic gaseous molecule). S and Se occur as S_8 and Se_8 with Puckered ring structure as seen below

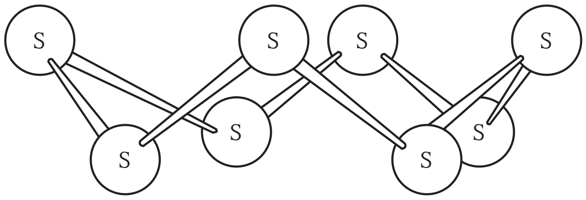


Fig. 7.8 Puckered ring structure of S_8 molecule

The reason for such a difference is the tendency of O–atom to form multiple bonds ($p\pi$ - $p\pi$ bonds) which is missing in the case of sulphur and selenium.

(l) Catenation

Oxygen has some while sulphur has a high tendency to catenate. *e.g.,* H—O—O—H (H_2O_2)., H—S—S—S—S—H (H_2S_4)

(m) Allotropy

Oxygen exist in two allotropic forms-O_2 and O_3. Sulphur exists as–**rhombic** or α**-form, monoclinic** or β**-form, plastic** or γ**-form, colloidal** or δ**-form,** λ**-sulphur** and μ**-sulphur.** Selenium exists in two forms- **red form** and **grey form.** Tellurium exists in two forms- one of which is metallic and other is non-metallic. Polonium exists in two forms namely α and β**-forms** both of which are metallic.

Chemical Properties

Elements of the group form compound with several elements.

The properties of these compounds are described below

(a) Oxides

Among the compounds of group 16 elements the most important ones are oxides. The oxides of metals are basic, that of non-metals are acidic and that of semi-metals are amphoteric in nature. The acidic character of oxides increases across a period from left to right and basic character of oxides increases down a group. The oxides are mainly **monoxides** (AO type)**, dioxides** (AO_2) type and trioxides (AO_3 type). However, sulphur forms heptoxide also with formula S_2O_7. Out of these the oxides of sulphur are most important commercially. The oxides, formed by S, Se, Te and Po are tabulated below.

Table 7.7 **Different Oxides of 16 Group Elements**

S.N.	Type of oxide	S	Se	Te	Po
1.	Monoxide	SO	—	TeO	PoO
2.	Dioxide	SO_2	SeO_2	TeO_2	PoO_2
3.	Trioxide	SO_3	SeO_3	TeO_3	PoO_3
4.	Heptoxide	S_2O_7	—	—	—

Some important facts related to oxides are

(i) All elements except Se forms **monoxides** but all the monoxide are not so stable. Out of these, SO is formed by passing electric discharge through SO_2 while TeO and PoO are formed by heating corresponding trioxides.

(ii) Dioxides are formed by all the members (except oxygen of course). These dioxides differ from each other considerably *e.g.,* SO_2 and SeO_2 are acidic oxides with good solubility in water while TeO_2 and PoO_2 are amphoteric in nature and have poor solubility in water.

(iii) SO_2 has angular structure. SeO_2 in gaseous phase has angular structure but in solid state (white volatile solid) it has polymeric structure comprising of infinite chains as

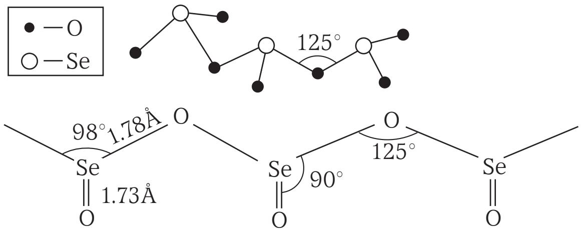


Fig. 7.9 Polymeric structure of SeO_2 in solid state

Dioxides of Te and Po are also non-volatile crystalline ionic solids, out of which TeO_2 has a layer structure consisting of TeO_4 units.

Dioxides show differences in their reaction with water as

(i) SO_2 dissolves in water giving H_2SO_3 (known in solution only).

(ii) SeO_2 gives selenious acid with water which can be isolated in crystalline state.

(iii) TeO_2 is almost insoluble in water. It however dissolves in alkalies (to form tellurites) and in acids (to form basic salts) showing its amphoteric nature.

(iv) PoO_2 shows similar behaviour.

Among trioxides, SO_3 is the most important. They all are acidic in nature, *i.e.,* form acids with water and this nature decreases on moving down the group. SO_3, in gaseous phase exists as planar triangular geometry while in solid state, has linear cyclic trimer or a polymeric chain structure. SeO_3 on the other hand, exists as a cyclic tetramer (Se_4O_{12}) in the solid state as shown below

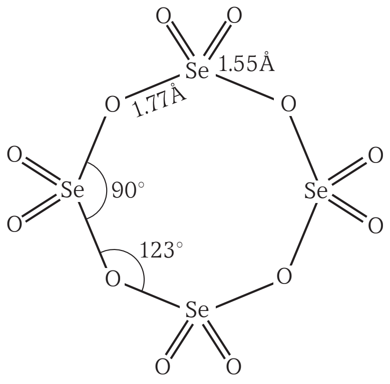


Fig. 7.10 The cycle structure of tetrameric Se_4O_{12}

TeO_2 exists in polymeric form.

(b) **Hydrides**

Group 16 elements form binary hydrides of general formula M_2A (where, A = O, S, Se, Te or Po). The thermal stability of these hydrides decreases from oxygen to polonium. Unlike H_2O, other hydrides are unpleasant foul smelling poisonous gases. The unique behaviour of H_2O is due to extensive intermolecular H–bonding. Hydrides of H_2R_2 type are also known.

Hydrides of S, Se and Te are prepared by the action of metals on metal sulphides, selenides and tellurides respectively. H_2S, H_2Se and H_2Te are weak diprotic acids in aqueous solutions. The acidity increases in the series as $H_2S < H_2Se < H_2Te$. H_2O is neutral in nature. Increase in acidic strength of hydrides can be easily explained on the basis of increase in the size of central atom from oxygen to Te. As the result of such an increase, the length of R–H bond also increases gradually which is always inversely proportional to bond strength. Thus, bond strength decreases.

The other properties of these hydrides are summarised as

Table 7.8 **Properties of Hydrides of Group 16 Elements**

Property	H_2O	H_2S	H_2Se	H_2Te
Melting point (°C)	0	– 85.5	– 65.7	–51.1
Boiling point (°C)	100.0	– 60.75	– 41.5	–1.8
Bond angle H—X—H	104.5°	92.5°	90°	89°
Bond length H—X (Å)	0.95	1.30	1.45	1.72
Dissociation constant as an acid at 25°C	1.0×10^{-14}	1.0×10^{-7}	1.7×10^{-4}	2.3×10^{-3}

As the size of central atom increases, the M—H (M = O to Po) bond becomes weaker and longer. Consequently, the thermal stability decreases. Since, reducing power varies inversely with bond strength, it increases as the bond strength decreases or bond length increases.

First two members of the family also form hydrides of the formula H_2R_2 (*i.e.*, H_2O_2 and H_2S_2). However, these two hydrides differ considerably from each other *e.g.*, H_2O_2 is fairly stable but H_2S_2 is unstable. It decomposes readily to give S and H_2S as

$$H_2S_2 \xrightarrow{OH^-} H_2S + S$$

Similarly, H_2O_2 on account of hydrogen bonding is highly associated while, H_2S_2 forms discrete molecules.

(c) **Halides**

Oxygen forms halides only with fluorine (OF_2 or F_2O-oxygen difluoride) and its compounds with rest of the halogens are called oxides (not halides) as its electronegativity is more than any other halogen. S and other chalcogens form a number of halides.

All the halides of these elements can be tabulated as

Table 7.9 **Halides of Oxygen Family**

	F	Cl	Br	I
O	OF_2, F_2O_2	Cl_2O_6, Cl_2O_7, Cl_2O, ClO_2 etc	Br_2O, BrO_2, BrO_3	I_2O, I_2O_4, I_2O_5
S	S_2F_2, SF_4, SF_6, S_2F_{10}	S_2Cl_2, SCl_2, SCl_4	S_2Br_2	
Se	SeF_2, SeF_4 SeF_6	Se_2Cl_2, $SeCl_4$	Se_2Br_2, $SeBr_4$	
Te	TeF_4, Te_2F_{10}, TeF_6	$TeCl_2$, $TeCl_4$	$TeBr_2$, $TeBr_4$	TeI_4
Po	—	$PoCl_2$, $PoCl_4$	$PoBr_2$, $PoBr_4$	PoI_4

Some important facts related to halides of 16 *group elements are as follows*

(i) The stability of halides decreases in the order F > Cl > Br > I. The highest oxidation state is realised only in fluorides.

(ii) The general preparative routes for chalcogen halides involve the direct reaction of chalcogen with respective halogen *i.e.*,

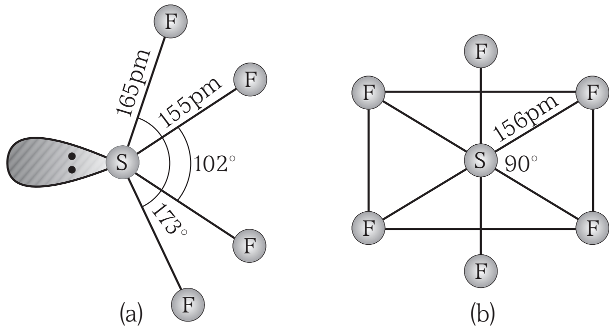
$$\frac{1}{8}S_8(s) + 3F_2(g) \longrightarrow SF_6(g)$$

$$Te\,(s) + 2Cl_2(g) \longrightarrow TeCl_4(s)$$

(iii) Direct fluorination of elemental sulphur yields mainly SF_6 alongwith traces of $SF_4 \cdot SF_4$ is prepared by the fluorination of SCl_2 with NaF in acetonitrile at 350 K as

$$3SCl_2 + 4NaF \xrightarrow{\text{MeCOCN, 350 K}} S_2Cl_2 + SF_4 + 4NaCl$$

(iv) SF_6 is an inert non-toxic gas at room temperature. It is inert due to sterically protected atom. In contrast, less sterically hindered SeF_6 and SF_4 undergo hydrolysis readily.



(a) (b)

Fig. 7.11 The structure of (a) SF_4 (b) SF_6

Compared to sulphur halides, the halides of Se and especially Te adopt oligomeric or polymeric structures in +4 oxidation state, $SeCl_4$, $SeBr_4$, $TeCl_4$, $TeBr_4$ and TeI_4 exist as tetramer while, TeF_4 has polymeric structure.

(v) All hexafluorides have a high degree of covalency and low boiling points.

(vi) The tetrahalides act as Lewis bases (electron donor) and Lewis acids (electron acceptors).

(d) Oxyacids

Among the group, only oxy acids of S, Se and Te are known. S forms many oxy acids while Se and Te forms two oxy acids each.

Some of these oxyacids are given in the following table

Table 7.10 **Oxyacids of S, Se and Te**

S	Se	Te
H_2SO_3 (sulphurous acids)	H_2SeO_3 (selenous acid)	H_2TeO_3 (tellurous acid)
H_2SO_4 (sulphuric acid or oil of vitriol)	H_2SeO_4 (selenic acid)	H_6TeO_6 (telluric acid)
H_2SO_5 (peroxomono sulphuric acid or Caro's acid)		
$H_2S_2O_8$ (peroxodisulphuric acid or Marshall's acid)		

Anomalous Behaviour of Oxygen

Owing to its small size, high charge density and non-availability to *d*-orbitals, oxygen differs from rest of the members in following respects.

1. Oxygen is a diatomic gas while all other members are solid with eight membered puckered ring structure.
2. Most of the compounds of oxygen are ionic and polar covalent due to its high electronegativity.
3. Maximum covalency that can be exhibited by oxygen in its compounds is two while rest of the members can show a maximum covalency of six.
4. Oxygen forms $p\pi$-$p\pi$ multiple bond while, S form $d\pi$-$p\pi$ bonds.
5. Only the hydride of oxygen, *ie*, H_2O is non-poisonous and is a liquid while, the hydrides of other members are poisonous gases.
6. Oxygen is paramagnetic while, rest are not.

Sample Problem 12 *The correct order of thermal stability of the hydrides of group 16 elements is* **[NCERT]**

(a) $H_2Po > H_2Te > H_2Se > H_2S > H_2O$

(b) $H_2O < H_2S > H_2Se > H_2Te > H_2Po$

(c) $H_2O = H_2S = H_2Se = H_2Te = H_2Po$

(d) $H_2O > H_2S > H_2Se > H_2Te > H_2Po$

Interpret (c) Thermal stability ∝ bond dissociation energy,

$$\Delta_{diss}H(H-E)/\text{kJ mol}^{-1} \propto \frac{1}{\text{Size of central atom}}$$

(where, $E = 16$ group elements)

On moving down the group, bond dissociation energy decreases because bond length increases.

Thus, the order of bond dissociation energy is

$$H_2O > H_2S > H_2Se > H_2Te > H_2Po$$

This is also the order of thermal stability.

7.5 Ozone (O_3)

It is formed in the upper layer of atmosphere by the action of UV rays from sun on oxygen. It prevents the UV rays from entering the earth's atmosphere. CFCs, common refrigerants deplete the ozone layer.

Method of Preparation

It is prepared in ozoniser by subjecting dry and cold dioxygen to the action of silent electric discharge.

$$3O_2(g) \xrightleftharpoons{\text{Silent electric discharge}} 2O_3(g)$$

Physical Properties

It is a pale blue gas with a characteristic pungent odour. It condenses to a deep blue liquid (b.p. 161.2 K) and to a violet black solid (m.p. 80.6 K). It is diamagnetic in nature and acts as a powerful oxidising agent due to liberation of O_2. The colour of O_3 is due to intense absorption of red light.

Chemical Properties

Chemical properties of O_3 involves :

1. O_3 is thermodynamically unstable and decomposes to O_2.
$$2O_3 \longrightarrow 3O_2; \quad \Delta G = -163 \text{ kJ mol}^{-1}$$
2. O_3 is an extremely powerful oxidising agent.
$$O_3 + 2H^+ + 2e^- \rightleftharpoons O_2 + H_2O$$
$$O_3 + H_2O + 2e^- \rightleftharpoons O_2 + 2OH^-$$

It oxidises

(i) $3PbS + 4O_3 \longrightarrow 3PbSO_4$

(ii) $6NO_2 + O_3 \longrightarrow 3N_2O_5$

(iii) $S + H_2O + O_3 \longrightarrow H_2SO_4$

(iv) $2KOH + 5O_3 \longrightarrow 2KO_3 + 5O_2 + H_2O$

(Potassium ozonide KO_3 is an orange coloured solid and contains the paramagentic O_3^- ion)

(v) $O_3 + 2KI + H_2O \longrightarrow I_2 + 2KOH + O_2$

The amount of O_3 in a gas mixture can be determined by passing the gas into a KI solution (at a constant pH 9.2 using borate buffer). The iodine that is liberated is titrated with sodium thiosulphate solution.

$$O_3 + 2I^- + H_2O \longrightarrow I_2 + 2OH^- + O_2$$

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

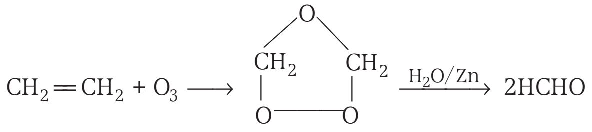
(vi) $3SnCl_2 + 6HCl + O_3 \longrightarrow 3SnCl_4 + 3H_2O$

(vii) $2[Fe(CN)_6]^{4-} + H_2O + O_3 \longrightarrow 2[Fe(CN)_6]^{3-} + O_2 + 2OH^-$

3. O_3 can also be decomposed catalytically and change in volume measured:

$$\underset{\text{(2 volume)}}{2O_3} \longrightarrow \underset{\text{(3 volume)}}{3O_2}$$

4. O_3 also adds to unsaturated organic compounds at room temperature forming ozonides which can be cleaved as aldehydes and ketones in solution.



Uses

Some important uses of ozone are

(i) O_3 is used as a disinfectant.

(ii) It is used to purify drinking water, since it can destroy bacteria and viruses.

(iii) It is better than Cl_2 since, it (O_3) avoids the unpleasant smell and taste of Cl_2 and any excess O_3 soon decomposes to O_2.

(iv) It also absorbs UV light. This is particularly important since, there is a layer of O_3 in the upper atmosphere which absorbs harmful UV radiation from the sun, thus protecting people on the earth. The use of chlorofluorocarbons (CFC) in aerosols and refrigerators, and their subsequent escape into the atmosphere, is blamed for making **holes in the ozone layer** over the Antarctic and Arctic. It is feared that this will allow an excessive amount of UV light to reach the earth which will cause melanoma (skin cancer) in humans. Oxides of nitrogen (from car exhausts) and the halogens can also damage the O_3 layer. Ozone destroying reactions

1. Based on oxides of nitrogen.

$$NO + O_3 \longrightarrow NO_2 + O_2$$
$$O_3 + h\nu \longrightarrow O_2 + O$$
$$NO_2 + O \longrightarrow NO + O_2$$

Net reaction

$$2O_3 + h\nu \longrightarrow 3O_2$$

2. Based on reactive chlorine species from CFC.

$$Cl + O_3 \longrightarrow ClO + O_2$$
$$O_3 + h\nu \longrightarrow O + O_2$$
$$ClO + O \longrightarrow Cl + O_2$$

Net reaction

$$2O_3 + h\nu \longrightarrow 3O_2$$

Structure

Structure of O_3 is best described as a resonance hybrid of following canonical forms

Both the O—O bond here are of equal length, *i.e.,* 128 pm.

Sample Problem 13 *Ozone with* KI *solution produces*

(*a*) IO_3 (*b*) I_2 (*c*) Cl_2 (*d*) HI

Interpret (*b*)

$$\begin{array}{rcl} O_3 & \longrightarrow & O_2 + [O] \\ 2KI + H_2O + [O] & \longrightarrow & 2KOH + I_2 \\ \hline 2KI + H_2O + O_3 & \longrightarrow & 2KOH + I_2 + O_2 \end{array}$$

7.6 Sulphur

It is found in free as well as in combined state. Elemental S mixed with gangue is called **native sulphur**. In combined state, S occurs as sulphides and sulphates in the form of galena (PbS), iron pyrites (FeS_2), gypsum ($CaSO_4 \cdot 2H_2O$) barytes ($BaSO_4$) etc.

Allotropes of sulphur

Sulphur exists in several allotropic forms, The properties of these forms are as follows

1. **Rhombic, octahedral or α-sulphur** is the most common form of sulphur and is stable at temperatures below 95.6°C. Its specific gravity is 2.06. It melts at 114°C. It is soluble in carbon disulphide. Its crystal structure contains cyclic S_8 rings packed in a manner which leads to the formation of rhombic crystals.

2. **Monoclinic, prismatic** or **β-sulphur** is stable above 95.6°C. It is prepared by melting rhombic sulphur in a dish and allowing it to cool until a crust is formed at the surface. On removing the crust, small needle-like crystals of monoclinic sulphur become visible. Its specific gravity is 1.96. It melts at 120°C. It is soluble in carbon disulphide. Like α-sulphur, its crystal structure also contains cyclic S_8 rings but the mode of packing is different than that in α-sulphur. The packing in this case is such that it leads to the formation of monoclinic crystals.

3. γ-**sulphur** is best obtained by decomposing ethylene xanthate of copper (I) in pyridine or by chilling hot solution of sulphur in carbon disulphide. Its crystal structure also consists of cyclic S_8 rings which are packed in lattice in a more compact manner than in the crystals of α or β-sulphur. Its specific gravity is 2.18. γ-sulphur slowly changes into α and β-forms of sulphur.
4. **Colloidal** or δ-**sulphur** is obtained, when hydrogen sulphide is passed through an oxidising solution such as nitric acid, potassium permanganate, etc.

$$2HNO_3 + H_2S \longrightarrow \underset{\substack{\text{colloidal}\\\text{sulphur}}}{S} + 2NO_2 + 2H_2O$$

Colloidal sulphur is also obtained by passing hydrogen sulphide through water containing dissolved sulphur dioxide.

$$2H_2S + SO_2 \longrightarrow 2H_2O + 3S$$

5. **Plastic** or χ-**sulphur** is obtained, when molten sulphur heated to about 350°C is poured into cold water. It is a soft rubber-like mass. It hardens on standing and changes gradually into rhombic sulphur. It is soluble in carbon disulphide and has no sharp melting point. This form is a mixture of allotropes of sulphur containing cyclic S_8 rings and long helical chains of a large number of S atoms. Plastic sulphur can be converted into fibres when it is heated in an atmosphere of nitrogen at 300°C for a few minutes and then quenched in water. Their structure contains open polymeric helical chains of S atoms.

It is also considered as **supercooled liquid,** *i.e.*, the liquid which due to rapid cooling below its freezing point had no time to settle into a crystalline form.

6. Sulphur allotropes containing cyclic S_6, S_7, S_{10}, S_{12}, S_{18} and S_{20} rings are also found. **Cyclohexasulphur** (Engel's sulphur) containing cyclic S_6 rings and can be prepared by the following reaction :

$$S_2Cl_2 + H_2S_4 \longrightarrow S_6 + 2HCl$$

The structure of cyclohexa sulphur consists of closely packed cyclic S_6 rings in chair form. As a result of this close packing the specific gravity (2.2 at −110°C) of this form is higher than specific gravities of all the other forms. This form of sulphur is highly reactive. The cyclosulphurs are quite unstable with the exception of S_{18} and S_{20}.

Properties and Uses

Sulphur is a yellow solid which is tasteless and odourless. It is freely soluble in CS_2, sparingly soluble in alcohol and ether and totally insoluble in water. Its vapours are poisonous for bacteria and fungi but not for other animals or human beings.

Sulphuric Acid (Oil of Vitriol)

In ancient days, it was called **oil of vitriol,** since it was prepared by distilling green vitriol (ferrous sulphate) $FeSO_4 \cdot 7H_2O$.

$$\underset{\text{green vitriol}}{2[FeSO_4 \cdot 7H_2O]} \xrightarrow{\text{Distillation}} Fe_2O_3 + SO_2 + 13H_2O + \underset{\substack{\text{oil of}\\\text{vitriol}}}{H_2SO_4}$$

Methods of Preparation

Sulphur is burnt in air so that it is oxidised to SO_2. SO_2 thus, obtained is oxidised to SO_3 which, when dissolved in H_2O, gives H_2SO_4. The whole process can be summarised as :

$$S \xrightarrow{+O_2} SO_2 \xrightarrow{+\frac{1}{2}O_2} SO_3 \xrightarrow{+H_2O} H_2SO_4$$

Industrial Preparation of H_2SO_4

Sulphuric acid is manufactured these days by the following two processes

1. **Lead chamber process** in which H_2SO_4 is obtained, when a mixture containing SO_2, air and NO is treated with steam (H_2O). In this reaction NO acts as a catalyst.

$$2SO_2 + \underset{\text{(from air)}}{O_2} + 2H_2O + \underset{\text{catalyst}}{[NO]} \rightarrow 2H_2SO_4 + \underset{\text{catalyst}}{[NO]}$$

The steps involved during this process are

Step I **Preparation of SO_2** By heating sulphur or iron pyrites (FeS_2) in the excess of air.

$$S + O_2 \longrightarrow SO_2$$
$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

Step II **Oxidation of SO_2 to SO_3 by HNO_3 or by NO_2**

$$2HNO_3 + 2SO_2 \longrightarrow H_2 + NO + NO_2 + 2SO_3$$
$$SO_2 + NO_2 \longrightarrow SO_3 + NO$$

Step III **Preparation of H_2SO_4** By allowing SO_3 obtained in step (II) to react with steam (H_2O).

$$SO_3 + H_2O\text{ (steam)} \longrightarrow H_2SO_4$$

2. **Contact process** *Involves the following steps*

Step I **Preparation of SO_2** By burning sulphur or iron pyrites (FeS_2) in the excess of air.

$$S + O_2 \longrightarrow SO_2$$
$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

Step II **Oxidation of SO_2 to SO_3** by the atmospheric O_2 in presence of a catalyst which may be **Pt-asbestos,** V_2O_5 or a mixture of ferric and cupric oxide.

$$2SO_2 + O_2 \overset{V_2O_5}{\rightleftharpoons} 2SO_3;\quad \Delta H = -196.6\text{ kJ}$$

The gases (*i.e.,* SO_2 and O_2) must be purified before allowing them to combine to form SO_3. If they are not purified, the impurities will poison the catalyst used in the reaction. These days V_2O_5 is used as catalyst, as it is cheaper and not poisoned by impurities. The oxidation of SO_2 to SO_3 by atmospheric O_2 as shown at step (II) is a reversible and exothermic process. According to Le Chatelier's principle, the favourable conditions for the maximum yield of SO_3 are

(i) **Low temperature,** since the forward reaction is exothermic, but a minimum temperature of 450°C, called optimum temperature, is needed to get the maximum yield of SO_3. Even at this temperature, the rate of reaction is slow and to accelerate the rate of reaction, a suitable catalyst is required.

(ii) **High pressure,** since the volume of the gaseous product (*i.e.*, SO_3) is less than that of the gaseous reactants (*i.e.*, SO_2 and O_2), But a very high pressure is likely to cause the corrosion of the vessel in which oxidation is carried out. The optimum pressure of 2–3 atmospheres is sufficient for oxidation.

(iii) **Excess of atmospheric** O_2 Maximum yield of SO_3 is obtained when SO_2 and atmospheric O_2 are taken in 2 : 3 ratio.

Step III **Dissolution of SO_3 in 98% H_2SO_4,** to get **oleum,** $H_2S_2O_7$ (fuming sulphuric acid).

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$

(**Fuming sulphuric acid** is that acid which contains dissolved SO_3 in it).

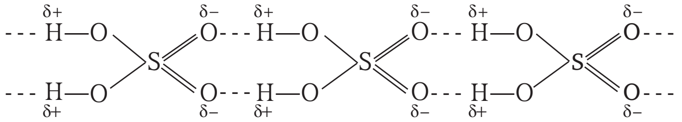
It may be noted that SO_3 cannot be dissolved in water because it produces a dense fog which does not easily condense.

Step IV **Dilution of oleum by water** to get the H_2SO_4 of any desired concentration.

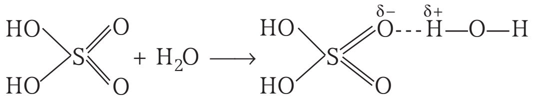
$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

Physical Properties

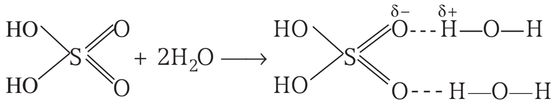
(i) Pure H_2SO_4 is a colourless viscous, heavy and syrupy oily liquid of density 1.84 (at 15°C) which does not fume. It forms a constant boiling mixture with water. This mixture contains 98% H_2SO_4 and its boiling point is 340°C. 95% acid boils at 295°C. High boiling point and high viscosity of H_2SO_4 is due to the fact that H_2SO_4 molecules are associated together by H-bonding as shown below :



(ii) It is highly soluble in water. When water is added to the acid, a large amount of heat is produced and the temperature rises as high as 120°C. The heat produced is so large that the acid spurts out of the container. Therefore, if the acid is to be diluted, the acid should be added to water slowly with constant stirring and not water to the acid. The production of heat is due to the formation of hydrates like $H_2SO_4 \cdot H_2O$ (m.p. = 8.5°C) and $H_2SO_4 \cdot 2H_2O$ (m.p. = 38°C).



monohydrate, $H_2SO_4 \cdot H_2O$



dihydrate, $H_2SO_4 \cdot 2H_2O$

(iii) It is a good conductor of heat and electricity.

Chemical Properties

H_2SO_4 *exhibits the following chemical reactions*

1. (i) **H_2SO_4, when heated undergoes dissociation into steam** (H_2O) **and SO_3**

$$H_2SO_4 \overset{\Delta}{\rightleftharpoons} H_2O \text{ (steam)} + SO_3$$

The dissociation is almost complete at 444°C.

(ii) When the acid vapours are passed through a strongly heated Pt or quartz tube, it gets decomposed into SO_2, steam (H_2O) and O_2.

$$2H_2SO_4 \longrightarrow 2SO_2 + H_2O \text{ (steam)} + O_2$$

2. **The aqueous solution of the acid behaves as a strong dibasic acid,** since it ionises in two stages and gives two H^+ ions.

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \text{ (bisulphate ion)}$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \text{ (sulphate ion)}$$

Thus, H_2SO_4 forms two types of salts which are called bisulphates (*e.g.,* $NaHSO_4$) and sulphates (*e.g.,* Na_2SO_4). The acidic nature of H_2SO_4 is confirmed by the following reactions or properties shown by H_2SO_4 :

(i) H_2SO_4 is sour in taste and turns blue litmus red.

(ii) It neutralises alkalies and forms bisulphates (HSO_4^-) and sulphates (SO_4^{2-}).

$$NaOH + H_2SO_4 \longrightarrow NaHSO_4 + H_2O$$
$$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$$

(iii) It decomposes carbonates and bicarbonates into CO_2.

$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2$$
$$2NaHCO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O + 2CO_2$$

(iv) Dilute H_2SO_4 usually reacts with all metals (except Pb) such as Al, Sn, Mn, Zn, Fe, Mg etc., evolve H_2 gas.

$$M(M = \text{Zn, Fe, Mg etc.}) + H_2SO_4 \longrightarrow MSO_4 + H_2\uparrow$$

[Less reactive metals like Cu, Ag, Hg, Pb etc, are not attacked by dil H_2SO_4. However, these metals react with hot conc H_2SO_4 (oxidising properties)].

3. H_2SO_4 is a strong acid and hence, decomposes the salts of more volatile acids (*e.g.,* chlorides, nitrates, sulphides, sulphites, carbonates etc.). The more volatile acid is liberated in each case. Some examples are as follows :

$$2NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2HCl$$
$$2KNO_3 + H_2SO_4 \longrightarrow K_2SO_4 + 2HNO_3$$
$$FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S$$
$$Ca_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 3CaSO_4 + 2H_3PO_4$$
$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$
$$2NaNO_2 + H_2SO_4 \longrightarrow Na_2SO_4 + \underset{\substack{\downarrow \\ NO + NO_2 + H_2O}}{2HNO_2}$$

4. Hot concentrated H_2SO_4 (not dilute) acts as a **powerful oxidising agent,** since it can lose nascent oxygen quite readily. When H_2SO_4 oxidises any substance, it is reduced to SO_2.

$$\underset{\substack{\text{(hot and} \\ \text{concentrated)}}}{H_2SO_4} \longrightarrow H_2O + SO_2 + [O]$$

Occasionally, H_2SO_4 is also reduced to sulphur, sulphide or H_2S.

$$SO_4^{2-} + 8H^+ + 6e^- \longrightarrow S + 4H_2O$$
$$SO_4^{2-} + 8H^+ + 8e^- \longrightarrow S^{2-} + 4H_2O$$
$$SO_4^{2-} + 10H^+ + 8e^- \longrightarrow H_2S + 4H_2O$$

(i) H_2SO_4 oxidises non-metals like carbon and sulphur to their corresponding oxides *viz,* CO_2 and SO_2.

$$2H_2SO_4 + C \longrightarrow 2H_2O + 2SO_2 + CO_2$$
$$2H_2SO_4 + S \longrightarrow 2H_2O + 3SO_2$$

It oxidises phosphorus to H_3PO_4, since P_2O_5 formed reacts with water to form H_3PO_4.

$$2P + 5H_2SO_4 \longrightarrow 2H_3PO_4 + 5SO_2$$

(ii) Metals like Cu, Ag, Hg, Pb etc., react with hot conc. H_2SO_4 and are oxidised to their oxides which get convert into sulphate. Here, H_2SO_4 is reduced to SO_2 *e.g.,*

$$\begin{array}{rcl} H_2SO_4 & \longrightarrow & H_2O + SO_2 + O \\ Cu + O & \longrightarrow & CuO \\ CuO + H_2SO_4 & \longrightarrow & CuSO_4 + H_2O \\ \hline Cu + 2H_2SO_4 & \longrightarrow & CuSO_4 + SO_2 + 2H_2O \end{array}$$

Some other examples are given below

$$2Ag + 2H_2SO_4 \longrightarrow Ag_2SO_4 + 2H_2O + SO_2$$
$$Hg + 2H_2SO_4 \longrightarrow HgSO_4 + SO_2 + 2H_2O$$
$$Pb + 2H_2SO_4 \longrightarrow PbSO_4 + 2H_2O + SO_2$$

Dil. H_2SO_4 reacts with commercial Zn, evolving H_2. Hot and conc H_2SO_4 attacks Zn, giving off SO_2.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + SO_2 + H_2O$$

Moderately conc acid (20%) when heated with Zn metal gives H_2S and precipitates a little sulphur.

$$4Zn + 5H_2SO_4 \longrightarrow 4ZnSO_4 + H_2S + 4H_2O$$
$$3Zn + 4H_2SO_4 \longrightarrow 3ZnSO_4 + S + 4H_2O$$

(iii) H_2SO_4 cannot oxidise HF (or CaF_2) and HCl (or NaCl, KCl etc.) but it can oxidise HBr (or NaBr, KBr) and HI (or NaI, KI) to Br_2 and I_2 respectively. When H_2SO_4 oxidises HBr (or NaBr or KBr), it is reduced to SO_2 but when it oxidises HI (or NaI or KI), it is reduced to SO_2, S or H_2S depending on the amount of HI used in the reaction.

$$H_2SO_4 + 2HBr \longrightarrow SO_2 + 2H_2O + Br_2$$
$$\text{Similarly, } H_2SO_4 + 2HI \longrightarrow SO_2 + 2H_2O + I_2$$
$$H_2SO_4 + 6HI \longrightarrow S + 4H_2O + 3I_2$$
$$H_2SO_4 + 8HI \longrightarrow H_2S + 4H_2O + 4I_2$$

(iv) In presence of Hg (catalyst) naphthalene ($C_{10}H_8$) is oxidised to phthalic acid ($C_8H_6O_4$).

$$9H_2SO_4 + C_{10}H_8 \longrightarrow 10H_2O + 9SO_2 + C_8H_6O_4 + 2CO_2$$

(v) H_2SO_4 oxidises H_2S to S

$$H_2SO_4 + H_2S \longrightarrow 2H_2O + SO_2 + S$$

(vi) H_2SO_4 oxidises H_2 (H = 0) to H_2O(H = +1).

$$H_2SO_4 + H_2 \longrightarrow 2H_2O + SO_2$$

5. **Conc. sulphuric acid is a strong dehydrating agent** It dissolves in water and forms sulphuric acid hydrates, $H_2SO_4 \cdot nH_2O$. Due to this property, conc. H_2SO_4 shows dehydrating properties. Thus, it absorbs water from many organic compounds and dehydrates them. Absorption of water is highly exothermic.

(i) Cane sugar, glucose and starch are dehydrated to carbon.

$$\underset{\text{cane sugar}}{C_{12}H_{22}O_{11}} + H_2SO_4 \longrightarrow \underset{\text{sugar charcoal}}{12C} + \underset{\text{hydrate}}{[H_2SO_4\cdot 11H_2O]}$$

$$\underset{\text{starch}}{(C_6H_{10}O_5)_n} + H_2SO_4 \longrightarrow 6C + [H_2SO_4\cdot 5nH_2O]$$

(ii) Oxalic acid, $(COOH)_2$ is dehydrated to CO and CO_2 and formic acid (HCOOH) gets dehydrated to CO only.

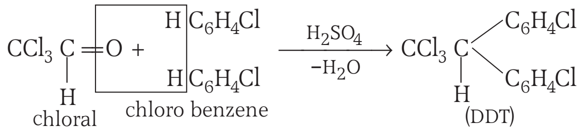
$$(COOH)_2 + H_2SO_4 \longrightarrow CO + CO_2 + [H_2SO_4\cdot H_2O]$$

$$HCOOH + H_2SO_4 \longrightarrow CO + [H_2SO_4\cdot H_2O]$$

(iii) Ethyl alcohol (C_2H_5OH) is dehydrated to diethyl ether.

$$2C_2H_5OH + H_2SO_4 \longrightarrow C_2H_5OC_2H_5 + [H_2SO_4\cdot H_2O]$$

(iv) Dehydration of a mixture of chlorobenzene (C_6H_5Cl) and trichloroacetaldehyde (CCl_3CHO), also called chloral, gives DDT.



It is due to the dehydrating property of conc H_2SO_4 that cloth, wood, starch paper etc [which are largely cellulose $(C_6H_{10}O_5)_x$ materials] get charred in this acid, *i.e.,* conc H_2SO_4 removes water from these substances and thus, chars them. The dehydrating property of conc H_2SO_4 is used :

(i) in drying the gases which do not react with the acid (*e.g.,* Cl_2, SO_2, HCl etc.)

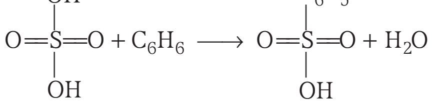
(ii) in many reactions like esterification etc.

(iii) in the manufacture of dyes and explosives.

H_2SO_4 has very corrosive action on skin because it acts as dehydrating agent and absorption of water is accompanied by the release of heat.

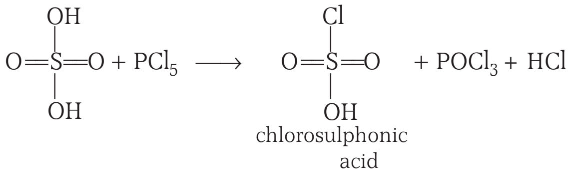
6. The molecule of H_2SO_4 contains two OH groups. One or both these groups can be replaced by other groups or atoms by treating H_2SO_4 with the appropriate compound. *e.g.,* :

(i) When conc H_2SO_4 is heated with C_6H_6, one OH group of H_2SO_4 is replaced by phenyl group (C_6H_5) and benzene sulphonic acid, $C_6H_5(OH)SO_2$ (also called benzene sulphuric acid) is obtained.

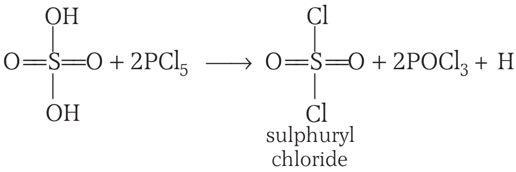


$$O{=}S(OH)_2{=}O + C_6H_6 \longrightarrow O{=}S(C_6H_5)(OH){=}O + H_2O$$

(ii) One or both the —OH groups of H_2SO_4 can be replaced by Cl-atom when H_2SO_4 is treated with PCl_5.



$$O{=}S(OH)_2{=}O + PCl_5 \longrightarrow \underset{\text{chlorosulphonic acid}}{O{=}S(Cl)(OH){=}O} + POCl_3 + HCl$$



$$O{=}S(OH)_2{=}O + 2PCl_5 \longrightarrow \underset{\text{sulphuryl chloride}}{O{=}S(Cl)_2{=}O} + 2POCl_3 + HCl$$

(iii) One Cl-atom can also be replaced by the action of $POCl_3$ on it. Thus, the action of $POCl_3$ on H_2SO_4 produces chlorosulphonic acid.

$$2O_2S(OH)_2 + POCl_3 \longrightarrow 2Cl\cdot SO_2\cdot OH + HCl + HPO_3$$

7. **On heating** $KClO_3$ with conc. H_2SO_4, ClO_2 is evolved with explosion.

$$3KClO_3 + 3H_2SO_4 \xrightarrow{\Delta} 3KHSO_4 + HClO_4 + 2ClO_2 + H_2O$$

8. H_2SO_4 when treated with P_2O_5, loses water which combines with **P_2O_5 and forms HPO_3**.

$$H_2SO_4 \xrightarrow{-H_2O} H_2O + SO_3$$

$$H_2O + P_2O_5 \longrightarrow 2HPO_3$$

$$\overline{H_2SO_4 + P_2O_5 \longrightarrow SO_3 + 2HPO_3}$$

Uses

Sulphuric acid is used

1. as a laboratory reagent.
2. for preparation of important acids such as HCl, HNO_3, H_3PO_4.
3. for making of fertilizers.
4. for sulphonation of organic compounds.
5. for making of lead storage batteries.
6. in the purification of petrolium.

Sample **Problem 14** *Hot conc.* H_2SO_4 *acts as moderately strong oxidising agent. It oxidises both metals and non-metals. Which of the following element is oxidised by conc.* H_2SO_4 *into two gaseous products?* [NCERT]

(*a*) Cu

(*b*) S

(*c*) C

(*d*) Zn

Interpret (*c*) $2H_2SO_4 + Cu \longrightarrow CuSO_4 + SO_2\uparrow + 2H_2O$

$$2H_2SO_4 + S \longrightarrow 2H_2O + SO_2\uparrow$$

$$2H_2SO_4 + C \longrightarrow 2H_2O + 2SO_2\uparrow + CO_2\uparrow$$

$$4H_2SO_4 + Zn \longrightarrow ZnSO_4 + SO_2\uparrow + H_2O$$

Hot Spot 2

OXYACIDS OF Sulphur

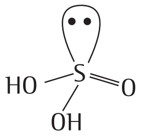
It is an important topic for JEE Main examination. Question of this topic are generally based upon their structures or oxidation state and their level vary from easy to moderate.

Sulphur shows following oxyacids

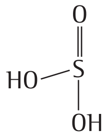
1. Sulphurous acid, H_2SO_3
2. Sulphuric acid or oil of vitroil, H_2SO_4
3. Peroxomono sulphuric acid or Caro's acid, H_25O_5
4. Peroxodisulphuric acid or Marshall's acid, $H_2S_2O_8$
5. Thiosulphuric acid, $H_2S_2O_3$
6. Dithionic acid, $H_2S_2O_5$
7. Pyrosulphuric acid or oleum or disulphuric acid, $H_2S_2O_7$

Among the above written acids, H_2SO_3 (sulphurous acid) and oil of vitriol, *i.e.*, H_2SO_4 are of commercial importance.

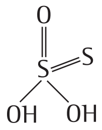
The structure of some of oxyacids of sulphur with their oxidation states are given below



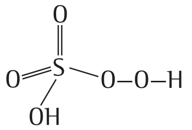
$H_2SO_3(+4)$
(strong reducing agent)



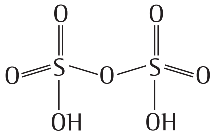
$H_2SO_4(+6)$
(strong dehydrating agent)



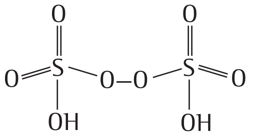
$H_2S_2O_3(+2)$
(reducing agent)



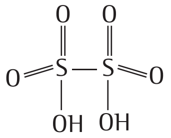
$H_2SO_5(+6)$
(strong oxidising agent)



$H_2S_2O_7(+6)$
(strong oxidising agent)



$H_2S_2O_8(+6)$
(strong oxidising agent)

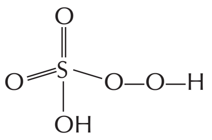


$H_2S_2O_6(+5)$
(oxidising agent)

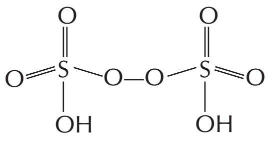
Sample **Problem 15** *Which of the following are peroxoacids of sulphur?* [**NCERT**]

(a) H_2SO_5 *and* $H_2S_2O_8$ (b) H_2SO_5 *and* $H_2S_2O_7$
(c) $H_2S_2O_7$ *and* $H_2S_2O_8$ (d) $H_2S_2O_6$ *and* $H_2S_2O_5$

Interpret (a) In peroxoacids, —O—O— linkage is present H_2SO_5 and $H_2S_2O_8$ are peroxoacids of sulphur.



H_2SO_5
peroxomonosulphuric acid or Caro's acid



$H_2S_2O_8$
peroxodisulphuric acid or Marshall's acid

Check Point 2

1. Why does oxygen exist as O_2 but sulphur as S_8 molecule?
2. H_2S is a gas while H_2O is liquid at room temperature. Explain.
3. Explain, why does addition of HNO_3 to concentrated H_2SO_4 result in the formation of NO_2^+ and NO_3^- ions? How could one test experimentally that such ions exist in H_2SO_4 solution?
4. SO_2 can act as an oxidising agent as well as reducing agent while, SO_3 can act as an oxidising agent. Account for it.
5. SO_2 is a more powerful reducing agent in alkaline medium than in acidic medium. Explain.

Group 17 Elements and Their Compounds

7.7 Group 17 Elements

This group consists of five elements namely **fluorine** (F), **chlorine** (Cl), **bromine** (Br), **iodine** (I) and **astatine** (At). These elements are also called **halogen** (means sea salts), *i.e.,* their salts are abundantly present in sea water.

Occurrence

They do not occur free in nature but in combined state these occur abundantly. Astatine is radioactive and occur very sparsely. These are mainly found as metal halides although iodine also occurs as iodate (IO_3^-). Chlorine is most abundant among halogen and its commercial source is NaCl (common salt). Sources of halogens and their abundance are seen as

Table 7.11 **Sources of Halogens**

Halogen	Abundance		Main sources
	Crystal rocks	Oceans	
Fluorine	5.44×10^{-2}	7.0×10^{-6}	Fluorspar (CaF_2), Fluorapatite [$Ca_5(PO_4)_3F$], Cryolite (Na_3AlF_6) etc.
Chlorine	1.26×10^{-2}	1.9	Sea water, salt wells, salt beds (NaCl, KCl, $MgCl_2$, $CaCl_2$) etc.
Bromine	0.25×10^{-3}	6.5×10^{-3}	Sea water, salt lakes (NaBr, KBr, $MgBr_2$) etc.
Iodine	4.6×10^{-5}	5.0×10^{-6}	Brine wells, sea weeds (I^-), chile salt petre ($NaIO_3$ present as impurity) etc.

General and Physical Properties

Trends of general and physical properties exhibited by these elements are as follows

(a) Electronic Configuration

The general electronic configuration of halogens is ns^2p^5 (where, $n = 2, 3, 4, \ldots$). Due to the presence of 7 electrons in their valence shell, these elements have a high tendency to gain one electron and achieve nearest noble gas configuration.

(b) Atomic and Ionic Radii

Halogens have small atomic radii than the elements of group 16th due to increased effective nuclear charge. On moving down the group, it increases as the number of shells increases by one.

(c) Physical State

On moving down the group, the tendency to form condensed molecules increases. Thus, fluorine and chlorine are gases at ordinary temperature, bromine is a highly fuming liquid while iodine is a volatile solid.

(d) Melting and Boiling Points

On moving down from F to At, there is an increase in melting and boiling points. This is because van der Waals' forces increase as the size increases.

(e) Ionisation Energy

They all have high ionisation energy, *i.e.,* have a little tendency to lose electrons. On moving down the group this tendency and thus, the ionisation energy decreases. Iodine because of the lowest IE, has some tendency to form I^+ ion as it forms compounds like ICl, ICN, etc, which in molten state conduct electricity showing the existence of I^+ cation.

(f) Electronegativity

Halogens have the high values of electronegativities and on moving downward from F to I, electronegativity decreases. Thus, fluorine has the maximum value of electronegativity. As a result of the decrease of electronegativity, the non-metallic character increases from F to I. Hence, somewhat metallic character is observed in iodine, *e.g.,* it forms in a few cases a positive ion and has a metallic lustre.

(g) Electron Gain Enthalpy

These elements have maximum electron gain enthalpies in their respective periods because they have only one electron less than ns^2np^6 configuration. On moving down the group the magnitude of electron gain enthalpy (*i.e.,* electron affinity) usually decreases. But electron affinity of fluorine is unexpectedly lower than Cl. This is because of the smaller size of F. As a result of which the incoming electron does not feel much attraction but feels somewhat repulsion. Chlorine has the highest electron affinity in the periodic table.

(h) Molecular State

Halogens exist as diatomic covalent molecules. In between their atoms weak van der Waals' forces exist. On account of which, the halogens are volatile in nature. With the increase in size, these forces increase and hence, change in physical state occurs from gas (F_2 and Cl_2) to solid (I_2).

(i) Oxidation State

When a halogen atom combines with an element of lesser electronegativity, it shows −1 oxidation state. On the other hand, when it combines with an element having higher electronegativity, it exhibits +1 oxidation state. However, F being most electronegative always shows −1 oxidation state. Other elements show +3, +5 and +7 oxidation states also due to the presence of vacant *d*-orbitals in their valence shell.

(j) Solubility

Halogens, being non-polar molecules, do not dissolve to a considerable extent in a polar solvent like water. However, fluorine reacts with water readily and forms mixture of oxygen and ozone as

$$2F_2 + 2H_2O \longrightarrow 4HF + O_2$$
$$3F_2 + 3H_2O \longrightarrow 6HF + O_3$$

Cl_2, Br_2 and I_2 are more soluble in non-polar solvents like $CHCl_3$, paraffins etc and give yellow, brown and violet colour respectively in chloroform or carbon tetrachloride. In non-polar solvents, halogens exist as free molecules while in nucleophilic solvents like alcohols, liquid SO_2 etc halogens produce brown solution due to the formation of complex. I_2 is more soluble in KI solution due to the formation of KI_3 (I_3^- ion), which also increases its solubility in water.

(k) Oxidising Power

Standard reduction potentials of halogens are positive and decrease down the group. Thus, halogens act as strong oxidising agents and their oxidising power decreases from fluorine to iodine. The strength of an oxidising agent depends on several energy terms as

$$E = \frac{1}{2} H_f + \frac{1}{2} H_{\text{ev}} + \frac{1}{2} H_d - EA - H_{\text{hyd.}}$$

where, H_f = enthalpy of fusion
H_{ev} = enthalpy of evaporation
H_d = enthalpy of dissociation
H_{hyd} = enthalpy of hydration
EA = electron affinity

The value of E decreases from fluorine to iodine. Hence, fluorine is the strongest oxidising agent.

(l) Nature of Bonds

Halogens due to the presence of seven electrons in their valence shell, are highly reactive and form ionic compounds with highly electropositive metals readily. However, with weakly electropositive metals and non-metals, they form covalent bonds. F being most electropositive, form ionic compounds with less electropositive metals.

(m) Bond Dissociation Energy

With the increase of size, the bond length increases from fluorine to iodine. Since, the bond length of fluorine is minimum, its bond dissociation energy should be highest. However, the bond dissociaition energy of fluorine is less than Cl—Cl and Br—Br. It is due to the high interelectronic repulsions between non-bonding electrons in the 2*p*-orbitals of fluorine. Consequently, F—F bond becomes weaker in comparison to Cl—Cl and Br—Br bonds.

(n) Colour

All the halogens are coloured and as the atomic number increases, the colour get deepens.

F	Cl	Br	I
light yellow	yellow green	reddish brown	deep violet

The colour is because of the absorption of energy from visible light by the halogen molecules for excitation of outer electrons to higher energy levels. Fluorine absorbs violet portion of the light and thus, appears yellow while iodine absorbs yellow and green portions of the light and thus, appears violet. Thus, it is clear that on moving down the group the colour changes. This is called **blue shift** or **bathchromic shift.**

The physical properties described above can be summarised as

Table 7.12 **Physical Properties of Halogens**

Property	Fluorine	Chlorine	Bromine	Iodine
Atomic number	9	17	35	53
Atomic mass (u)	18.998	35.453	79.909	126.904
Physical state	Gas	Gas	Liquid	Solid
M.P. (°C)	–218.6	–101.0	–7.2	113.9
B.P. (°C)	–188.1	–34.6	59.5	185.2
Density in liquid state ($g\,cm^{-3}$)	1.108	1.1557	2.948	3.76 (in solid state)
Colour of vapour	Pale yellow	Greenish yellow	Orange red	Violet
Colour of liquid	Clear yellow	Amber yellow	Reddish brown	Shining dark solid
Atomic radius (Å)	0.72	0.99	1.14	1.33
Ionic radius of X^- ion (Å)	1.33	1.84	1.96	2.20
Atomic volume (cc)	17.1	18.7	23.5	25.7
Electronegativity	4.0	3.0	2.8	2.5
Electron affinity ($kJ\,mol^{-1}$)	332.6	348.6	324.5	295.5

Property	Fluorine	Chlorine	Bromine	Iodine
Ionisation energy (kJ mol^{-1})	1680.8	1255.5	1142.8	1008.3
Oxidation states	–1	–1, +1, +3, +4, +5, +6, +7	–1, +1, +3, +4, +5, +6	–1, +1, +3, +4, +5, +6, +7
Bond energy (kJ mol^{-1})	158.8	242.6	192.8	151.1
Standard electrode potential (volt)	+2.8	+1.36	+1.08	+0.54

Chemical Properties

Halogens are most reactive non-metals and their reactivity decreases on moving down the group. The important factors that are responsible for the low reactivity of fluorine are (i) the small size and (ii) the highest electronegativity of fluorine.

(a) Reaction with Water

Fluorine decomposes water very readily even at low temperaure and in dark forming mixture of O_2 and O_3, Cl_2 decomposes water in the presence of sunlight while bromine decomposes water very slowly in presence of sunlight. Iodine, however, does not decompose water.

(b) Reaction with Hydrogen

All the halogens react with hydrogen to form volatile covalent hydrides, of formula H*X*. Since, H-atom has less electronegativity than each of the halogens, the oxidation state of H in these compounds is +1 and that of halogen is −1. It is the positive oxidation state of H and negative oxidation state of halogens due to which these compounds are called hydrogen halides (H^+X^-). Since, these compounds ionise in aqueous solution to produce H^+ (or H_3O^+) these are also called **'halogen acids'.**

$$HX + H_2O \longrightarrow H_3O^+ + X^-$$

These compounds are also known by other names like **hydroacids** or **hydrohalic acid** etc. The reactivity of halogens towards hydrogen decreases from fluorine to iodine. These are colourless, irritating gases at room temperature.

As we move down the group, boiling point increases with increase in size of halogen. However, boiling point of HF is abnormally high due to H-bonding.

Acidic character and reducing character of these hydrides increase on moving from F to I.

(c) Reaction with Metals and Non-metals

Halogens combine with metals and non-metals to form halides such as $MgBr_2$, XeF_6, PCl_3, PCl_5, SF_6 etc. The ionic character of *M*—*X* bond decreases as the size of halogen atom increases.

$$M\text{—F} > M\text{—Cl} > M\text{—Br} > M\text{—I}$$

(d) Reaction with Oxygen

Halogens form binary compounds with oxygen but most of them are unstable. Fluorine forms only two binary compounds, *i.e.*, OF_2 and O_2F_2 (called **oxygen fluorides).** Chlorine, bromine and iodine form oxides in which the oxidation state of halogen varies from +1 to +7. *e.g.*,

Anomalous Behaviour of Fluorine

Fluorine also, because of its small size, high charge density, non-availability of *d*-orbitals and low bond dissociation energy differs from the rest of the halogens in following characteristics

1. Fluorine shows only −1oxidation state due to its maximum electronegativity, whereas the other halogens can show negative as well as positive oxidation state, *i.e.*, between −1 and +7.
2. Maximum covalency of fluorine is one as there is no *d*-orbital in its valence shell. Other members can have maximum covalency of 7 because of vacant *d*-orbitals.
3. Fluorine because of its low bond dissociation energy is very reactive. However, in Cl_2 and Br_2, *X*—*X* bond is stronger.
4. HF has a high tendency to form H-bond, thus, it is a liquid (b.p. 19°C) while HCl, HBr and HI due to lack of such a tendency, are gases under ordinary conditions.
5. Hydrofluoric acid being a dibasic acid (H_2F_2), forms two series of salt such as $NaHF_2$, Na_2F_2 while HCl, HBr and HI are monobasic in nature.
6. Mostly fluorides are ionic and contain F^- ion while other halides have frequently molecular lattices.
7. Fluorine when combines with sulphur, forms SF_6 while no other halogen forms the hexahalide with sulphur.
8. Fluorine does not form any oxo acid but other halogens form a number of oxyacids.
9. Fluorides are more stable than corresponding chlorine compounds.
10. Fluorine does not form polyhalides like F_3^- but other halogens do so, *e.g.*, I_3^-, Br_3^- etc.

7.8 Compounds of Elements of Group 17

Being highly reactive, halogens form several compounds but we will study some important of them which are also included in the syllabus.

Halogen Acids

Methods of Preparation

Halogen acids are prepared by the following methods

1. **By the direct combination of H_2 and** X_2 (X = Cl, Br, I) **under different conditions,**
   (i) HCl is produced by burning Cl_2 in the excess of H_2 or by the action of H_2 on Cl_2 in presence of sunlight.

$$Cl_2 + H_2(\text{excess}) \xrightarrow{\text{Burn}} 2HCl$$

$$Cl_2 + H_2 \xrightarrow{\text{Sunlight}} 2HCl + \text{heat}$$

   (ii) HBr can be prepared by passing a mixture of H_2 and Br_2 over a platinum spiral heated to redness by an electric current.

$$H_2 + Br_2 \xrightarrow[\text{Pt spiral}]{\text{Heat}} 2HBr$$

   (iii) HI can be prepared in small quantities by passing H_2 and I_2 vapours over red hot fine platinum.

$$H_2 + I_2 \underset{\text{Pt}}{\overset{\text{Heat (450°C)}}{\rightleftharpoons}} 2HI$$

2. **By heating an appropriate halide with conc. H_2SO_4 or conc. H_3PO_4.**
   (i) HF and HCl can be prepared by heating CaF_2 and NaCl respectively with conc H_2SO_4.

$$CaF_2 + H_2SO_4 \xrightarrow{\Delta} CaSO_4 + 2HF$$

$$2NaCl + H_2SO_4 \xrightarrow{\Delta} Na_2SO_4 + 2HCl$$

   (ii) When NaBr (or KBr) and NaI (or KI) are heated with conc. H_2SO_4, HBr and HI are produced respectively.

$$2MBr(M = \text{Na, K}) + H_2SO_4 \xrightarrow{\Delta} M_2SO_4 + 2HBr$$

$$2MI(M = \text{Na, K}) + H_2SO_4 \xrightarrow{\Delta} M_2SO_4 + 2HI$$

The HBr and HI so formed react with conc. H_2SO_4 and are oxidised to Br_2 and I_2 respectively. These acids are consumed and hence, are not obtained. In other words, we can say that HBr and HI cannot be prepared by the action of their halides on conc. H_2SO_4.

$$2HBr + H_2SO_4 \longrightarrow SO_2 + 2H_2O + Br_2$$
$$2HI + H_2SO_4 \longrightarrow SO_2 + 2H_2O + I_2$$
$$6HI + H_2SO_4 \longrightarrow S + 4H_2O + 3I_2$$
$$8HI + H_2SO_4 \longrightarrow H_2S + 4H_2O + 4I_2$$

Now as HBr and HI are not able to reduce conc H_3PO_4, these acids are obtained by heating NaBr and NaI respectively with conc H_3PO_4.

$$3NaBr + H_3PO_4 \xrightarrow{\Delta} Na_3PO_4 + 3HBr$$

$$3NaI + H_3PO_4 \xrightarrow{\Delta} Na_3PO_4 + 3HI$$

3. **By the action of water on a mixture of red phosphorus and Br_2 or I_2** (for HBr and HI) *e.g.,* HBr and HI can be prepared in the laboratory by slowly pouring water from a dropping funnel, fitted to a flask containing a mixture of red phosphorus (1 part) and Br_2 or I_2 (20 parts).

$$8H_2O + 2P + 5Br_2 \longrightarrow 10HBr + 2H_3PO_4$$
$$8H_2O + 2P + 5I_2 \longrightarrow 10HI + 2H_3PO_4$$

Methods of Preparation of only HCl

1. HCl can be prepared in the laboratory by heating NaCl with conc. H_2SO_4.

$$2NaCl + H_2SO_4 \xrightarrow{\Delta} Na_2SO_4 + 2HCl$$

The gas HCl obtained as above cannot be dried over P_2O_5 or quick lime (CaO), since HCl reacts with both of these substances.

$$2P_2O_5 + 3HCl \longrightarrow POCl_3 + 3HPO_3$$
$$CaO + 2HCl \longrightarrow CaCl_2 + H_2O$$

2. Pure HCl is obtained by the action of water on $SiCl_4$. (hydrolysis $SiCl_4$).

$$SiCl_4 + 2H_2O \longrightarrow SiO_2 + 4HCl$$

3. Considerable quantities of HCl are obtained as a by-product in the manufacture of Na_2CO_3 from NaCl by **Le-Blanc process.**

Physical Properties of Halogen Acids

1. Hydrofluoric acid exists as a dimeric molecule, (H_2F_2) even in the gaseous state because of intermolecular H-bonding. Due to its dimeric nature, H_2F_2 gives two types of salts which contain HF_2^- and F_2^{2-} ions.

$$2HF \rightleftharpoons HF_2^- + H^+$$

$$HF_2^- \rightleftharpoons F_2^{2-} + H^+$$

Salts (*e.g.,* Na_2F_2 or NaF), which contain F_2^{2-} or F^- ions, are called **"normal salts"** while those (*e.g.,* $NaHF_2$) which contain HF_2^- ions are known as *"acid salts". As an acid,* H_2F_2 *is weaker than* H_3PO_4, *but stronger than* HNO_2.

Other HX molecules (X = Cl, Br, I) are monomeric and hence, form only one type of salts, which contain X^- ion.

$$\text{H}X \rightleftharpoons \text{H}^+ + X^-$$
$$(X = \text{Cl, Br, I})$$

2. Anhydrous HF is a liquid at ordinary temperature and fumes strongly in air, while each of the remaining hydrogen halides, is a colourless gas, with pungent smell and acidic taste.
3. As the size of the halogen atom increases from F to I, **H—*X* bond length in H*X* molecules also increases from H—F to H—I** (HF < H—Cl < H—Br < H—I). The increase in H—*X* bond length decreases the strength of H—*X* bond from H—F to H—I (H—F > H—Cl > H—Br > H—I). Due to successive decrease in the strength of H—*X* bond from H—F to H—I, thermal stability of H*X* (HF > HCl > HBr > HI). Maximum thermal stability of HF is also evident from the fact that this acid is not oxidised even by strong oxidising agents.
4. As we move down the group from HF to HI, the magnitude of van der Waals' forces increases and hence, the boiling point of the hydrides should increase as HF < HCl < HBr < HI. But, this order is not correct. Actually boiling point first decreases from HF to HCl and then increases until we reach HI. The anomaly is due to the presence of H-bonding in HF.
5. HF is the least volatile and HCl is the most volatile. The least volatility of HF molecule is due to much stronger H—F bond and association of HF molecules to form dimer, H_2F_2 through H-bonding. The maximum volatility of HCl is due to its monomeric nature and less strength of H—Cl bond in HCl molecule.
6. All the hydrogen halides are highly soluble in water and give a constant boiling mixture, which is called azeotropic mixture. The azeotropic mixture of each acid contains a particular weight-percentage of the acid and boils at a fixed temperature. The dilute solution of the acid cannot be concentrated by boiling it beyond the weight-percentage of the acid. Dilute solution of HCl cannot be concentrated by boiling beyond 20.2%.
7. All the halogen acids are neither combustible nor supporter of combustion *i.e.*, they are incombustible and non-supporter of combustion.
8. H—*X* bond in gaseous H*X* molecules is largely covalent and has very small amount of ionic character. The covalent character of H—*X* bond is also confirmed by the fact that melting and boiling points of hydrogen halides are low and pure liquid halides are poor conductors of electricity. The ionic character of H–*X* bond in gaseous H*X* molecules is in the order :

   H—F > H—Cl > H—Br > H—I. This order shows that HF is the most ionic and HI is the least.

   The above order of the ionic character of H—*X* bond in gaseous H*X* molecules has been explained on the basis of

   (i) electronegativity difference value, $(\chi_X - \chi_H)$.
   (ii) dipole moment values of H*X* molecules.
   (iii) polarisation in between cations and anions (see chemical bonding).

Acidic Nature of Hydrogen Halides

H*X* molecules in the gaseous state are essentially covalent and hence, are not able to ionise to yield proton (H^+) but in aqueous solution, they give hydrated proton, $H^+(aq)$ and hence, act as Bronsted acids.

$$\text{H}X(g) + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{O}^+ + X^-(aq)$$

The acidic strength (*i.e.,* proton releasing power) of halogen acids in aqueous solution is in the order :

$$\text{HF}(aq) < \text{HI}(aq) < \text{HCl}(aq) < \text{HBr}(aq)$$

However, the relative order of the acidic strength of HX molecules, in methanol solvent, has been found as

$$\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$$

Sample Problem 16 *Afinity for hydrogen decreases in the group from fluorine to iodine. Which of the halogen acids should have highest bond dissociation enthalpy?* **[NCERT]**

(*a*) HF (*b*) HCl
(*c*) HBr (*d*) HI

Interpret (*a*) As the size of the halogen atom increases from F to I, H—*X* bond length in H*X* molecules also increases from H—F to HI (HF < HCl < HBr < HI). The increase in H*X* bond length decreases the strength of H*X* bond from HF to HI (HF > HCl > HBr > HI). Due to decrease in the strength of H*X* bonds, H*X* bond dissociation enthalpy decreases from HF to HI.

HX	HF	>	HCl	>	HBr	>	HI
Bond dissociation enthalpy (kJ/mol)	574.0		428.1		362.5		294.6

The important properties of halogen acids are summarised as

Table 7.13 **Properties of Halogen Acids**

S.N.	Property	HF	HCl	HBr	HI
1.	Monomeric or dimeric	Dimeric (H_2F_2)	Monomeric (HCl)	Monomeric (HBr)	Monomeric (HI)
2.	Physical state at 15°C	Liquid	Gas	Gas	Gas
3.	H—X bond length (Å)	0.92	1.27	1.41	1.61
			Increases →		
4.	Strength of H—X bond or thermal stability of HX molecule	Maximum	High	Not so high	Very little
			Decreases →		
5.	H—X bond dissociation energy or heat of dissociation (kJ mol^{-1})	+ 574.0	+ 428.1	+ 362.5	+ 294.6
			Decreases →		
6.	Dissociation temperature (°C)	Does not dissociate	1500	800	180
			Decreases →		
7.	Melting point (°C)	–83	–111	–86	–50.8
8.	Boiling point (°C)	+ 19.4 (Maximum)	– 85 (Minimum)	– 67	–35.0
9.	Hydrogen bonding	Maximum	Little	Very little	Very little
10.	Solubility in water at 0°C (g/L)	85.3	42.0	49.0	57.1
11.	Dipole moment values when HX molecules are assumed to be completely ionic [calculated values (C.m.)]	1.47×10^{-29}	2.03×10^{-29}	2.25×10^{-29}	2.57×10^{-29}
			Increases →		
12.	% of ionic character in the gaseous HX molecules	43.5	16.8	11.6	4.9
			Decreases →		
	(a) as calculated from their moment values	40.14	19.5	15.04	8.87
	(b) as calculated from Hanny-Smith's equation				
13.	Heat evolved (kJ mol^{-1}) in the reaction, $HX(g) + aq \rightarrow HX(aq) \rightarrow H^+(aq) + X^-(aq)$ or $HX(g) + H_2O \rightarrow H_3O^+ + X^-(aq)$ (called heat of ionisation)	–9.0 Weakest acid	– 60.8 Very strong acid	– 64.6 Strongest acid	– 58.4 Strong acid
			Decreases →		
14.	Reducing property	Not a reducing agent	Mild reducing agent	Strong reducing agent	Strongest reducing agent
			Increases →		
15.	Heat of formation (kJ mol^{-1}) $[\frac{1}{2} X_2 (s, l, g) + \frac{1}{2} H_2(g) \rightarrow HX(g)$ ΔH = heat required (+) or released (–)]	–271.1 (g)	– 92.3 (g)	–36.4 (g)	+25.4 (g)
			Increases →		
16.	Heat of dehydration (kJ mol^{-1}) $[HX(aq) + \text{heat} \rightarrow HX(g)]$	+48.0	+18.0	+21.0	+23.0
17.	Heat of neutralisation with NaOH (kJ mol^{-1})	+ 68.2	+57.3	+57.9	+57.6
18.	Apparent degree of dissociation in 0.1 N solution at room temperature	0.08	0.93	0.94	0.95
			Increases →		
19.	Solubility of silver salt (g/100 g)	172	0.00154	0.000084	0.000028
20.	Solubility of calcium salt (g/100 g)	0.0016	42.7	58.8	67.6
			Increases →		

Chemical Properties of Halogens Acids

Following reactions are common to halogen acids

1. Anhydrous hydrofluoric acid does not show acidic property and hence, does not attack metals except potassium. However, its concentrated solution shows acidic character. A concentrated solution of H_2F_2 reacts with metals (*e.g.,* Zn), their hydroxides, carbonates, oxides etc to form metallic fluorides.

$$\mathrm{Zn + H_2F_2 \longrightarrow ZnF_2 + H_2}$$
$$\mathrm{2NaOH + H_2F_2 \longrightarrow Na_2F_2 + 2H_2O}$$
$$\mathrm{B_2O_3 + 3H_2F_2 \longrightarrow 2BF_3 + 3H_2O}$$

The aqueous solution of HCl, HBr and HI show acidic nature and hence, turn blue litmus red. Each of them reacts with metals, their hydroxides, carbonates, oxides etc to form metallic halides as

$$\mathrm{Zn + 2H}X\ (X = \mathrm{Cl, Br, I}) \longrightarrow \mathrm{Zn}X_2 + \mathrm{H_2}$$
$$\mathrm{NaOH + H}X \longrightarrow \mathrm{Na}X + \mathrm{H_2O}$$
$$\mathrm{Na_2CO_3 + 2H}X \longrightarrow \mathrm{2Na}X + \mathrm{CO_2 + H_2O}$$

2. HCl, HBr and HI do not react with SiO_2 and glass. HF *attacks on* SiO_2 *and gives hydro fluosilicic acid* (H_2SiF_6)

$$\mathrm{SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O}$$

The white fumes of SiF_4 form a gelatinous mass of H_2SiO_3 or H_4SiO_4 and hydro-fluorosilicic acid (H_2SiF_6) with a drop of water held in these fumes.

$$\mathrm{3SiF_4 + 3H_2O \longrightarrow H_2SiO_3 + 2H_2SiF_6}$$
$$\text{or } \mathrm{3SiF_4 + 4H_2O \longrightarrow H_2SiO_3 \cdot H_2O} \text{ or } \mathrm{H_4SiO_4 + 2H_2SiF_6}$$

(Now, we know that glass is composed of Na_2SiO_3 and $CaSiO_3$. HF reacts with these silicates and form sodium and calcium fluosilicate (Na_2SiF_6 and $CaSiF_6$) respectively.

$$\mathrm{Na_2SiO_3 + 6HF \longrightarrow Na_2SiF_6 + 3H_2O}$$
$$\mathrm{CaSiO_3 + 6HF \longrightarrow CaSiF_6 + 3H_2O}$$

Since, HF *reacts with glass as shown above, it should not be kept in glass vessels; it should be stored in waxed glass vessels because wax prevents the action of* HF *on glass. The property of* HF *to act on glass has been utilised in the etching of glass and in making scales on the glass instruments.* For etching glass, commercial H_2F_2 (40–60%) is used.

3. HCl decomposes the salts of weaker acids like carbonates, bicarbonates, sulphides, sulphites, thiosulphates and nitrites as

$$\mathrm{2Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2}$$
$$\mathrm{NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2}$$
$$\mathrm{Na_2S + 2HCl \longrightarrow 2NaCl + H_2S}$$
$$\mathrm{Na_2SO_3 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2}$$
$$\mathrm{Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + S + H_2O + SO_2}$$
$$\mathrm{2NaNO_2 + 2HCl \longrightarrow 2NaCl + H_2O + NO + NO_2}$$

With metal oxides and hydroxides, HCl forms salt and water.

4. With $AgNO_3$ solution, HF forms AgF which becomes soluble in water. On the other hand, HCl, HBr and HI give the precipitate of AgCl (white), AgBr (pale yellow) and AgI (yellow) respectively.

$$\mathrm{AgNO_3 + HF \longrightarrow \underset{soluble}{AgF} + HNO_3}$$
$$\mathrm{AgNO_3 + H}X\ (X = \mathrm{Cl, Br, I}) \longrightarrow \underset{\text{ppt.}}{\mathrm{Ag}X} + \mathrm{HNO_3}$$

5. HF does not give any precipitate with the solution of Pb (II) salts like $Pb(NO_3)_2$, $(CH_3COO)_2Pb$ etc, HCl, HBr and HI give the precipitate of $PbCl_2$ (white) $PbBr_2$ (white) and PbI_2 (yellow) respectively.

$$\mathrm{Pb(NO_3)_2 + 2H}X(X = \mathrm{Cl, Br, I}) \longrightarrow \mathrm{Pb}X_2 + \mathrm{2HNO_3}$$
$$\mathrm{(CH_3COO)_2Pb + 2H}X \longrightarrow \mathrm{Pb}X_2 + \mathrm{2CH_3COOH}$$

[All the three precipitates (*i.e.,* $PbCl_2$, $PbBr_2$ and PbI_2) are soluble in hot water.]

6. HF does not give any precipitate with mercurous and mercuric salts. HCl forms a white precipitate of Hg_2Cl_2 with $Hg_2(NO_3)_2$ solution.

$$\mathrm{2HCl + Hg_2(NO_3)_2 \longrightarrow Hg_2Cl_2 + 2HNO_3}$$

Hg_2Cl_2 is soluble in aqua-regia. HI forms scarlet precipitate of HgI_2 with $HgCl_2$ solution.

$$\mathrm{2HI + HgCl_2 \longrightarrow HgI_2 + 2HCl}$$

7. HF, HCl and HBr do not react with $CuSO_4$ solution, but HI gives CuI_2 which, being unstable, decomposes into CuI and I_2 as

$$\mathrm{2HI + CuSO_4 \longrightarrow CuI_2 + H_2SO_4}$$
$$\mathrm{2CuI_2 \longrightarrow 2CuI + I_2}$$

8. With the solution of $BaCl_2$, $SrCl_2$ and $CaCl_2$ salts, H_2F_2 forms white precipitate of BaF_2, SrF_2 and CaF_2 respectively. Other acids do not give any precipitate since MX_2 (M = Ba, Sr, Ca; X = Br, I) are soluble.

$$M\mathrm{Cl_2 + H_2F_2} \longrightarrow \underset{\text{ppt.}}{M\mathrm{F_2}} + \mathrm{2HCl}$$
$$M\mathrm{Cl_2 + 2H}X \longrightarrow \underset{\text{soluble}}{MX_2} + \mathrm{2HCl}$$

9. Anhydrous HF does not attack any metal under ordinary conditions except potassium while acid reacts with many metals to form their fluorides with the evolution of H_2. *e.g.,*

$$Zn + 2HF \longrightarrow ZnF_2 + H_2$$
$$Mg + 2HF \longrightarrow MgF_2 + H_2$$

In these reactions, the metal is oxidised and HF is reduced to H_2.

Gaseous HCl reacts with heated metals while aqueous HCl reacts with most metals in cold. The reaction between aqueous HCl and Pt, Au, Ag and Hg is not preceptible. Some examples of the reaction between metal and HCl are as.

(i) Aqueous HCl reacts with Ag in presence of air.

$$4Ag + 4HCl + O_2 \longrightarrow 4AgCl + 2H_2O$$

(ii) Cu dissolves in conc HCl. Fe reacts with HCl and gives lower chloride *viz*, $FeCl_2$ (not $FeCl_3$).

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2$$

HBr dissolves Fe, Zn, Sn, Cu, Ag, Pb etc., with the liberation of H_2 and formation of bromides. HBr attacks Hg very slowly, forming H_2 and $HgBr_2$.

10. When H*X* molecule or X^- ion reacts with an oxidising agent, it reduces the oxidising agent and is itself oxidised to X_2 molecule.

$$2HX + O_2 \longrightarrow 2H_2O + 2X_2 \quad \text{(molecular equation)}$$

It has been found that the tendency of X^- ions to lose electrons increases from F^- to I^- ion. *Accordingly, the reducing power of X^- ions or* H*X* *molecules increases from* F^- *to* I^- *ions or from* HF *to* HI *molecules.*

$$F^- < Cl^- < Br^- < I^- \quad \text{or} \quad HF < HCl < HBr < HI$$

As a matter of fact, HF or F^- does not show reducing properties at all (even with very strong oxidising agent).

The increasing order of the reducing power of H*X* molecules or X^- ion can be explained on the basis of decrease in electronegative character from F to I *i.e.*, **good electron acceptors are bad electron loosers and *vice-versa*.**

As reducing agent, HCl *molecule or* Cl^- *ion is weaker than* HBr *and* HI *both and hence, reduces only strong oxidising agents* and is itself oxidised to Cl_2 which is evolved as a yellowish green gas. Thus, HCl reduces

(i) **MnO_2** (acidified with conc. H_2SO_4) to $MnSO_4$

$$MnO_2 + H_2SO_4 + 2HCl \longrightarrow MnSO_4 + 2H_2O + Cl_2$$

(ii) **MnO_2 to $MnCl_2$**

$$MnO_2 + 4HCl\,(\text{conc.}) \longrightarrow MnCl_2 + 2H_2O + Cl_2$$

(iii) **$KMnO_4$ to $MnCl_2$**

$$2KMnO_4 + 16HCl\,(\text{conc.}) \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

(iv) **$K_2Cr_2O_7$ to $CrCl_3$**

$$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$$

(v) **PbO_2 to $PbCl_2$**

$$PbO_2 + 4HCl(\text{hot and conc.}) \longrightarrow PbCl_2 + 2H_2O + Cl_2$$

(vi) **Pb_3O_4** (red lead) **to $PbCl_2$**

$$Pb_3O_4 + 8HCl \longrightarrow 3PbCl_2 + 4H_2O + Cl_2$$

(vii) **O_2 to H_2O in presence of Cu-salts** (catalyst)

$$O_2 + 4HCl \longrightarrow 2H_2O + 2Cl_2$$

(viii) **Bleaching powder ($CaOCl_2$) to $CaCl_2$**

$$CaOCl_2 + 2HCl \longrightarrow CaCl_2 + H_2O + Cl_2$$

(ix) **F_2 to HF but neither Br_2 to HBr nor I_2 to HI**

$$\left.2HCl + F_2 \longrightarrow 2HF + Cl_2\right] \text{possible}$$
$$\left.\begin{array}{l}2HCl + Br_2 \longrightarrow 2HBr + Cl_2\\ 2HCl + I_2 \longrightarrow 2HI + Cl_2\end{array}\right] \text{not possible}$$

(x) **HCl cannot reduce H_2SO_4 to SO_2**

Since, HBr or Br^- is a weaker reducing agent than HI or I^-, **it reduces some oxidising agents and is itself oxidised to** Br_2 which is evolved as reddish brown vapour. Thus, HBr reduces

(i) H_2SO_4 to SO_2

$$2HBr + H_2SO_4 \longrightarrow SO_2 + 2H_2O + Br_2$$

(ii) **Atmospheric O_2 to H_2O**

$$4HBr + O_2 \longrightarrow 2H_2O + 2Br_2$$

(iii) **Acidified solution of $KMnO_4$ to $MnSO_4$**

$$2KMnO_4 + 3H_2SO_4 + 10HBr \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5Br_2$$

(iv) **Acidified solution of $K_2Cr_2O_7$ to $Cr_2(SO_4)_3$**

$$K_2Cr_2O_7 + 4H_2SO_4 + 6HBr \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3Br_2$$

(v) **H_2O_2 to H_2O**

$$2HBr + H_2O_2 \longrightarrow 2H_2O + Br_2$$

(vi) **$FeCl_3$ to $FeCl_2$**

$$FeCl_3 + 2HBr \longrightarrow 2FeCl_2 + 2HCl + Br_2$$

(vii) **F_2 to HF and Cl_2 to HCl but not I_2 to HI**

$$\left.\begin{array}{l}2HBr + F_2 \longrightarrow 2HF + Br_2\\ 2HBr + Cl_2 \longrightarrow 2HCl + Br_2\end{array}\right] \text{possible}$$
$$\left.2HBr + I_2 \longrightarrow 2HI + Br_2\right] \text{not possible}$$

(viii) **Acidified MnO_2 to $MnSO_4$**

$$MnO_2 + H_2SO_4 + 2HBr \longrightarrow MnSO_4 + 2H_2O + Br_2$$

Being the strongest reducing agent, HI *or* I^- *reduces even very strong oxidising agents and is itself oxidised to* I_2 which is evolved as violet vapour. Thus, HI or I^- reduces

(i) H_2SO_4 to SO_2, S or H_2S (or S^{2-})

$$2HI + H_2SO_4 \longrightarrow SO_2 + 2H_2O + I_2$$
$$6HI + H_2SO_4 \longrightarrow S + 4H_2O + 3I_2$$
$$8HI + H_2SO_4 \longrightarrow H_2S + 4H_2O + 4I_2$$

(ii) HNO_3 to NO or NO_2

$$2HNO_3 + 6HI \longrightarrow 2NO + 4H_2O + 3I_2$$
$$2HNO_3 + 2HI \longrightarrow 2NO_2 + 2H_2O + I_2$$

(iii) **HNO_2 to NO**

$$2HNO_2 + 2HI \longrightarrow 2NO + 2H_2O + I_2$$

(iv) **$FeCl_3$ to $FeCl_2$**

$$2FeCl_3 + 2HI \longrightarrow 2FeCl_2 + 2HCl + I_2$$

(v) **$CuSO_4$ to CuI**

$$2CuSO_4 + 4HI \longrightarrow 2CuI + 2H_2SO_4 + I_2$$

(vi) **Atmospheric O_2 to H_2O**

$$4HI + O_2 \longrightarrow 2H_2O + 2I_2$$

(due to the liberation of free I_2, the solution of HI turns brown, when kept in air).

(vii) **Acdified MnO_2 to $MnSO_4$**

$$MnO_2 + H_2SO_4 + 2HI \longrightarrow MnSO_4 + 2H_2O + I_2$$

(viii) **Iodic acid (HIO_3) to I_2**

$$5HI + HIO_3 \longrightarrow 3H_2O + 3I_2$$

(ix) **Arsenate** (AsO_4^{3-}) **to arsenite** (AsO_3^{3-})

$$2I^- + AsO_4^{3-} + 2H^+ \longrightarrow AsO_3^{3-} + H_2O + I_2$$

(x) **Acidified solution of $KMnO_4$ to $MnSO_4$**

$$10HI + 2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5I_2$$

Interhalogen Compounds

Halogens react with each other to produce a number of interhalogen compounds (XX_n' where, $n = 1, 3, 5$ or 7). An interhalogen compound, infact, is regarded as the halide of more electropositive halogen, with a halogen with less electropositive character (electropositive character increases down the group). Thus, as far as this trend is concerned, F *cannot form any interhalogen compound as central atom, while* I *has the maximum tendency to form interhalogen compounds*.

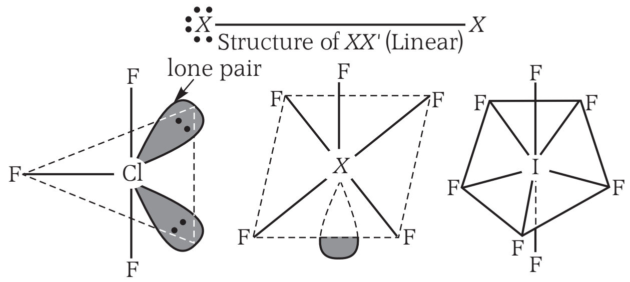
Interhalogens can be grouped into four categories namely XX' (*e.g.*, ClF, BrF etc,) XX'_3 (*e.g.*, ClF_3 BrF_3 etc.) XX'_5 (*e.g.*, ClF_5, IF_5 etc,) and XX'_7 (*e.g.*, IF_7) The oxidation states of *X* atom in these are +1, +3, +5 and +7 respectively.

Some important examples of these are

Table 7.14 **Examples of Interhalogens Compounds**

XX'	XX_3'	XX_5'	XX_7'
ClF	ClF_3	ClF_5	IF_7
BrF	BrF_3	BrF_5	
BrCl	IF_3	IF_5	
ICl	$ICl_3(I_2Cl_6)$		
IBr			
IF			

The stability of interhalogen compounds increases as the size of central atom increases. Out of two halogens the one with smaller size and higher electronegativity assigned negative oxidation state. ***XX′*** *interhalogen compounds have linear structure,* ***XX_3'*** *compounds have bent T structure* ***XX_5'*** *compounds have square pyramidal structure and* **IF_7** *have pentagonal bipyramidal structure.*



Structure of $XX¢_3$ type (T-shape)

Structure of $XX¢_5$ type (Square pyramidal)

Structure of $XX¢_7$ type (Pentagonal bipyramidal)

Fig. 7.14 Structure of interhalogen compounds

Pseudohalides

There are several uni-negative groups which show characteristics of halide ions. These are called **pseudohalides** or **pseudohalide ions.** As the halides of halide ions are called halogens, the covalent dimers of pseudohalide ions are called **pseudohalogens.** Some of them are

Table 7.15 **Some Pseudohalides and their Formulae**

Pseudohalide ions	Formulae	Pseudohalogens	Formulae
Cyanide	CN^-	Cyanogen	$(CN)_2$
Cyanate	OCN^-	Oxocyanogen	$(OCN)_2$
Thiocyanate	SCN^-	Thiocyanogen	$(SCN)_2$
Selenocyanate	$SeCN^-$	Selenocyanogen	$(SeCN)_2$
Azidothiocarbonate	$SCSN_3^-$	Azidocarbon disulphide	$(SCSN_3)_2$
Isocyanate	ONC^-		

Important similarities between halide and pseudohalide ions are

1. Both can form ionic compounds, such as AgCl (AgCN), $PbCl_2$ $[Pb(NCS)_2]$, covalent compounds, *e.g.,* ICl(ICN), $SiCl_4$ $[Si(NCS)_4]$, complex ions with transition metal ions, *e.g.,* $[FeF_6]^{3-}$, $Fe(CN)_6^{3-}$; $[CoCl_4]^{2-}$, $[Co(SCN)_4]^{2-}$ etc.
2. As halide ions combine together to form interhalogen compounds, pseudohalide ions also combine together to form interpseudohalogen compounds like $CN \cdot N_3$, $CN \cdot SCN$ etc.
3. Both of them combine with H_2 to form monobasic hydracids *e.g.,* HCl, HCN etc.
4. Both give insoluble salts with Ag^+, Pb^{2+} and Hg^+ ions.
   e.g.,
   $$Ag^+ + Cl^- \longrightarrow AgCl\downarrow$$
   $$Ag^+ + CN^- \longrightarrow AgCN\downarrow$$
5. Both of them can coordinate with two metal ions simultaneously, *i.e.,* can acts as bridging ligands, *e.g.,* CN^- in $R_2Au(CN)_4$, similarly Cl^- in R_2AuCl_2.

However, halide and pseudohalide ions differ in following respects

1. Pseudohalide ions are stronger ligands than halide ions due to the ability of former to form the σ as well as π-bond.
2. Pseudohalide ions, being made up of two hetero atoms can function as **ambidentate ligands**
   (see coordination compounds for detail). However, halide ions do not show this behaviour.

Similarities between halogens and pseudohalogens are

1. Both are dimeric and fairly volatile (with the exception of polymeric thiocyanogen) in the free state.
2. Pseudohalogens are **isomorphous** to halogens when in the free or solid state. *e.g.,* Cl_2 is isomorphous to $(CN)_2$; Br_2 is isomorphous to $(SCN)_2$.
3. Both can be added to ethylenic double bond linkage as
   $$CH_2{=}CH_2 + Cl_2 \longrightarrow CH_2Cl{-}CH_2Cl$$
   $$CH_2{=}CH_2 + (SCN)_2 \longrightarrow CH_2SCN{-}CH_2SCN$$
4. Both react with alkalies as
   $$(SCN)_2 + 2KOH\text{ (cold and dilute)} \longrightarrow KSCN + KOSCN + H_2O$$
   $$Cl_2 + 2KOH\text{ (cold and dilute)} \longrightarrow KCl + KOCl + H_2O$$

Halogen and pseudohalogens differ from each other in the fact that pseudohalogens have the ability to undergo polymerisation as $n(CN)_2 \xrightarrow{500°C} 2(CN)_n$

Similarly, $n(SCN)_2 \xrightarrow[\text{temp.}]{\text{Room}} 2(SCN)_n$

Halogens on the other hand do not have such a tendency.

Oxides of Halogens

Halogens form following oxides

Table 7.16 **Oxides of Halogens**

Oxides of chlorine	Oxides of bromine	Oxides of iodine
Cl_2O	Br_2O	I_2O_5
ClO_2	BrO_2	
Cl_2O_6	BrO_3	
Cl_2O_7		

In these oxides, bonds are mainly covalent, since there is a very small difference between the electronegativity of oxygen and the halogens.

Oxides of chlorine are acidic and the acidic nature increases as the percentage of oxygen increases. Moreover, these are powerful oxidising agents and decompose explosively when exposed to mechanical shock or on heating.

All the three monoxides *viz,* OF_2, Cl_2O and Br_2O have **tetrahedral structure** involving sp^3 hybridisation of oxygen. The bond angle increases as the size of halogen atom increases. Thus, the bond angle varies in the order **FOF < ClOCl < BrOBr.** This is because electrons in the case of OF_2 are nearer to fluorine due to high electronegativity of F compared to Cl to Br. The bonded electron pairs in Cl_2O and Br_2O are closer to oxygen making the repulsion between them more and thereby reducing the lone pair-lone pair repulsion on oxygen to some extent. Also due to the bulkiness of Cl and Br, the angles ClOCl and BrOBr increase to such an extent that 109°28′, (the tetrahedral angle), is approached.

Oxoacids of Halogens

Because of its high electronegativity and small size, fluorine forms only one oxoacid, HOF (known as **fluoric acid** or **hypofluorous acid).** Other halogens form many oxoacids. These are stable in aqueous solution or in the form of their salts. *These are as follows*

Table 7.17 **Oxoacids of Halogens**

Halogen	Hypohalous acids, HXO ($X = +1$)	Halous acids, HXO_2 ($X = +3$)	Halic acids, HXO_3 ($X = +5$)	Perhalic acids, HXO_4 ($X = +7$)
Chlorine	HClO	$HClO_2$	$HClO_3$	$HClO_4$
Bromine	HBrO	—	$HBrO_3$	—
Iodine	HIO	—	HIO_3	HIO_4, $HIO_4 \cdot 2H_2O$, $HIO_4 \cdot 2H_2O$, $2HIO_4 \cdot H_2O$

Some of the general properties of oxoacids are as follows

1. **Thermal stability** of these oxoacids depends on the oxidation number and electronegativity of the central halogen atom. Greater is the oxidation number or electronegativity of halogen atom, greater will be the thermal stability of the acid and *vice-versa*. Thus, the following two cases may be studied
   (i) **In case of oxoacids of a given halogen atom** since the electronegativity of the central halogen atom *viz*, Cl-atom in this case remains the same, the thermal stability depends only upon the oxidation number of the central atom. As the oxidation number of the central atom increases, *X*—O bond in the acids becomes more and more covalent and hence, thermal stability of the acids increases. *i.e.,* thermal stability of the given acids is in the order : $HClO < HClO_2 < HClO_3 < HClO_4$.

   (ii) **In case of oxoacids, having the same formula and different halogen atom** since, the oxidation number of the halogen atoms remains the same, the thermal stability depends only upon the electronegativity of the halogen atom. Thermal stability decreases with the decrease in electronegativity of halogen atom. Thus, thermal stability of the given acids is in the order :

   $$HClO > HBrO > HIO.$$

   Reaction with alkalies Fluorine reacts with cold dilute alkalies to give OF_2 (oxygen difluoride) while with concentration alkalies, it evolves oxygen.

   $$\underset{\text{(cold and dilute)}}{2NaOH} + 2F_2 \longrightarrow 2NaF + OF_2 + H_2O$$

   $$\underset{\text{(conc.)}}{4NaOH} + 2F_2 \longrightarrow 4NaF + O_2 + 2H_2O$$

   Cl_2, Br_2 and I_2 behaves similarly but differently than fluorine. They form a mixture of halide and hypohalites with cold dilute alkalies while a mixture of halides and halate with concentrated hot alkalies.

   $$\underset{\text{cold and dilute}}{2NaOH} + X_2 \longrightarrow \underset{\text{halide}}{NaX} + \underset{\text{hypohalite}}{NaXO} + H_2O$$

   $$\underset{\text{hot and conc.}}{6NaOH} + 3X_2 \longrightarrow 5NaX + \underset{\text{halate}}{NaXO_3} + 3H_2O$$

   (where, X = Cl, Br, I)

2. **Acidity** (or acid strength) of oxoacids also follows the same trend as thermal stability.
3. **Oxidising power** Here also following two cases may be possible
   (i) **Oxidising power of oxoacids of a given halogen atom** (*e.g.,* $HClO$, $HClO_2$, $HClO_3$, $HClO_4$) decreases with the increase in the oxidation number of the central halogen atom. This is because the *XX*—O bond becomes more and more covalent as the oxidation number of the central atom increases. Thus, the oxidising power of the given acids is in the order

   $$HClO > HClO_2 > HClO_3 > HClO_4.$$

   (ii) **In case of oxoacids, having the same formula and different halogen atom** (*e.g.,* $HClO_3$, $HBrO_3$ and HIO_3), oxidising power decreases with the decrease in the electronegativity of the halogen atom. Thus, oxidising power of the given acids is in the order

   $$HClO_3 > HBrO_3 > HIO_3.$$

4. **Stability and basicity of the oxo-anions of a given halogen atom** (*e.g.,* ClO^-, ClO_2^-, ClO_3^- and ClO_4^-) have been found to be in the following order

   Stability $ClO_4^- > ClO_3^- > ClO_2^- > ClO^-$

   Basicity $ClO_4^- < ClO_3^- < ClO_2^- < ClO^-$

Some important oxyacids of halogens as discussed below.

Hypochlorous Acid, HClO

Hypochlorous acid, HClO is known only in solution.

Methods of Preparation

It is prepared by following methods.

1. By passing Cl_2 into H_2O or into a suspension of $CaCO_3$ in water or into an aqueous solution of potassium hypochlorite (KClO) or bleaching powder ($CaOCl_2$).

   $$Cl_2 + H_2O \longrightarrow HCl + HClO$$

   In this reaction, Cl_2 undergoes disproportionation into HCl and HClO.

2. By the action of atmospheric CO_2 on sodium hypochlorite, NaOCl.

   $$NaOCl + CO_2 + H_2O \longrightarrow NaHCO_3 + HOCl$$

3. By distilling the aqueous solution of bleaching powder ($CaOCl_2$) with a calculated quantity of 5% HNO_3 or by passing CO_2 into aqueous solution of $CaOCl_2$ and then distilling.

   $$2CaOCl_2 + 2HNO_3 \longrightarrow CaCl_2 + Ca(NO_3)_2 + 2HClO$$

   $$CaOCl_2 + H_2O + CO_2 \longrightarrow CaCO_3 + 2HClO$$

4. By shaking Cl_2 water with freshly precipitated HgO (General method for the preparation of hypohalous acids).

   $$2Cl_2 + 2HgO + H_2O \longrightarrow HgCl_2 \cdot HgO\downarrow + 2HClO$$

   The insoluble $HgCl_2 \cdot HgO$ is removed by filtration. The filtrate is distilled when dilute HClO passes over.

Physical Properties

The concentrated solution of HClO is yellow in colour, while the dilute solution is colourless. It is a weak acid, even weaker than H_2CO_3. Its dissociation constant is 3×10^{-8} at 20°C.

Chemical Properties

1. (i) The dilute solution of the acid is fairly stable in the dark, but when concentrated solution is exposed to light, it becomes unstable and hence, undergoes **disproportionation** into Cl_2 (Cl = 0) and $HClO_3$ (Cl = +5).

$$\underset{(Cl\,=\,+1)}{5HClO} \longrightarrow \underset{(Cl\,=\,0)}{2Cl_2} + \underset{(Cl\,=\,+5)}{HClO_3} + 2H_2O$$

(Molecular equation)

The decomposition is accelerated by Pt-black, MnO and CoO.

(ii) When aqueous solution of HClO is heated, it undergoes disproportionation into HCl and $HClO_3$.

$$3HClO \xrightarrow{\Delta} 2HCl + HClO_3$$

2. On distillation, HClO decomposes into H_2O and Cl_2O.

$$2HClO \longrightarrow Cl_2O + H_2O$$

3. It reacts with metals, *e.g.,* it dissolves in Mg, with the evolution of H_2, in Fe and Al, with the evolution of H_2 and Cl_2, while with Co, Ni and Cu, Cl_2 and O_2 are evolved.

$$Mg + 2HClO \longrightarrow Mg(OCl)_2 + H_2$$

When HClO is shaken with Hg, a light brown precipitate of basic mercuric chloride, HgCl(OH), which is soluble in HCl, is obtained

$$2Hg + 2HClO \longrightarrow 2HgCl(OH)\ (\text{Light brown ppt.})$$

4. The aqueous solution of HClO and its salts (*e.g.*, NaOCl) are **oxidising** and **bleaching agents.** This property is due to the fact that HClO or NaOCl decomposes to give nascent oxygen.

$$HClO \xrightarrow{\text{Reduction}} HCl + O$$

$$NaClO \xrightarrow{\text{Reduction}} NaCl + O$$

5. HClO is a **monobasic acid,** since its aqueous solution gives only one H^+ ion on ionisation.

$$HClO\,(aq) \rightleftharpoons H^+(aq) + ClO^-(aq)$$

ClO^- ion is called **hypochlorite ion.** Its monobasic nature shows that HClO molecule has one OH group attached directly with the central Cl-atom. Being an acid, HClO reacts with alkalies to form the salts which are called hypochlorites, *e.g.*,

$$NaOH + HClO \longrightarrow NaOCl + H_2O$$

6. HClO reacts with $AgNO_3$ and gives silver hypochlorite (AgClO). This compound is unstable and hence, undergoes disproportionation into AgCl and $AgClO_3$.

$$HOCl + AgNO_3 \longrightarrow AgOCl + HNO_3$$

$$3AgOCl \longrightarrow AgCl + AgClO_3$$

Chloric Acid, $HClO_3$

This acid is known only in solution.

Methods of Preparation

$HClO_3$ *is prepared by following methods.*

1. By the action of dil H_2SO_4 on $Ba(ClO_3)_2$.

$$Ba(ClO_3)_2 + H_2SO_4 \longrightarrow BaSO_4\ (\text{ppt.}) + 2HClO_3$$

The precipitate of $BaSO_4$ is obtained by filtration. The unused H_2SO_4 is precipitated with baryta water. The filtrate is evaporated in a vacuum desicator over concentrated H_2SO_4 until a 4% solution of $HClO_3$ is obtained.

(If the solution containing $HClO_3$ is evaporated further more, it gets decomposed into perchloric acid, $HClO_4$.

$$3HClO_3 \longrightarrow HClO_4 + Cl_2 + 2O_2 + H_2O$$

2. By the action of hydrofluorosilicic acid (H_2SiF_6) on $KClO_3$.

$$2KClO_3 + H_2SiF_6 \longrightarrow K_2SiF_6(\text{ppt.}) + 2HClO_3$$

Physical and Chemical Properties

1. Concentrated solution of the acid is colourless and is a pungent smelling liquid.
2. It is fairly stable in dark. In light it decomposes and becomes yellow. On heating, $HClO_3$ decomposes to give $HClO_4$.

$$3HClO_3 \xrightarrow{\Delta} HClO_4 + Cl_2 + 2O_2 + H_2O$$

3. When organic substances like cotton, wool, paper etc, come in contact with the acid, they catch fire.
4. The acid is a powerful oxidising and bleaching agent.
5. When iodine is evaporated with 25% $HClO_3$, iodic acid (HIO_3) is obtained.

$$2HClO_2 + I_2 \longrightarrow 2HIO_3 + Cl_2$$

This reaction has been used for the preparation of HIO_3.

6. $HClO_3$ is a monobasic acid.

$$HClO_3 \rightleftharpoons H^+ + ClO_3^-$$

Perchloric Acid, $HClO_4$

Methods of Preparation

Perchloric acid, $HClO_4$ is prepared as

1. By heating $HClO_3$

$$3HClO_3 \xrightarrow{\Delta} HClO_4 + Cl_2 + 2O_2 + H_2O$$

2. By treating $Ba(ClO_4)_2$ with calculated quantity of dil. H_2SO_4 and then removing the insoluble $BaSO_4$ by filtration.

$$Ba(ClO_4)_2 + H_2SO_4 \longrightarrow 2HClO_4 + BaSO_4 \downarrow$$

3. By adding NH_4ClO_4 dissolved in conc. HCl to warm conc HNO_3 and then evaporating.

$$NH_4ClO_4 + 8HCl + 3HNO_3 \longrightarrow HClO_4 + 2N_2O + 4Cl_2 + 7H_2O$$

4. Anhydrous acid is obtained by distilling a mixture of potassium perchlorate ($KClO_4$) with conc. H_2SO_4 under reduced pressure.

$$KClO_4 + H_2SO_4 \longrightarrow HClO_4 + KHSO_4$$

Physical and Chemical Properties

These include

1. Anhydrous $HClO_4$ is a colourless mobile hygroscopic and oily liquid. It fumes strongly in moist air and dissolves in water with hissing sound due to the liberation of much heat.
2. It forms hydrates with 1, 2, 2.5, 3 and 3.5 molecules of water of crystallisation.
3. It is unstable and decomposes with explosion on heating and sometimes merely on standing for a few days even in the dark. Aqueous solution of the acid is quite stable and does not decompose and hence, can be kept indefinitely.
4. It is highly dangerous acid and produces severe wounds on the skin.
5. It is powerful oxidising agent and inflames paper and wood.
6. On dehydration with P_2O_5 at $-10°C$, it gives Cl_2O_7 which is the anhydride of perchloric acid.

$$2HClO_4 + P_2O_5 \longrightarrow Cl_2O_7 + 2HPO_3$$

This reaction has been used for the preparation of Cl_2O_7.

7. $HClO_4$ is the strongest acid of all the acids.
8. The metals like Zn, Fe etc, dissolve in the aqueous solution of the acid and form the soluble perchlorates.

$$Zn + 2HClO_4(aq) \longrightarrow Zn(ClO_4)_2(aq) + H_2 \downarrow$$

9. The acid is not reduced by nascent hydrogen but gets reduced to chloride by strong reducing agents like $SnCl_2$ $CrCl_2$ etc.
10. When a suspension of iodine is heated with $HClO_4$, paraperiodic acid (H_5IO_6) is obtained.

$$2HClO_4 + I_2 + 4H_2O \longrightarrow 2H_5IO_6 + Cl_2$$

Uses

The aqueous solution of the acid is used for the estimation of potassium gravimetrically.

Metaperiodic Acid, HIO_4

Methods of Preparation

1. HIO_4 is obtained by heating paraperiodic acid, H_5IO_6.

$$H_5IO_6 \xrightarrow{100°C} HIO_4 + 2H_2O$$

2. Its salts which are called metaperiodates is prepared by the thermal decomposition of iodates, *e.g.*,

$$4KIO_3 \xrightarrow{\Delta} 3KIO_4 + KI$$

Properties

These include

1. It is a weak acid and dissociates as

$$HIO_4 \rightleftharpoons H^+ + IO_4^-$$

2. When dissolved in water, it changes back to H_2IO_6.

$$HIO_4 + 2H_2O \longrightarrow H_5IO_6$$

3. HIO_4 and its salts are strong oxidising agents in acidic medium.

$$2IO_4^- + 16H^+ + 14e^- \longrightarrow I_2 + 8H_2O$$

Sample **Problem 17** *Which of the following is correct order of acidity of oxoacids of chlorine?* **[NCERT]**

(*a*) $HClO_4 < HClO_3 < HClO_2 < HClO$
(*b*) $HClO < HClO_2 < HClO_3 < HClO_4$
(*c*) $HClO_2 < HClO < HClO_3 < HClO_4$
(*d*) $HClO_4 < HClO_3 > HClO_2 > HClO$

Interpret (*b*) Oxygen is more electronegative than chlorine, therefore dispersal of negative charge present on chlorine increases from ClO^- to ClO_4^- ion because number of oxygen atoms attached to chlorine is increasing. Therefore, stability of ions will increaase in the order given below

$$ClO^- < ClO_2^- < ClO_3^- < ClO_4^-$$

Due to increase in stability of conjugate base, acidic strength of corresponding acid increases in the same order.

$$HClO < HClO_2 < HClO_3 < HClO_4$$

Check Point 3

1. Bond dissociation energy and electron affinity of fluorine are low, nevertheless it is a very good oxidising agent. Explain.
2. Interhalogen compounds, are more reactive than halogens. Why?
3. When a blue litmus is dipped into a solution of hypochalorous acid, it first turns red and later gets decolourised. Explain.
4. Why is HF not stored in glass bottles and kept in wax bottles?

18 Group Elements and Their Compounds

7.9 Group 18 Elements

This group of Periodic Table contains He, Ne, Ar, Kr, Xe and Rn. These were called **inert gases** due to their inert nature. However, these are now called **noble gases** because some of these elements form compounds under specific conditions.

Occurrence

All these gases except radon (Rn) are present in atmosphere. Rn results from disintegration of radium is itself radioactive. The total abundance of these elements in dry air (except Rn) is ~1% by volume, out of which Ar is the major component.

General and Physical Properties

(a) Electronic Configuration

These gases have highly stable $ns^2\ np^6$ configuration thus, have very little tendency to form chemical compounds with other elements (inert gases).

(b) Atomic and Ionic Radii

The atomic radii of 18th group elements correspond to the van der Waals' radii and increases on moving down the group.

(c) Boiling Points

They have low boiling points in comparison to other elements and their boiling point increases with increases in atomic sizes.

(d) Ionisation Energy and Electron Affinity

Noble gases have stable ns^2np^6 (fully filled) configuration, thus, have no tendency to add or lose electron. Therefore, their ionisation energy is very high. On the other hand, their electron affinity is zero.

(e) Heat of Vaporisation and Polarisability

They possess very low values of heat of vaporisation due to the presence of very weak van der Waals' forces of attraction between their monatomic molecules. However, the value of heat of vaporisation increases with atomic number and this shows that there is an increasing polarizability of the larger electronic clouds of the elements with higher atomic number. In other words, the polarizability increases down the group as He < Ne < Ar < Kr < Xe.

(f) Solubility

They are slightly soluble in water and their solubility generally increases on moving down the group.

(g) Adsorption

Except He, all the noble gases are adsorbed by coconut charcoal and the ease of adsorption increases down the group.

(h) Conductivity

They have high electrical conductivity at low pressures.

(i) Spectra

All of them give characteristic spectra, by which they can be identified.

(j) Liquification

Due to the presence of weak van der Waals' forces of attraction, it is difficult to liquify noble gases. Ease of liquification increases down the group from He to Rn due to increase in intermolecular forces.

The above mentioned physical properties can be summarised as

Table 7.18 **Physical Properties of Noble Gases**

Property	Helium	Neon	Argon	Krypton	Xenon	Radon
Atomic number	2	10	18	36	54	86
Molar mass (amu)	4.003	20.183	39.948	83.30	131.30	222
Boiling point (°C)	–268.93	–246.06	–185.86	–153.35	–108.1	–62
Melting point (°C)	–272.1	–246.61	–189.37	–157.2	–111.8	–71
Ionisation energy (kJ mol^{-1})	2372.1	2080.4	1520.6	1350.6	1170.2	1037.0
Heat of vaporisation (kJ mol^{-1})	0.08	1.74	6.52	9.05	12.65	18.1
Atomic radius (Å)	1.4	1.54	1.88	2.02	2.16	—
Critical temperature (°C)	–267.9	–228.7	–122.4	–62.5	+16.6	+14.5
Critical pressure (atm)	2.26	26.9	50.0	54.3	58.3	62.4
$\gamma = C_p / C_V$	1.652	1.642	1.60	1.689	1.60	—
Absorption coefficient in water at 25°C	0.0097	0.0114	0.0053	0.1105	0.2420	0.5100

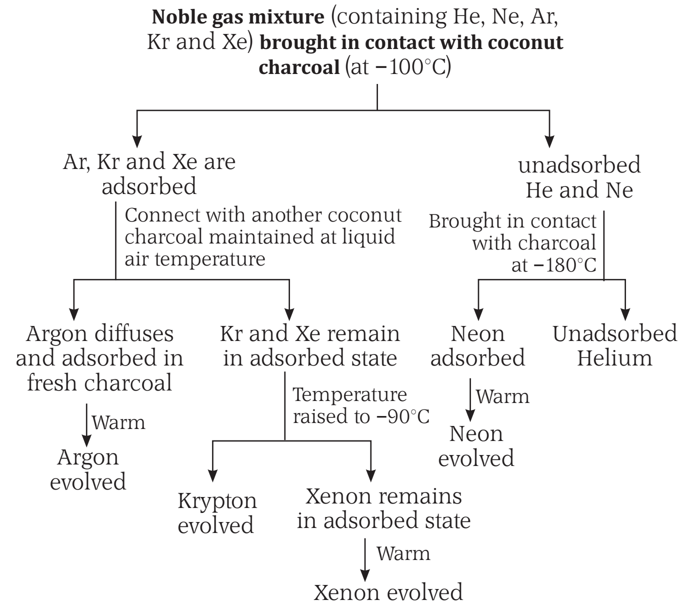
Chemistry of Noble Gases

The real chemistry of noble gases began in 1962 when

Neil Bartlett isolated an orange yellow solid from the reaction of Xe and PtF_6 (the possibility of reaction arise due to similarity in ionisation enthalpies of O_2 and Xe). After this discovery many compounds of Xe were prepared (with oxygen and F only). Kr forms comparatively fewer compounds (only KrF_2 have been studied in detail). Compounds of Rn have not been isolated but are identified with radiotracer techniques.

Extraction of Noble Gas

Helium, argon, neon, krypton and xenon are prepared by the fractional distillation of liquid air. Fractional distillation of air gives O_2, N_2 and mixture of noble gases. The individual gases may be obtained by adsorption of air on coconut charcoal. The charcoal adsorbs different gases at different temperatures and thus, these gases can be collected.



However, radon is obtained by radioactive disintegration of radium (226) as ${}_{88}Ra^{226} \longrightarrow {}_{86}Rn^{222} + {}_{2}\alpha^{4}$

Properties and Uses of Noble gases

The important properties along with the uses and discoverer of noble gases can be summarised as

Table 7.19 **Discovery and Uses of Noble Gases**

Noble gas	Discoverer	Uses	Reasons
He	Lockyer and Janssen (1868)	(i) He/O_2 mixture for deep-sea breathing, instead of N_2/O_2 mixture	Low solubility in blood; prevents nitrogen narcosis and "bends".
		(ii) Diluent for gaseous anaesthetics	Non-flammable, non-reactive.
		(iii) Filling of observation balloons and other lighter air craft	Non-flammable; 93% lifting power as compared to flammable H_2.
		(iv) Liquid He to maintain very low temperature in research (cryogenics)	Extremely low boiling point.
		(v) He/O_2 mixtures for respiratory patients	Low density flows easily through restricted assages.
		(vi) Heat transfer agent in gas cooled nuclear reactors.	Transfers heat readily; does not becomes radioactive; chemically inert.
Ne	Ramsay and Travers	Neon signs.	Even at low pressure Ne, moderate electric current causes bright orange-red glow; can be modified by coloured glass or mixing with Ar or Hg vapour.
Ar	L. Rayleigh and Ramsay	(i) Inert atmosphere for welding	Chemically inert.
		(ii) Filling incandescent light bulbs.	Inert; prevents vaporisation of tungsten and blackening of bulbs.
Kr	Ramsay and Travers (1898)	Airport runway and approach lights	Gives longer life to incandescent lights than Ar, but more expensive.
Xe	Ramsay and Travers (1898)	Xe and Kr mixture in high-intensity, short-exposure photographic flash tubes	Both have fast response to electric current.
Rn	Dorn (1900)	For the treatment of cancer (radiotherapy).	Because of radioactive nature.

7.10 Compounds of Elements of Group 18

Xe because of its low ionisation energy forms several compounds. However no true compounds of He, Ne and Ar are known. Most of the compounds of Xe are with F and O.

Xenon Fluorides

Xe forms three binary fluorides, *i.e.*, XeF_2, XeF_4 and XeF_6 by the direct union of elements under appropriate experimental conditions. In these fluorides, Xe is in +2, +4 and +6 oxidation states respectively.

(a) Xenon Difluorine

XeF_2 is prepared by the following method as

1. $\underbrace{Xe + F_2}_{2\,:\,1 \text{ ratio}} \xrightarrow[\text{tube (400°C)}]{\text{Sealed Ni}} XeF_2$
2. $\underbrace{Xe + F_2}_{2\,:\,1 \text{ ratio}} \xrightarrow[\text{discharge}]{\text{Electric}} XeF_2$
3. $Xe + F_2 \xrightarrow[\text{(Hg vapours)}]{\text{Photochemical combination}} XeF_2$
4. XeF_2 can also be prepared by the fluorination of Xe by oxygen monofluoride, O_2F_2 at −178°C.

$$Xe + O_2F_2 \xrightarrow{-178°C} XeF_2 + O_2$$

The important properties exhibited by XeF_2 are as

1. It is a colourless crystalline solid with m.p. is 140°C.
2. XeF_2 is reduced by H_2O to Xe and H_2O is oxidised to O_2.

$$2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$$

However, it is rapidly hydrolysed by an aqueous solution of a base.

$$2XeF_2 + 4OH^- \longrightarrow 2Xe + 4F^- + 2H_2O + O_2$$

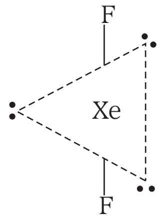
3. XeF_2 is a mild fluorinating agent. Thus, it reacts with C_6H_6 to give C_6H_5F.
4. It can oxidise many substances and itself gets reduced to xenon. *e.g.,*

$$XeF_2 + H_2 \longrightarrow Xe + 2HF$$
$$2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$$
$$XeF_2 + I_2 \xrightarrow{BF_3} Xe + 2IF$$
$$XeF_2 + 2SO_3 \longrightarrow Xe + S_2O_6F_2$$
$$XeF_2 + 2HCl \longrightarrow Xe + 2HF + Cl_2$$
$$XeF_2 + 2Ce^{3+} \longrightarrow 2Ce^{4+} + Xe + 2F^-$$

5. In BrF_3 solution, XeF_2 forms adducts with MF_5 molecules (M = P, A, Sb etc).

$$XeF_2 + MF_5 \longrightarrow XeF_2 \cdot MF_5$$
$$XeF_2 + 2MF_5 \longrightarrow XeF_2 \cdot 2MF_5$$
$$2XeF_2 + MF_5 \longrightarrow 2XeF_2 \cdot MF_5$$

XeF_2 has sp^3d hybridisation and linear geometry (due to the presence of 3 lone pairs) which is represented as



Linear XeF_2

(b) Xenon Tetrafluoride

XeF_4 is prepared as

1. $\underbrace{Xe + 2F_2}_{1\,:\,5 \text{ ratio}} \xrightarrow[\text{400°C, 5–6 atm}]{\text{Ni tube}} XeF_4$
2. $\underbrace{Xe + 2F_2}_{1\,:\,2 \text{ ratio}} \xrightarrow[-80°C]{\text{Electric discharge}} XeF_4$

Its important properties are as

1. It is also a colourless crystalline solid. Its mp is 117.1°C. It sublimes readily.
2. XeF_4 undergoes disproportionation in water, giving XeO_3 which is a highly explosive solid.

$$2XeF_4 + 3H_2O \longrightarrow Xe(g) + XeO_3(s) + 6HF(aq) + F_2(g)$$

If the reaction is carried out at −80°C, $XeOF_2$ is formed. In this reaction, slow and partial hydrolysis of XeF_4 takes place as

$$XeF_4 + H_2O \xrightarrow{-80°C} XeOF_2 + 2HF$$

3. XeF_4 is a stronger fluorinating agent than XeF_2. Thus, it converts Hg to HgF_2, Pt to PtF_4, NO to NOF, NO_2 to NO_2F, SF_4 to SF_6, BCl_3 to BF_3 etc.

$$2Hg + XeF_4 \longrightarrow Xe + 2HgF_2$$
$$Pt + XeF_4 \longrightarrow Xe + PtF_4$$
$$2SF_4 + XeF_4 \longrightarrow Xe + 2SF_6$$
$$4BCl_3 + 3XeF_4 \longrightarrow 3Xe + 4BF_3 + 6Cl_2$$

4. It also acts as an oxidising agent and in these reactions, itself get reduced to Xe.

$$XeF_4 + 2H_2 \longrightarrow Xe + 4HF$$
$$3XeF_4 + 4BCl_3 \longrightarrow 3Xe + 4BF_3 + 6Cl_2$$
$$XeF_4 + 4I^- \longrightarrow Xe + 4F^- + 2I_2$$

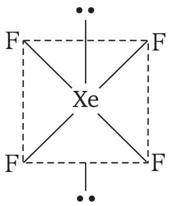
5. **XeF_4 dissolves in molten SbF_5 and gives the addition compound, $XeF_4 \cdot SbF_5$** which is an ionic compound and hence, is represented as $[XeF_3]^+ [SbF_6]^-$.

$$XeF_4 + SbF_5 \longrightarrow XeF_4 \cdot SbF_5 \longrightarrow [XeF_3]^+ [SbF_6]^-$$

It also dissolves in molten TaF_5, giving a straw coloured compound, $Xe(TaF_6)_2$ which is described as an addition compound, $XeF_2 \cdot 2TaF_5$.

$$XeF_4 + 2TaF_5 \longrightarrow Xe(TaF_6)_2 \text{ or } XeF_2 \cdot 2TaF_5 + F_2$$

XeF_4 has sp^3d^2 hybridisation but square planar geometry because of the presence of two lone pairs of electrons.



Square planar XeF_4

(c) Xenon Hexafluoride

XeF_6 can be prepared as

1. $\underbrace{Xe + 3F_2}_{1\,:\,20 \text{ ratio}} \xrightarrow[250\text{–}300°C,\ 50\text{–}60 \text{ atm}]{\text{Ni vessel}} XeF_6$
2. $\underbrace{Xe + 3F_2}_{1\,:\,3 \text{ ratio}} \xrightarrow[\text{low temp.}]{\text{Electric discharge}} XeF_6$
3. XeF_6 can also be prepared by the fluorination of XeF_4 by O_2F_2 or by F_2 under pressure.

$$XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$$
$$XeF_4 + F_2 \longrightarrow XeF_6$$

Its properties include

1. It is colourless crystalline solid with melting point 49.5°C.
2. XeF_6 undergoes hydrolysis in water. The final product obtained is XeO_3 (an explosive solid).

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$
$$XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$$
$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

3. In strongly basic solution, the reaction proceeds as

$$XeF_6 + 7OH^- \longrightarrow 6F^- + 4H_2O + \underset{(Xe\,=\,+\,6)}{HXeO_4^-} \text{ (xenate ion)}$$

$$HXeO_4^- \xrightarrow{+2OH^-} \frac{6}{4} H_2O + \frac{1}{4} Xe + \frac{3}{4} \underset{(Xe\,=\,+8)}{XeO_6^{4-}} \text{ (perxenate ion)}$$

In acidic solution, main species is $XeOF_4$ (Xe = + 6) and H_6XeO_6 (Xe = + 6) H_6XeO_6 is called **xenic acid.**

4. It also acts as an oxidising agent as

$$XeF_6 + 3H_2 \longrightarrow Xe + 6HF$$

XeF_6 can also oxidise NH_3 (N = – 3) to N_2 (N = 0) and HCl (Cl = – 1) to Cl_2 (Cl = 0). In these reactions XeF_6 is reduced to Xe.

$$XeF_6 + 8NH_3 \longrightarrow Xe + 6NH_4F + N_2$$
$$XeF_6 + 6HCl \longrightarrow Xe + 6HF + 3Cl_2$$

5. XeF_6 dissolves in HF, giving a solution which is a good conductor of electricity. The electrical conductivity of the solution is because of the formation of XeF_5^+ and HF_2^+.

$$XeF_6 + HF \longrightarrow XeF_5^+ + HF_2^+$$

6. XeF_6 gives addition compound with AsF_5 and SbF_5 molecules.

$$XeF_6 + \underset{(M\,=\,\text{As, Sb})}{MF_5} \longrightarrow XeF_6 \cdot MF_5 \longrightarrow [XeF_5]^+[MF_6]^-$$

In these reactions, XeF_6 molecule acts as F^- ion donor while MF_5 molecule behaves as F^- ion acceptor.

7. XeF_6 also reacts with alkali metal fluorides (except LiF) and gives species containing XeF_7^- and XeF_8^{2-} ions. Thus, in these reactions XeF_6 molecule acts as F^- ion acceptor and MF molecule (M = Na, K, Rb) behaves as F^- ion donor.

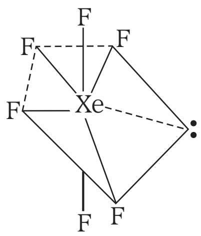
$$XeF_6 + \underset{(M\,=\,\text{Na, K})}{2MF} \longrightarrow \underset{\text{(octafluoro xenate)}}{M_2XeF_8}$$

$$XeF_6 + \underset{\text{molten}}{2RbF} \xrightarrow{200°C} \underset{\text{(heptafluoroxenate)}}{2RbXeF_7} \xrightarrow{50°C} \underset{\text{(octafluoroxenate)}}{Rb_2XeF_8} + XeF_6$$

8. XeF_6 is the most volatile of all the fluorides. Its vapours have a greenish yellow colour.
9. XeF_6 is extremely reactive. Thus, cannot be stored in glass or quartz vessels, since it readily reacts with SiO_2 present in glass as one of its constituents. With SiO_2, XeF_6 gives dangerously explosive XeO_3 as a final product.

$$2XeF_6 + 3SiO_2 \longrightarrow 2XeO_3 + 3SiF_4$$

XeF_6 has sp^3d^3 hybridisation and distorted octahedral geometry because of the presence of one lone pair of electrons.



Distorted octahedral XeF_6

Xenon Oxides

(a) **Xenon Trioxide,** XeO_3

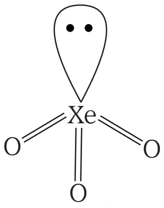
It is prepared by complete hydrolysis of XeF_4 and XeF_6 as

$$6XeF_4 + 12H_2O \longrightarrow 2XeO_3 + 4Xe + 3O_2 + 24HF$$

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

It is a colourless solid, highly explosive and powerful oxidising agent.

XeO_3 has sp^3 hybridisation trigonal pyramidal geometry because of the presence of one lone pair of electrons over Xe. The molecule has three Xe$=$O double bonds containing $p\pi$ - $d\pi$ overlapping as



Structure of XeO_3

(b) **Xenon Tetraoxide,** XeO_4

It is prepared by the action of conc H_2SO_4 on sodium or barium xenate (Na_4XeO_6; Ba_2XeO_6) at room temperature.

$$Na_4XeO_6 + 2H_2SO_4 \longrightarrow XeO_4 + 2Na_2SO_4 + 2H_2O$$

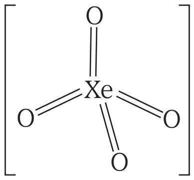
$$Ba_2XeO_6 + 2H_2SO_4 \longrightarrow XeO_4 + 2BaSO_4 + 2H_2O$$

XeO_4 is purified by vacuum sublimation at 195 K.

It is quite unstable gas and decomposes to xenon and oxygen,

$$XeO_4 \longrightarrow Xe + 2O_2$$

XeO_4 has tetrahedral structure due to sp^3 hybridization of Xe. There are four Xe—O double bonds containing $p\pi$ - $d\pi$ overlapping.



Structure of XeO_4

Clathrates

Noble gases form a number of compounds in which these are trapped into the cavities of crystal lattices of certain organic and inorganic compounds. These are called **cage compounds** or **clathrates,** *e.g.*, $Xe \cdot 6H_2O$, quinol clathrate. He and Ne do not form clathrate compounds as the size of the cavity is more than the size of the He or Ne atom.

Uses of Clathrates

Important uses of clathrates include

1. Separation of noble gases. Ne can be separated from other gases (Ar and Kr) as it does not form clathrate with quinol.
2. As an anaesthetic.
3. The clathrates are convenient form of handling. processing and transporting of isotopes of noble gases.

Sample **Problem 18** *Which one of the following does not exist?* [**NCERT**]

(*a*) $XeOF_4$ (*b*) NeF_2
(*c*) XeF_2 (*d*) XeF_6

Interpret (*b*) NeF_2 does not exist due to very high ionization enthalpy (2080 kJ mol^{-1}) of neon (Ne). Ionization enthalpy of xenon is low (1170 kJ mol^{-1}) so, its compounds like $XeOF_4$, XeF_2, XeF_6 etc. exist.

Check Point 4

1. Explain, why are noble gases inert under ordinary conditions?
2. Why do noble gases form compounds with fluorine and oxygen?
3. The boiling points of noble gases increase with increase in atomic number. Explain
4. Why does xenon not form fluorides such as XeF, XeF_3 or XeF_5?

WORKED OUT
Examples

Example 1 *Copper metal on treatment with dilute* HNO_3 *produces a gas* (*X*). (*X*) *when passed through acidic solution of stannous chloride, a nitrogen containing compound* (*Y*) *is obtained.* (*Y*) *on reaction with nitrous acid produces a gas* (*Z*). *Gas* (*Z*) *is*

(*a*) NO (*b*) N_2
(*c*) NO_2 (*d*) N_2O

Solution (*d*) Cu produces NO gas when treated with dil. HNO_3. This gas is reduced by $SnCl_2/HCl$ and then oxidised by HNO_2 to give N_2O. The reactions are as follows:

$$Cu + \text{dil. } HNO_3 \longrightarrow \underset{(X)}{NO} \xrightarrow{SnCl_2/HCl} \underset{(Y)}{NH_2OH \cdot HCl} \xrightarrow{HNO_2} \underset{(Z)}{N_2O}$$

$$\underset{(X)}{NO} \xrightarrow{SnCl_2/HCl} NH_2OH \cdot HCl$$

$$\underset{(Y)}{NH_2OH \cdot HCl} \xrightarrow{HNO_2} \underset{(Z)}{N_2O}$$

Example 2 *White phosphorus on reaction with lime water gives calcium salt of an acid* (*A*) *along with a gas* (*X*). *Which of the following statement is correct with respect to above?*

(*a*) (*A*) *on heating gives* (*X*) *and* O_2
(*b*) *The bond angle in* (*X*) *is less than that in case of ammonia*
(*c*) (*A*) *is a dibasic acid*
(*d*) (*X*) *is more basic than ammonia*

Solution (*b*) $8P + 3Ca(OH)_2 + 6H_2O \rightarrow 3Ca(H_2PO_2)_2 + \underset{(X)}{2PH_3}$

(*A*) is H_3PO_2 (hypophosphorous acid), a monobasic acid. PH_3 is less basic than NH_3. The bond angle in (*X*) is less than that present in NH_3. H_3PO_2 on heating gives orthophosphoric acid and phosphine (*X*).

Example 3 *A certain compound on burning in air produces three oxides. Out of these, one oxide turned lime water milky, the second one turned anhydrous* $CuSO_4$ *blue and the third formed a solution of* $pH = 9$. *The compound is made up of*

(*a*) S, N *and* H (*b*) S, H *and* Na
(*c*) S, *and* N (*d*) S, C *and* H

Solution (*b*) Since, the gas turns lime water milky, it may be CO_2 or SO_2, H_2O turns the colour of anhydrous $CuSO_4$ blue and the oxide of metals are usually alkaline. Thus, the compound is made up of S, H and Na.

Example 4 *An oxide of a non-metal has the following properties*

(*i*) *It acts both as a proton donor as well as proton acceptor*
(*ii*) *It reacts readily with basic and acidic oxides*
(*iii*) *It oxidises* Fe *at its boiling point.*

The oxide is

(*a*) P_2O_5 (*b*) SiO_2
(*c*) H_2O (*d*) CO_2

Solution (*c*) H_2O is a amphoteric oxide. It can accept protons and also can donate them. Thus, it readily reacts with basic as well as acidic oxides. Only water vapour react with Fe.

Example 5 *Which of the following solutions does not change its colour on passing ozone through it?*

(*a*) *Starch iodide solution*
(*b*) *Alcoholic solution of benzidine*
(*c*) *Acidic solution of* $K_2Cr_2O_7$
(*d*) *Acidified solution of* $FeSO_4$

Solution (*c*) Ozone does not react with acidified solution of $K_2Cr_2O_7$, thus, does not change its colour.

Example 6 *A greenish yellow gas reacts with an alkali metal hydroxide to form a halate which can be used in fireworks and safety matches. The gas and the halate are*

(*a*) $Br_2, KBrO_3$ (*b*) $Cl_2, KClO_3$
(*c*) I_2, $NaIO_3$ (*d*) I_2, KIO_3

Solution (*b*) $KClO_3$ is the halate that is used in fireworks and safety matches thus, the gas is Cl_2

$$\underset{\substack{\text{greenish}\\ \text{yellow gas}}}{3Cl_2} + 6KOH \longrightarrow KClO_3 + 5KCl + 3H_2O$$

Example 7 $AgClO_3 + (A) \longrightarrow (B) + (C) + (D)$

$MnO_2 + \underset{\text{conc}}{HCl} \longrightarrow$

The substance (A), (B), (C) and (D) are

(a) Cl_2, AgCl, ClO_2, O_2
(b) Cl_2, Ag, Cl_2O_6, O_2
(c) H_2, AgCl, H_2O, O_2
(d) HClO, AgCl, Cl_2O, O_2

Solution (a) $2AgClO_3 + \underset{(A)}{Cl_2} \longrightarrow \underset{(B)}{2AgCl} + \underset{(C)}{2ClO_2} + \underset{(D)}{O_2}$

Example 8 $KClO_3$ *on reaction with* SO_2 *gives (A) and on reaction with conc.* H_2SO_4 *gives (B). (A) and (B) are*

(a) KCl, $HClO_4$
(b) Cl_2, ClO_2
(c) KCl, $HClO_3$
(d) Cl_2, $HClO_4$

Solution (a) $KClO_3 + 3SO_2 + 3H_2O \longrightarrow \underset{(A)}{KCl} + 3H_2SO_4$

$$3KClO_3 + 3H_2SO_4 \longrightarrow 3KHSO_4 + 3HClO_3$$

$$2HClO_3 \longrightarrow 2ClO_2 + H_2O + O$$

$$HClO_3 + O \longrightarrow HClO_4$$

$$3KClO_3 + 3H_2SO_4 \longrightarrow \underbrace{3KHSO_4 + 2ClO_2 + \underset{(B)}{HClO_4} + H_2O}_{\text{products}}$$

Example 9 *A liquid X is treated with* Na_2CO_3 *solution. A mixture of two salts Y and Z are produced in the solution. The mixture on acidification with sulphuric acid and distillation produces the liquid X again. Identify X.*

(a) Cl_2
(b) Br_2
(c) Hg
(d) I_2

Solution (b) The liquid X is bromine which on treatment with sodium carbonate forms a mixture of NaBr and $NaBrO_3$ (sodium bromate). The mixture with conc. H_2SO_4 on distillation, gives the liquid bromine again.

$$3Br_2 + 3Na_2CO_3 \longrightarrow 5NaBr + NaBrO_3 + 3CO_2$$

$$5NaBr + NaBrO_3 + 3H_2SO_4 \longrightarrow 3Na_2SO_4 + 3Br_2 + 3H_2O$$

Start **Practice** *for* JEE Main

Round I (Topically Divided Problems)

Group 15 Elements and their Compounds

1. Pure nitrogen can be prepared from
(a) NH_4OH (b) NH_4NO_2
(c) $Ba(NO_3)_2$ (d) Ca_3N_2

2. The element which catches fire in air at 30°C and is stored under water is
(a) sodium (b) phosphorus
(c) magnesium (d) zinc

3. By the action of hot conc. H_2SO_4, phosphorus changes to
(a) phosphorous acid
(b) metaphosphoric acid
(c) pyrophosphoric acid
(d) orthophosphoric acid

4. Each of the following is true for white and red phosphorus except that they
(a) can be oxidised by heating in air
(b) are both soluble in CS_2
(c) consists of same kind of atoms
(d) can be converted into one another

5. White phosphorus (P_4) does not contain
(a) six P—P single bond
(b) four P—P single bond
(c) four lone pairs of electrons
(d) P—P—P angle of 60°

6. Which oxide do not act as a reducing agent?
(a) N_2O_5 (b) N_2O
(c) NO (d) NO_2

7. Which of the following is not hydrolysed?
(a) PF_3 (b) $SbCl_3$
(c) $AsCl_3$ (d) NF_3

8. The number of P—O—P bonds in cyclic metaphosphoric acid is
(a) zero (b) three
(c) two (d) four

9. Which of the following will be obtained on heating phosphorus acid? **[NCERT]**
(a) Metaphosphoric acid (b) Orthophosphorous acid
(c) Hypophosphorous acid (d) Phosphene

10. PCl_5 can act as **[NCERT]**
(a) reducing agent
(b) oxidising agent
(c) both reducing as well as oxidising agent
(d) neither reducing nor oxidising agent

11. On comparing with bond angle of PH_3, the bond angle in PH_4^+ ion is **[NCERT]**
(a) greater (b) lesser
(c) equal (d) cannot predict

12. Which of the following oxides of nitrogen is the anhydride of nitrous acid?
(a) NO (b) N_2O_4
(c) N_2O_3 (d) N_2O_5

13. PCl_3 on hydrolysis gives
(a) HPO_3 (b) H_3PO_2
(c) H_3PO_4 (d) H_3PO_3

14. Maximum covalency of nitrogen is **[NCERT Exemplar]**
(a) 3 (b) 5 (c) 4 (d) 6

15. Elements of group-15 form compounds in +5 oxidation state. However, bismuth forms only one well characterised compound in +5 oxidation state. The compound is **[NCERT Exemplar]**
(a) Bi_2O_5 (b) BiF_5 (c) $BiCl_5$ (d) Bi_2S_5

16. In solid state PCl_5 is a **[NCERT Exemplar]**
(a) covalent solid
(b) octahedral structure
(c) ionic solid with $[PCl_6]^+$ octahedral and $[PCl_4]^-$ tetrahedral
(d) ionic solid with $[PCl_4]^+$ tetrahedral and $[PCl_6]^-$ octahedral

17. Nitrogen dioxide
(a) does not dissolve in water
(b) dissolves in water forming nitric acid
(c) dissolves in water to form a mixture of nitrous and nitric acid
(d) dissolves in water to form nitrous acid and gives off oxygen

18. The basicity of orthophosphoric acid is
(a) 2 (b) 4 (c) 3 (d) 5

19. Which oxide is alkaline?
(a) P_2O_3 (b) B_2O_3 (c) Bi_2O_3 (d) As_2O_3

20. Phosphine is produced by adding water to
(a) CaC_2 (b) HPO_3 (c) Ca_3P_2 (d) P_4O_{10}

21. What may be expected to happen when phosphine gas is mixed with chlorine gas?
(a) PCl_5 and HCl are formed and the mixture cools down
(b) $PH_3 \cdot Cl_2$ is formed with warming up
(c) PCl_3 and HCl are formed and the mixture warms up
(d) The mixture only cools down

22. Liquid ammonia is used for refrigeration because
(a) it is basic
(b) it is a stable compound
(c) it has a high dipole moment
(d) it has high heat of vaporisation

23. What would happen when a solution of potassium chromate is treated with an excess of dilute nitric acid?
(a) CrO_4^{2-} is reduced to +3 state of Cr
(b) CrO_4^{2-} is oxidized to +7 state of Cr
(c) $Cr_2O_7^{2-}$ and H_2O are formed
(d) Cr^{3-} and $Cr_2O_7^{2-}$ are formed

24. Which of the following compound show sublimation?
(a) $CaHPO_3$ (b) NH_4Cl
(c) $BaSO_4$ (d) $CaCO_3$

25. In the reaction, $HNO_3 + P_4O_{10} \longrightarrow 4HPO_3 + x$, the product x is
(a) NO_2 (b) N_2O_5 (c) N_2O_3 (d) H_2O

Group 16 Elements and their Compounds

26. The S—S—S bond angle in S_8 molecule is
(a) 109.5° (b) 105° (c) 110° (d) 60°

27. Sulphur in +3 oxidation state is present in
(a) dithionous acid (b) sulphurous acid
(c) thionous acid (d) pyrosulphuric acid

28. Sulphur is present in [NCERT]
(a) Baryte (b) zinc blende
(c) garlic (d) All of these

29. Sulphur on boiling with NaOH solution gives
(a) $Na_2SO_3 + H_2S$ (b) $Na_2S_2O_3 + Na_2S$
(c) $Na_2S_2O_3 + NaHSO_3$ (d) $Na_2SO_3 + SO_2$

30. At room temperature, H_2O is liquid while H_2S is a gas. The reason is
(a) electronegativity of O is greater than S
(b) difference in the bond angles of both the molecules
(c) association takes place in H_2O due to H-bonding while no H-bonding in H_2S
(d) O and S belong to different periods

31. $SO_2 + H_2S \longrightarrow$ product, the final product is
(a) H_2SO_3 (b) H_2SO_4 (c) $H_2S_2O_3$ (d) $H_2O + S$

32. A gas that cannot be collected over water is
(a) SO_2 (b) N_2 (c) O_2 (d) PH_3

33. In the reaction, $HCOOH \xrightarrow{H_2SO_4} CO + H_2O$;

H_2SO_4 acts as
(a) reducing agent (b) oxidising agent
(c) dehydrating agent (d) All of these

34. Which one is known as oil of vitriol?
(a) $H_2S_2O_7$ (b) H_2SO_3 (c) $H_2S_2O_8$ (d) H_2SO_4

35. Bleaching action of SO_2 is due to
(a) reduction (b) hydrolysis
(c) oxidation (d) acidic nature

36. Copper turnings when heated with concentrated sulphuric acid will give
(a) H_2S (b) SO_2 (c) SO_3 (d) O_2

37. Sulphuric acid has great affinity for water because
(a) acid decomposes water
(b) it hydrolyses the acid
(c) it decomposes the acid
(d) acid forms hydrates with water

38. S—S bond is present in
(a) α-$(SO_3)_n$ (b) γ-(S_3O_9)
(c) $H_2S_2O_3$ (d) $H_2S_2O_8$

39. The compound of sulphur used as a solvent in rubber industry is
(a) $SO_2(OH)Cl$ (b) SO_2
(c) SO_3 (d) S_2Cl_2

40. Dry bleach is caused by
(a) Cl_2 (b) SO_2 (c) H_2O_2 (d) O_3

Elements of Group 17 and their Compounds

41. Fluorine reacts with water to give
(a) HF, O_2 and O_3 (b) HF and F_2
(c) HF and O_2 (d) HF and O_3

42. The chief source of iodine in which it is present as sodium iodate is
(a) carnallite
(b) sea weeds
(c) caliche
(d) iodine never exists as sodium iodate

43. Bleaching action of chlorine is due to [NCERT]
(a) Cl (b) O (c) H (d) N

44. Which of the following is strongest oxidising agent?
(a) I_2 (b) Br_2
(c) Cl_2 (d) F_2

45. Chlorine acts as a bleaching agent only in presence of
(a) dry air (b) moisture
(c) sunlight (d) pure oxygen

46. Concentrated HNO_3 reacts with I_2 to gives
(a) HI (b) HOI
(c) HIO_3 (d) $HOIO_2$

47. Among the halogens, the one which is oxidised by nitric acid is
(a) iodine (b) bromine
(c) fluorine (d) chlorine

48. Iodine is formed when potassium iodide reacts with a solution of
(a) $ZnSO_4$ (b) $CuSO_4$
(c) $(NH_4)_2SO_4$ (d) Na_2SO_4

49. Mark the strongest acid
(a) HI (b) HBr
(c) HCl (d) HF

50. Which of the following properties does not correspond to the order?

$$HI < HBr < HCl < HF$$

(a) Thermal stability (b) Reducing power
(c) Ionic character (d) Dipole moment

51. Reduction potentials of some ions are given below. Arrange them in decreasing order of oxidising power.

Ion	ClO_4^-	IO_4^-	BrO_4^-
Reduction potential E^V / V	$E^V = 1.19\,V$	$E^V = 1.65\,V$	$E^V = 1.74\,V$

[NCERT Exemplar]

(a) $ClO_4^- > IO_4^- > BrO_4^-$ (b) $IO_4^- > BrO_4^- > ClO_4^-$
(c) $BrO_4^- > IO_4^- > ClO_4^-$ (d) $BrO_4^- > ClO_4^- > IO_4^-$

52. Metal halide which is insoluble in water is
(a) AgF (b) AgI
(c) KBr (d) $CaCl_2$

53. The mixture of conc. HCl and HNO_3 made in 3 : 1 ratio contains
(a) ClO_2 (b) NOCl
(c) NCl_3 (d) N_2O_4

54. Which one liberates Br_2 from KBr?
(a) I_2 (b) HI (c) Cl_2 (d) SO_2

55. The acid employed for etching of glass is
(a) HCl (b) $HClO_4$
(c) HF (d) aqua regia

56. Which one is the anhydride of $HClO_4$?
(a) ClO_2 (b) Cl_2O_7
(c) Cl_2O (d) Cl_2O_6

57. The reaction of the type $2X_2 + S \longrightarrow SX_4$ is shown by sulphur when X is
(a) fluorine or chlorine
(b) chlorine only
(c) chlorine and bromine only
(d) F, Cl, Br, all

58. The following acids have been arranged in the order of decreasing acid strength. Identify the correct order

ClOH(I) BrOH(II) IOH(III)

(a) I > II > III (b) II > I > III
(c) III > II > I (d) I > III > II

59. Euchlorine is a mixture of
(a) $Cl_2 + ClO_2$ (b) $Cl_2 + Cl_2O$
(c) $Cl_2O_3 + ClO_2$ (d) $Cl_2O + Cl_2O_3$

60. T-shaped interhalogen compound is
(a) ClF_3 (b) ICl
(c) ClF_5 (d) IF_5

61. Which of the following form of interhalogen compounds does not exist?
(a) IF_7 (b) ClF_3
(c) ICl (d) $BrCl_7$

Group 18 Elements and their Compounds

62. Which of the following gases exists more abundantly in nature than the others?
(a) Helium (b) Neon
(c) Argon (d) Krypton

63. Welding of magnesium can be done in an atmosphere of
(a) Xe (b) He (c) Kr (d) Ne

64. Gradual addition of electronic shells in the noble gases causes a decrease in their
(a) ionisation energy (b) density
(c) boiling point (d) atomic radius

65. Noble gases are sparingly soluble in water due to
(a) dipole-dipole interaction
(b) dipole-induced dipole interaction
(c) induced dipole-induced dipole interaction
(d) hydrogen bonding

66. The noble gas which can diffuse through rubber and glass easily is
(a) Xe (b) Ne (c) Ar (d) He

67. The correct order of solubility in water for He, Ne, Ar, Kr, Xe is
(a) Xe > Kr > Ar > Ne > He
(b) Ar > Ne > He > Kr > Xe
(c) He > Ne > Ar > Kr > Xe
(d) Ne > Ar > Kr > He > Xe

68. When the mineral clevite is heated, it give off the inert gas
(a) helium (b) xenon (c) radon (d) argon

69. The noble gas which forms interstitial compounds is
(a) Helium (b) Argon (c) Neon (d) Xenon

70. The noble gas which shows abnormal behaviour in liquid state and behave as super fluid is
(a) Ne (b) He
(c) Ar (d) Xe

71. Which of the following is the life saving mixture for an asthma patient?
(a) Mixture of helium and oxygen
(b) Mixture of neon and oxygen
(c) Mixture of xenon and nitrogen
(d) Mixture of argon and oxygen

72. The noble gas which forms maximum number of compounds is
(a) Ar (b) He (c) Ne (d) Xe

73. XeF_2 on hydrolysis gives
(a) XeO_3 (b) XeO (c) Xe (d) XeO_2

74. Which of the following is not obtained by direct reaction of constituent elements?
(a) XeO_3 (b) XeF_2 (c) XeF_6 (d) XeF_4

75. Which of the following is formed by xenon?
(a) XeF_7 (b) XeF_4 (c) XeF_5 (d) XeF_3

76. Among the following molecule
(i) XeO_3 (ii) $XeOF_4$
(iii) XeF_6
those having same number of lone pairs on Xe are
(a) (i) and (iii) only (b) (i) and (ii) only
(c) (ii) and (iii) only (d) (i), (ii) and (iii)

77. The geometry of $XeOF_4$ molecule is
(a) tetrahedral (b) square pyramidal
(c) square planar (d) octahedral

78. The pair of species having identical shape for molecules of both species is
(a) XeF_2, IF_2^- (b) BF_3, NH_3
(c) CF_4, SF_4 (d) PCl_5, ICl_5

79. Number of $p\pi$ - $d\pi$ bonds present in XeO_4 are
(a) four (b) two (c) three (d) zero

80. Clathrates are
(a) non-stoichiometric compounds
(b) complex compounds
(c) interstitial compounds
(d) ionic compounds

Round II (Mixed Bag)

Only One Correct Option

1. The number of P—O—P bridges in the structure of phosphorus pentoxide and phosphorus trioxide are respectively
(a) 5, 5 (b) 6, 5 (c) 5, 6 (d) 6, 6

2. In compounds of type ECl_3, where E = B, P, As or Bi the angles Cl—E—Cl for different E are in the order
(a) B > P > As > Bi (b) B > P = As = Bi
(c) B < P = As = Bi (d) B < P < As < Bi

3. Ammonia on reaction with hypochlorite anion, can form
(a) NO (b) N_2H_4 (c) NH_4Cl (d) HNO_2

4. Which blue liquid is obtained on reacting equimolar amounts of two gases at –30°C?
(a) N_2O_4 (b) N_2O (c) N_2O_3 (d) N_2O_5

5. The percentage of p-character in the orbitals forming P—P bond in P_4 is
(a) 25 (b) 33
(c) 50 (d) 75

6. $(NH_4)_2Cr_2O_7$ on heating liberates a gas. The same gas will be obtained by
(a) heating NH_4NO_3
(b) heating NH_4NO_2
(c) treating H_2O_2 with $NaNO_2$
(d) treating Mg_3N_2 with H_2O

7. There is no S—S bond in
(a) $S_2O_4^{2-}$ (b) $S_2O_3^{2-}$
(c) $S_2O_5^{2-}$ (d) $S_2O_7^{2-}$

8. What are the conditions to maximize the yield of H_2SO_4 by contact process? **[NCERT]**
(a) Low temperature and high pressure
(b) High temperature and low pressure
(c) High temperature and high pressure
(d) Low temperature and low pressure

9. Sulphur hepto oxide is an anhydride of

(a) $H_2S_2O_8$ (b) $H_2S_2O_7$
(c) H_2SO_4 (d) H_2SO_5

10. The reason why conc. H_2SO_4 is used largely to prepare other acids is that conc H_2SO_4

(a) is highly ionised
(b) is dehydrating agent
(c) has high specific gravity and density
(d) has a high boiling point

11. A substance which gives a yellow precipitate when boiled with an excess of nitric acid and ammonium molybdate and red precipitate with $AgNO_3$ is

(a) orthophosphate (b) pyrophosphate
(c) metaphosphate (d) hypophosphate

12. The following two reactions HNO_3 with Zn are given as (equations are not balanced)

$$\text{Zn} + \text{conc. } HNO_3 \longrightarrow Zn(NO_3)_2 + X + H_2O(A)$$
$$\text{Zn} + \text{dil. } HNO_3 \longrightarrow Zn(NO_3)_2 + Y + H_2O(B)$$

In reactions *A* and *B*, the compounds *X* and *Y* respectively, are

(a) NO_2 and NO (b) NO_2 and NO_2
(c) NO and NO_2 (d) NO_2 and NH_4NO_3

13. Concentrated sulphuric acid can be reduced by

(a) NaCl (b) NaF (c) NaOH (d) NaBr

14. On heating lead (II) nitrate gives a brown gas "*A*". The gas "*A*" on cooling changes to colourless solid "*B*". Solid "*B*" on heating with NO changes to a blue solid "*C*". Identify "*C*". **[NCERT Exemplar]**

(a) NO_2 (b) N_2O_4 (c) N_2O_5 (d) N_2O_3

15. On heating, compound (*A*) gives a gas (*B*) which is a constituent of air. This gas when treated with 3 moles of hydrogen (H_2) in the presence of a catalyst gives another gas (*C*) which is basic in nature. Gas *C* on further oxidation in moist condition gives a compound (*D*) which is a part of acid rain. Identify compound (*D*). **[NCERT Exemplar]**

(a) HNO_2 (b) HNO_3 (c) H_2SO_4 (d) HCl

16. A black compound of manganese reacts with a halogen acid to give greenish yellow gas. When excess of this gas reacts with NH_3 an unstable trihalide is formed. In this process the oxidation state of nitrogen changes from **[NCERT Exemplar]**

(a) -3 to $+3$ (b) -3 to 0
(c) -3 to $+5$ (d) 0 to -3

17. Which of the following dissolves in water but does not give any oxyacid solution?

(a) SO_2 (b) OF_2
(c) SCl_4 (d) SO_3

18. Which one is correct statement?

(a) Basicity of H_3PO_4 and H_3PO_3 is 3 and 3 respectively
(b) Acidity of H_3PO_4 and H_3PO_3 is 3 and 3 respectively
(c) Acidity of H_3PO_4 and H_3PO_3 is 3 and 2 respectively
(d) Basicity of H_3PO_4 and H_3PO_3 is 3 and 2 respectively

19. Correct order of decreasing thermal stability is as

(a) $NH_3 > PH_3 > AsH_3 > SbH_3$
(b) $PH_3 > NH_3 > AsH_3 > SbH_3$
(c) $AsH_3 > PH_3 > NH_3 > SbH_3$
(d) $SbH_3 > AsH_3 > PH_3 > NH_3$

20. Which of the following is not oxidised by O_3?

(a) KI (b) $FeSO_4$
(c) $KMnO_4$ (d) K_2MnO_4

21. NH_3 gas is dried over

(a) CaO (b) HNO_3
(c) P_2O_5 (d) $CuSO_4$

22. The solubility of iodine in water increases in presence of

(a) chloroform (b) alcohol
(c) potassium iodide (d) sodium hydroxide

23. Which is the most volatile compound?

(a) HCl (b) HI (c) HBr (d) HF

24. Which one below is a pseudohalide?

(a) I_3^- (b) IF^- (c) ICl (d) CN^-

25. A dark brown solid (*X*) reacts with NH_3 to form a mild explosive which decomposes to give a violet coloured gas. (*X*) also reacts with H_2 to give an acid (*Y*). (*Y*) can also be prepared by heating its salt with H_3PO_4. *X* and *Y* are

(a) Cl_2, HCl (b) SO_2, H_2SO_4
(c) Br_2, HBr (d) I_2, HI

26. A green yellow gas reacts with an alkali metal hydroxide to form a halate which can be used in fireworks and safety matches. The gas and halate respectively are

(a) Br_2, $KBrO_3$ (b) Cl_2, $KClO_3$
(c) I_2, $NaIO_3$ (d) Cl_2, $NaClO_3$

27. Which reaction is not feasible?

(a) $2KI + Br_2 \longrightarrow 2KBr + I_2$
(b) $2KBr + I_2 \longrightarrow 2KI + Br_2$
(c) $2KBr + Cl_2 \longrightarrow 2KCl + Br_2$
(d) $2H_2O + 2F_2 \longrightarrow 4HF + O_2$

28. The least stable anion of oxo-acids of chlorine is

(a) ClO^- (b) ClO_2^- (c) ClO_3^- (d) ClO_4^-

29. XeO_2F_2 is obtained by partial hydrolysis of

(a) $XeOF_4$ (b) XeF_6
(c) Both (a) and (b) (d) None of these

30. Which of the following compounds can not be stored in glass vessels?

(a) XeF_4 (b) XeF_6
(c) XeO_3 (d) XeF_2

31. Which one of the following statements regarding helium is incorrect?

(a) It is used to produce and sustain powerful super conducting magnets
(b) It is used in gas-cooled nuclear reactors
(c) It is used to fill gas balloons instead of hydrogen because it is lighter and non-inflammable
(d) It is used as a cryogenic agent for carrying out experiments at low temperature

32. Bleaching powder is disinfectant for purification of water, when water born germs are killed, but disinfectant activity is destroyed. It is due to its disproportionation into

(a) $CaCl_2$ and Cl_2 (b) $CaCl_2$ and $Ca(ClO_3)_2$
(c) CaO and Cl_2 (d) CaO, Cl_2 and $CaCl_2$

33. $HClO_4 + P_2O_5 \longrightarrow (A)$ and (B)
A and *B* are

(a) $HClO_3, H_3PO_4$ (b) $Cl_2O_6 + HPO_3$
(c) ClO_2, H_2PO_4 (d) Cl_2O_7, HPO_3

34. Which of the following does not exist?

(a) $KrF^-[SbF_6]^-$ (b) $[KrF_3]^-[SbF_4]^+$
(c) $KrF^+[MoOF_5]$ (d) $KrF^+[WOF_5]^-$

35. Perxenate ion is

(a) XeO_6^{4-} (b) $HXeO_4^-$
(c) XeO_4^{2-} (d) XeO_4^-

36. The stability of interhalogen compounds follows the order

(a) $IF_3 > BrF_3 > ClF_3$ (b) $BrF_3 > IF_3 > ClF_3$
(c) $ClF_3 > BrF_3 > IF_3$ (d) $ClF_3 > IF_3 > BrF_3$

37. Xenon hexafluoride reacts with silica to form a xenon compound *X*. The oxidation state of xenon in *X* is

(a) +2 (b) +4
(c) +6 (d) 0

38. The electron affinity values (in kJ mol^{-1}) of three halogens *X*, *Y* and *Z* are respectively – 349, – 333 and – 325. Then *X*, *Y* and *Z* respectively, are

(a) F_2, Cl_2 and Br_2 (b) Cl_2, F_2 and Br_2
(c) Cl_2, Br_2 and F_2 (d) Br_2, Cl_2 and F_2

39. The formation of $O_2^+[PtF_6]^-$ is the basis for the formation of xenon fluorides. This is because

(a) O_2 and Xe have comparable sizes
(b) both O_2 and Xe are gases
(c) O_2 and Xe have comparable ionisation energies
(d) Both (a) and (b)

40. A metal, *M* forms chlorides in its +2 and +4 oxidation states. Which of the following statements about these chlorides is correct?

(a) MCl_2 is more volatile than MCl_4
(b) MCl_2 is more soluble in anhydrous ethanol than MCl_4
(c) MCl_2 is more ionic than MCl_4
(d) MCl_2 is more easily hydrolysed than MCl_4

41. What products are expected from the disproportionation reaction of hypochlorous acid?

(a) $HClO_3$ and Cl_2O (b) $HClO_2$ and $HClO_4$
(c) HCl and Cl_2O (d) HCl and $HClO_3$

42. Fluorine exhibits an oxidation state of only –1 because

(a) it can readily accept an electron
(b) it is strongly electronegative
(c) it is a non-metal
(d) it belongs to halogen family

43. D_3 line observed in the yellow region of the sun's spectrum is due to

(a) Na (b) Ne
(c) Kr (d) He

More than One Correct Option

44. If chlorine gas is passed through hot NaOH solution, two changes are observed in the oxidation number of chlorine during the reaction. These are … and … [**NCERT** Exemplar]

(a) 0 to +5 (b) 0 to +3
(c) 0 to –1 (d) 0 to +1

45. Which of the following options are not in accordance with the property mentioned against them? [**NCERT** Exemplar]

(a) $F_2 > Cl_2 > Br_2 > I_2$	Oxidising power
(b) $MI > MBr > MCl > MF$	Ionic character of metal halide
(c) $F_2 > Cl_2 > Br_2 > I_2$	Bond dissociation enthalpy
(d) $HI < HBr < HCl < HF$	Hydrogen-halogen bond strength

46. Which of the following statements are correct for SO_2 gas? [**NCERT** Exemplar]

(a) It acts as bleaching agent in moist conditions
(b) Its molecule has linear geometry
(c) Its dilute solution is used as disinfectant
(d) It can be prepared by the reaction of dilute H_2SO_4 with metal sulphide

47. Concentrated sulphuric acid is

(a) oxidising agent (b) hygroscopic
(c) efflorescent (d) sulphonating agent

48. Which of the following statements is/are correct?

(a) He_{II} has much lower entropy

(b) Transition of He_I to He_{II} takes place, across the line $\lambda - \lambda' = 2.2$ K

(c) It has very high viscosity

(d) He_{II} is unique liquid that exhibits superconductivity

Assertion and Reason

Directions (Q. Nos. 49 to 53) *Each of these questions contains two statements : Statement* I (*Assertion*) *and Statement* II (*Reason*). *Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes* (*a*), (*b*), (*c*), (*d*) *given below :*

(a) Statement I is true; Statement II is true; Statement II is a correct explanation for Statement I.

(b) Statement I is true; Statement II is true; Statement II is not a correct explanation for Statement I.

(c) Statement I is true; Statement II is false.

(d) Statement I is false; Statement II is true.

49. **Statement I** HNO_3 makes iron passive.

Statement II HNO_3 forms a protective layer of ferric nitrate on the surface of iron. [**NCERT** Exemplar]

50. **Statement I** Red phosphorus is less volatile than white phosphorus.

Statement II Red phosphorus has a discrete tetrahedral structure.

51. **Statement I** Oxygen is more electronegative than sulphur, yet H_2S is acidic, while H_2O is neutral.

Statement II H—S bond is weaker than O—H bond.

52. **Statement I** The aqueous solution of XeF_2 is powerful oxidising agent.

Statement II The hydrolysis of XeF_2 is slow in dilute acid but rapid in basic solution.

53. **Statement I** Helium is the only substance that can't be solidified at atmospheric pressure.

Statement II The zero point energy of helium is very high.

Comprehension Based Questions

Directions (Q. Nos. 54 to 56) Due to the presence of two lone pairs of electrons on the central atom, hydrides of group 16 elements have bent (V) shapes. The central atom in these hydrides is sp^3 hybridized. Due to strong H-bonding m.p. and b.p. of hydride of oxygen are very high. On moving down the group, the covalent character increases. This can be explained on the basis of Fajan's rule, which states that the tendency to form covalent bonds increases as the size of the anion M^{2-} increases. As the size of the atom in H_2M increases, the strength of H—M bond decreases. Hence, the tendency to release hydrogen as proton increases down the group.

54. Bond angle is minimum for

(a) H_2Se (b) H_2S (c) H_2Te (d) H_2O

55. Which one of the following hydrides is most acidic?

(a) H_2S (b) H_2Te (c) H_2O (d) H_2Se

56. Which of the following hydrides has the lowest boiling point?

(a) H_2Se (b) H_2S (c) H_2O (d) H_2Te

Directions (Q. Nos. 57 to 59) The trihalides of this group elements are predominantly covalent and have pyramidal structures, with a lone pair of electrons in the fourth orbital. Except NF_3 and PF_3, the trihalides are readily hydrolysed by water. They are Lewis bases because of the presence of lone pair of electrons. Due to absence of d-orbitals in its valence shell, nitrogen does not form pentahalides, while P, As and Sb form pentahalides due to unsymmetrical shape where some bond angles are of 90° and others are of 120°. PCl_5 is not very stable. It behave as a good chlorinating agent.

57. Which of the following compound is not known?

(a) NCl_5 (b) NI_3

(c) $SbCl_3$ (d) NCl_3

58. Which of the following halides undergoes hydrolysis?

(a) PF_5 (b) NCl_3

(c) NF_3 (d) PF_3

59. Which of the following is the weakest base?

(a) NF_3 (b) NCl_3

(c) NI_3 (d) NBr_3

Previous Years' Questions

60. The molecule having smaller bond angle is [AIEEE 2012]

(a) NCl_3 (b) $AsCl_3$

(c) $SbCl_3$ (d) PCl_3

61. Which of the following on thermal decomposition yields a basic as well as acidic oxide? [AIEEE 2012]

(a) $NaNO_3$ (b) $KClO_3$

(c) $CaCO_3$ (d) NH_4NO_3

62. Which of the following statement is wrong? [AIEEE 2011]

(a) The stability of hydrides increases from NH_3 to BiH_3 in group 15 of the Periodic table

(b) Nitrogen can't from $d\pi$-$p\pi$ bond

(c) Singe N—N bond is weaker than the single P—P bond.

(d) N_2O_4 has two resonance structure

63. Which of the following statements regarding sulphur is incorrect? [AIEEE 2011]

(a) S_2 molecule is paramagnetic

(b) The vapour at 200°C consists mostly of S_8 rings

(c) At 600°C the gas mainly consists of S_2 molecules

(d) The oxidation state of sulphur is never less than +4 in its compounds

64. Which one of the following reaction of xenon compounds is not feasible? [AIEEE 2009]

(a) $XeO_3 + 6HF \longrightarrow XeF_6 + 3H_2O$

(b) $3XeF_4 + 6H_2O \longrightarrow 2Xe + XeO_3 + 12HF + 1.5\,O_2$

(c) $2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$

(d) $XeF_6 + RbF \longrightarrow Rb[XeF_7]$

65. Identify the incorrect statement among the following. [AIEEE 2007]

(a) Ozone reacts with SO_2 to give SO_3

(b) Silicon reacts with NaOH (*aq*) in the presence of air to give Na_2SiO_3 and H_2O

(c) Cl_2 reacts with excess of NH_3 to give N_2 and HCl

(d) Br_2 reacts with hot and strong NaOH solution to give NaBr, $NaBrO_4$ and H_2O

66. Which of the following statements is true? [AIEEE 2006]

(a) H_3PO_3 is a stronger acid than H_2SO_3

(b) In aqueous medium HF is a stroonger acid than HCl

(c) $HClO_4$ is weaker acid than $HClO_3$

(d) HNO_3 is a stronger acid than HNO_2

67. The number of hydrogen atom (s) attached to phosphorus atom in hypophosphorous acid is [AIEEE 2005]

(a) three (b) one (c) two (d) zero

68. The substance used in Holme's signals of the ship is a mixture of [AIEEE 2013]

(a) $CaC_2 + Ca_3P_2$ (b) $Ca_3(PO_4)_2 + Pb_3O_4$

(c) $H_3PO_4 + CaCl_2$ (d) $NH_3 + HOCl$

69. Concentrated hydrochloric acid when kept in open air sometimes produces a cloud of white fumes. The explanation for it is that [AIEEE 2003]

(a) concentrated hydrochloric acid emits strongly smelling HCl gas all the time

(b) oxygen in air reacts with the emitted HCl gas to form a cloud of chlorine gas

(c) strong affinity of HCl gas for moisture in air results in forming of droplets of liquid solution which appears like a cloudy smoke

(d) due to strong affinity for water, concentrated hydrochloric acid pulls moisture of air towards itself. This moisture forms droplets of water and hence, the cloud

70. PCl_3 and PCl_5 both exist; NCl_3 exist but NCl_5 does not exist. It is due to [AIEEE 2002]

(a) lower electronegativity of P and N

(b) lower tendency of N to form covalent bond

(c) availability of vacant *d*-orbital in P but not in N

(d) statement is itslelf incorrect

Answers

Round I

1. (b)	**2.** (b)	**3.** (d)	**4.** (b)	**5.** (b)	**6.** (a)	**7.** (d)	**8.** (b)	**9.** (d)	**10.** (b)
11. (a)	**12.** (c)	**13.** (d)	**14.** (c)	**15.** (b)	**16.** (d)	**17.** (c)	**18.** (c)	**19.** (c)	**20.** (c)
21. (a)	**22.** (d)	**23.** (c)	**24.** (b)	**25.** (b)	**26.** (b)	**27.** (a)	**28.** (d)	**29.** (b)	**30.** (c)
31. (d)	**32.** (a)	**33.** (c)	**34.** (d)	**35.** (a)	**36.** (b)	**37.** (d)	**38.** (c)	**39.** (d)	**40.** (d)
41. (a)	**42.** (c)	**43.** (b)	**44.** (d)	**45.** (b)	**46.** (c)	**47.** (a)	**48.** (b)	**49.** (a)	**50.** (b)
51. (c)	**52.** (b)	**53.** (b)	**54.** (c)	**55.** (c)	**56.** (b)	**57.** (a)	**58.** (a)	**59.** (a)	**60.** (a)
61. (d)	**62.** (c)	**63.** (b)	**64.** (a)	**65.** (b)	**66.** (d)	**67.** (a)	**68.** (a)	**69.** (a)	**70.** (b)
71. (a)	**72.** (d)	**73.** (c)	**74.** (a)	**75.** (b)	**76.** (d)	**77.** (b)	**78.** (a)	**79.** (a)	**80.** (a)

Round II

1. (d)	**2.** (a)	**3.** (b)	**4.** (c)	**5.** (d)	**6.** (b)	**7.** (d)	**8.** (a)	**9.** (a)	**10.** (d)
11. (a)	**12.** (d)	**13.** (d)	**14.** (d)	**15.** (b)	**16.** (a)	**17.** (b)	**18.** (d)	**19.** (a)	**20.** (c)
21. (a)	**22.** (c)	**23.** (a)	**24.** (d)	**25.** (d)	**26.** (b)	**27.** (b)	**28.** (a)	**29.** (c)	**30.** (b)
31. (c)	**32.** (b)	**33.** (d)	**34.** (b)	**35.** (a)	**36.** (a)	**37.** (c)	**38.** (b)	**39.** (c)	**40.** (c)
41. (d)	**42.** (b)	**43.** (d)	**44.** (a,c)	**45.** (b,c)	**46.** (a,c)	**47.** (b,d)	**48.** (a,b,d)	**49.** (c)	**50.** (c)
51. (a)	**52.** (b)	**53.** (a)	**54.** (c)	**55.** (b)	**56.** (b)	**57.** (a)	**58.** (b)	**59.** (a)	**60.** (c)
61. (c)	**62.** (a)	**63.** (d)	**64.** (a)	**65.** (d)	**66.** (d)	**67.** (c)	**68.** (a)	**69.** (b)	**70.** (c)

the Guidance

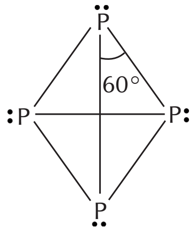
Round I

2. Because of very low ignition temperature (303K) of phosphorus, it is always kept under water.

3. $P_4 + 6H_2SO_4 \longrightarrow 4H_3PO_4 + 6SO_2$

4. White phosphorus, is soluble in CS_2 whereas red phosphorus is insoluble in it.

5. P_4 molecule,



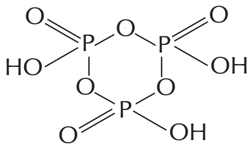
Bond angle = 60°

Six P—P single bonds, lone pair = 4

6. In N_2O_5, the oxidation state of N is +5. Further increase in oxidation state is not possible. That's why its does not behave as reducing agent.

7. Due to absence of *d*-orbitals in N-atom, it cannot accept electrons from H_2O for hydrolysis of NF_3.

8.

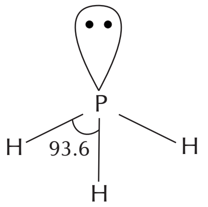


Cyclometa phosphoric acid $(HPO_3)_3$

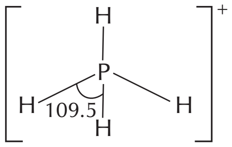
9. $\underset{\text{orthophosphorous acid}}{4H_3PO_3} \longrightarrow \underset{\text{orthophosphoric acid}}{3H_3PO_4} + \underset{\text{phosphene}}{PH_3}$

10. In PCl_5, the oxidation number of P is +5, *i.e.*, maximum which cannot be increased further. So PCl_5 cannot behave as a reducing agent. But it can decrease its oxidation number from +5 to +3, so it can behave as an oxidising agent.

11. In both PH_4^+ and PH_4, P is sp^3 hybridised. In PH_4^+, all the four orbitals are bonded whereas in PH_4, there is a lone pair of electron too. Due to lone pair-bonded pair repulsion in PH_4, the bond angle is less than 109.5°.



PH_3 (pyramidal)



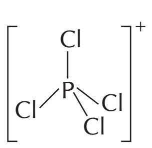
PH_4^+ (tetrahedral)

13. $3H_2O + PCl_3 \longrightarrow H_3PO_3 + 3HCl$

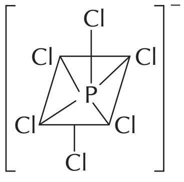
14. Due to absence of *d*-orbital, nitrogen show maximum covalency of 4 in NH_4^+. Rest of group 15 members can show maximum 5 covalency.

15. Bismuth forms BiF_5 only in which its oxidation state is +5.

16. Solid PCl_5 shows ionic lattices. It has tetrahedral cations $[PCl_4]^+$ and octahedral anions $[PCl_6]^-$.



$[PCl_4]^+$



$[PCl_6]^-$

19. $\underbrace{P_2O_3 \quad A_2O_3 \quad B_2O_3}_{\text{acidic oxides}} \quad \underbrace{Bi_2O_3}_{\text{alkaline}}\}$ as Bi is most metallic among the group.

20. $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$

21. $PH_3 + 4Cl_2 \longrightarrow PCl_5 + 3HCl$

22. Liquid ammonia is used in refrigeration because it has high heat of vaporisation.

23. $2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$

25. $4HNO_3 + P_4O_{10} \longrightarrow 4HPO_3 + 2N_2O_5$

27. Dithionous acid $(H_2S_2O_4)$ has sulphur in +3 oxidation state.

29. $3S + 4NaOH \xrightarrow{\text{Boiling}} Na_2S_2O_3 + Na_2S$

30. H_2O contain hydrogen bond while no hydrogen bonding is present in H_2S.

31. SO_2 acts as an oxidising agent particularly when treated with stronger reducing agents. SO_2 oxidises H_2S into S.

$$SO_2 + 2H_2S \longrightarrow 2H_2O + S$$

32. SO_2 is soluble in water.

$$H_2O + SO_2 \longrightarrow \underset{\text{sulphurous acid}}{H_2SO_3}$$

33. H_2SO_4 acts as dehydrating agent in the following reaction.

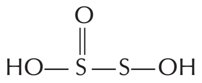
$$HCOOH \xrightarrow{H_2SO_4} CO + H_2O$$

35. $2H_2O + SO_2 \longrightarrow H_2SO_4 + \underset{\text{[nascent hydrogen]}}{2[H]}$

Coloured flower + $2[H] \longrightarrow$ Colourless flower

37. The great affinity of H_2SO_4 for water is because it forms hydrates with water.

38. $H_2S_2O_3$,



$$HO-\overset{\overset{\displaystyle O}{\|}}{S}-S-OH$$

41. $2F_2 + 2H_2O \longrightarrow 4HF + O_2$

$3F_2 + 3H_2O \longrightarrow O_3 + 6HF$

42. Caliche is crude chile salt petre ($NaNO_3$) which contains about 0.02% iodine as sodium iodate ($NaIO_3$), from which iodine is extracted.

44. Fluorine is the strongest oxidising agent. It will oxidise other halide ions to halogens in solution or even in dry.

$$F_2 + 2X^- \longrightarrow 2F^- + X_2$$

45. $Cl_2 + H_2O \longrightarrow 2HCl + [O]$ nascent oxygen

46. $I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$

47. Reducing properties increase from F to I so, I is oxidised by nitric acid.

$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

48. $CuSO_4 + 2KI \longrightarrow CuI_2 + K_2SO_4$

$$2CuI_2 \longrightarrow \underset{\text{cuprous iodide}}{2CuI} + I_2$$

49. HI is the strongest acid because H—I bond is weakest bond.

51. Oxidising power of species is directly proportional to reduction potentials. Therefore, order of oxidising power of given ions is as follows

Ion $\quad BrO_4^- > IO_4^- > ClO_4^-$

$E_c(V)\quad 1.74 \quad 1.65 \quad 1.19$

52. AgI is a covalent compound so it is insoluble in water.

54. $Cl_2 + 2KBr \longrightarrow Br_2 + 2KCl$

56. $2HClO_4 \longrightarrow H_2O + Cl_2O_7$

57. Fluorine and chlorine are more electronegative than sulphur, so they can displace it form its salt.

58. Acid strength decreases from HClO to HIO as the electronegativity of halogen decrease.

60. ClF_3, where Cl is sp^3d hybridised, has a T-shape structure due to presence of two lone pairs of electrons on Cl atom.

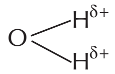
61. Chlorine, being only a slightly stronger oxidising agent than bromine cannot oxidise it to +7 oxidation state as is required for the formation of the compound $BrCl_7$.

62.

Gas	Abundance in air by volume (ppm)
Helium	5.2
Neon	18.2
Argon	93.4
Krypton	1.1
Xenon	0.09

63. Welding of Mg is done in the atmosphere of He due to its inert and non-inflammable nature.

64. As the number of shells increases, size increases and the effective nuclear charge on the outermost electron decreases. Thus, IE decreases.

65. Dipole of water  induces dipole in noble gases which interact and causes solubility in water.

66. He, because of its small size can diffuse through rubber, glass PVC etc. easily.

67. Solubility increases on moving down the group.

Xe > Kr > Ar > Ne > He

68. Clevite is uranium mineral, on heating it gives He.

69. Only He forms interstitial compounds since, the atomic size of He is smallest and matches the size of the interstices available is the lattice of most of the heavy metals.

73. $2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$

74. XeF_2, XeF_4 and XeF_6 can be directly prepared.

$$Xe + F_2 \xrightarrow[\text{673 K}]{\text{Ni tube}} XeF_2;$$

$$Xe + 2F_2 \xrightarrow[\text{6 atm}]{\text{673 K}} XeF_4$$

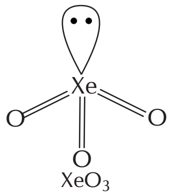
$$Xe + 3F_2 \xrightarrow[\text{50–60 atm}]{\text{523–573 K}} XeF_6$$

XeO_3 is obtained by the hydrolysis of XeF_6.

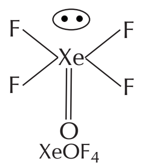
$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

75. XeF_2, XeF_4, XeF_6 are formed by xenon.

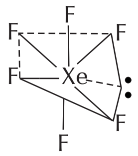
76.



XeO_3



$XeOF_4$



XeF_6

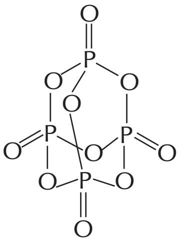
78. Both XeF_2 and IF_2^- are linear species but the central atoms Xe and I undergo sp^3d hybridisation with all the three equatorial positions occupied by the lone pairs of electrons.

79. XeO_4 is formed by promoting one 5*s* and three 5*p*-electrons of Xe to higher energy. 5*d* orbitals giving eight unpaired orbitals hybridize to give sp^3 hybridisation which form sigma bonds with four O atoms. The four unhybridised singly occupied 5*d* orbitals form four $p\pi$ - $d\pi$ bonds with oxygen atoms.

80. Clathrates are non-stoichiometric compounds where the ratio of guest and host molecules does not correspond to ideal chemical formula.

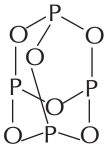
Round II

1. P_2O_5, *i.e.*, P_4O_{10}



$\Rightarrow$ Six P—O—P bridges

P_2O_3 *i.e.*, P_4O_6



$\Rightarrow$ Six P—O—P bridges

2. B > P > As > Bi

As we go down the group, bond angle decreases, since the repulsion between the bonded pairs of electrons decreases.

3. $3NH_3 + OCl^- \longrightarrow NH_2-NH_2 + NH_4Cl + OH^-$

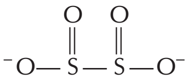
4. $NO(g) + NO_2(g) \longrightarrow N_2O_3(l)$

5. In P_4 each P is sp^3 hybridised so that the percentage of *p*-character in these orbitals is 75%.

6. $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2\uparrow + Cr_2O_3 + 4H_2O$

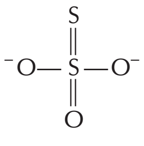
$NH_4NO_2 \longrightarrow N_2\uparrow + 2H_2O$

7. (a) $S_2O_4^{2-}$



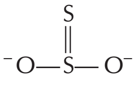
$^-O-\overset{\overset{O}{\|}}{S}-\overset{\overset{O}{\|}}{S}-O^-$

(b) $S_2O_3^{2-}$



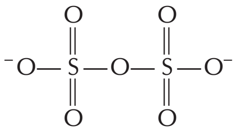
$^-O-\underset{\underset{O}{\|}}{\overset{\overset{S}{\|}}{S}}-O^-$

(c) $S_2O_2^{2-}$



$^-O-\overset{\overset{S}{\|}}{S}-O^-$

(d) $S_2O_7^{2-}$



$^-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O^-$

8. The key step in the manufacture of H_2SO_4 is catalytic oxidation of SO_2 to produce SO_3 in presence of V_2O_5.

$$2\,SO_2\,(g) + O_2\,(g) \underset{}{\overset{V_2O_5,\ 720\text{ K},\ 2\text{ bar}}{\rightleftharpoons}} 2\,SO_3(g)\,;$$

$$\Delta_r H^\circ = -196.6\text{ kJ mol}^{-1}$$

The reaction is exothermic, reversible and the forward reaction results in the decrease in volume. Thus according to Le-Chatelier's principle, the forward reaction should be favoured by **low temperature** and **high pressure**. But the temperature should not be very low otherwise the rate of reaction will become very slow.

In practise, H_2SO_4 is manufactured at 720 K temperature, 2 bar pressure and in the presence of V_2O_5 as catalyst.

9. $S_2O_7 + H_2O \longrightarrow H_2S_2O_8$

10. Concentrated H_2SO_4 is less volatile, *i.e.*, it has high boiling point.

11. Orthophosphate + Amm. molybdate $\xrightarrow[\Delta]{HNO_3}$ yellow ppt.

$\downarrow + AgNO_3$

Red ppt.

12. $Zn + \text{conc. } 4HNO_3 \longrightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$

$4Zn + \text{dil. } 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$

13. Concentrated sulphuric acid, being a strong acid, oxidises bromides and iodides but not chlorides and fluorides since, the later are more electronegative. Hence, it can be reduced only by NaBr among the given options.

$$H_2\overset{+6}{S}O_4 + 2Na\overset{-1}{Br} \longrightarrow NaH\overset{+6}{S}O_4 + H\overset{-1}{Br}$$

$$2H\overset{-1}{Br} + H_2\overset{+6}{S}O_4 \longrightarrow 2H_2O + \overset{0}{Br_2} + \overset{+4}{S}O_2$$

Reduction

14. $\underset{\text{lead nitrate}}{Pb\,(NO_3)_2} \xrightarrow[673\text{ K}]{\Delta} 2PbO + \underset{\substack{\text{brown}\\ [A]}}{4NO_2(g)}$

$$2NO_2(g) \underset{\text{Heating}}{\overset{\text{Cooling}}{\rightleftharpoons}} \underset{\text{colourless } [B]}{N_2O_4(g)}$$

$$2NO + N_2O_4 \xrightarrow{250\text{ K}} \underset{\text{blue } [C]}{2N_2O_3(s)}$$

15. The main constituent of air are nitrogen (78%) and oxygen (21%). Only N_2 reacts with three moles of H_2 in the presence of a catalyst to give NH_3 (ammonia) which is a gas having basic nature. On oxidation NH_3 gives NO_2 which is a part of acid rain. So the compounds *A* to *D* are as

$$A = NH_4NO_2;\ B = N_2;\ C = NH_3;\ D = HNO_3$$

16. $$\underset{\substack{\text{manganese oxide}\\ \text{(black)}}}{MnO_2} + H_2SO_4 + 2HCl \longrightarrow MnSO_4 + 2H_2O + \underset{\substack{\text{chlorine gas}\\ \text{(greenish yellow)}}}{Cl_2 \uparrow}$$

$$\underset{\text{ammonia}}{NH_3} + 3Cl_2 \longrightarrow \underset{\substack{\text{nitrogen trichloride}\\ \text{(unstable and explosive)}}}{NCl_3} + 3HCl$$

NH_3 Let the oxidation state of $N = x$

$$x + 3(+1) = 0$$
$$x = -3$$

NCl_3 Let the oxidation state of $N = y$

$$y + 3(-1) = 0$$
$$y = +3$$

Hence, in given process, oxidation state of nitrogen changes from −3 to +3.

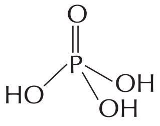
17. OF_2 dissolves in water but does not give any oxyacid solution while SO_2, SCl_4 and SO_3 give oxyacid solution in water.

$$SO_2 + H_2O \longrightarrow \underset{\text{sulphurous acid}}{H_2SO_3}$$

$$SCl_4 + 3H_2O \longrightarrow \underset{\text{sulphurous acid}}{H_2SO_3} + 4HCl$$

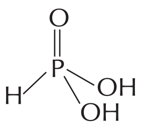
$$SO_3 + H_2O \longrightarrow \underset{\text{sulphuric acid}}{H_2SO_4}$$

18. Orthophosphoric acid (H_3PO_4) is a tribasic acid because it has three replaceable hydrogen atoms. Hence, the basicity of H_3PO_4 is 3. Its structure is as



H_3PO_4 (tribasic acid)

While phosphorous acid (H_3PO_3) is a dibasic acid because it has two replaceable hydrogen atom. Hence, the basicity of H_3PO_3 is 2. Its structure is as



H_3PO_3 (dibasic acid)

19. The thermal stability of the hydrides of nitrogen family or group 15 elements decreases on moving downwards in the group. Therefore, NH_3 is the most stable and BiH_3 is the least stable. The stability of the hydrides of group 15 elements decreases in the order

$$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$$

20. (a) $$2KI + H_2O + O_3 \longrightarrow 2KOH + O_2 + I_2$$

oxidised

(b) $$2FeSO_4 + H_2SO_4 + O_3 \longrightarrow Fe_2(SO_4)_3 + H_2O + O_2$$

oxidised

(c) $$KMnO_4 + O_3 \longrightarrow \text{No reaction}$$

because in $KMnO_4$, oxidation state of Mn is +7 and it is the highest oxidation state of Mn, so $KMnO_4$ is not oxidised by ozone.

(d) $$2K_2MnO_4 + H_2SO_4 + O_3 \longrightarrow 2KMnO_4 + K_2SO_4 + H_2O + O_2$$

oxidised

21. ∵ NH_3 reacts with P_2O_5 or $CaCl_2$ or conc. H_2SO_4.

∴ It cannot be dried over either of them.

$CuSO_4$ and HNO_3 are not drying agent. NH_3 can be dried over CaO only because it is a drying agent with which it does not react.

22. Iodine has the least affinity for water and is only slightly soluble in it. However, it dissolves in 10% aqueous solution of KI due to the formation of a complex ion *i.e.*, I_3^-

$$I_2 + KI \rightleftharpoons KI_3$$

or $$I_2 + I^- \rightleftharpoons I_3^-$$

(Complex ion)

23.

Hydride	HF	HCl	HBr	HI
B. pt (in K)	293	189	206	238

Because of having low boiling point HCl is more volatile..

25. $X = I_2$, $Y = HF$

$$3I_2 + 2NH_3 \longrightarrow \underset{\text{(explosive)}}{NH_3 \cdot NI_3}$$

$$8NI_3 \cdot NH_3 \longrightarrow 5N_2 + I_2 + 6NH_4I$$

$$I_2 + H_2 \longrightarrow \underset{(Y)}{2HI}$$

$$3NaI + H_3PO_4 \xrightarrow{\Delta} Na_3PO_4 + 3HI$$

26. A halate will be formed from halogen and the greenish yellow gas is Cl_2. The halate which is used in fireworks and safety matches is $KClO_3$.

$$3Cl_2 + 6KOH \longrightarrow KClO_3 + 5HCl + 3H_2O$$

27. I_2 cannot oxidise Br^- to Br_2.

28. The thermal stability of the anions of oxo-acids of chlorine increase with increasing oxidation number of halogen.

29. $$XeOF_4 + H_2O \longrightarrow XeO_2F_2 + 2HF$$

$$XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$$

30. XeF_6 cannot be stored in glass vessels because it reacts with SiO_2 of the glass to give highly explosive XeO_3.

$$2XeF_6 + 3SiO_2 \longrightarrow 2XeO_3 + 3SiF_4$$

31. Helium is twice as heavy as hydrogen, its lifting power is 92% of that of hydrogen. Helium has the lowest melting point of any element which makes liquid helium an ideal coolant for many extremely low temperature application such as crystals, a sophisticated measuring instrument based on super conducting magnet and cryogenic research where, temperature close to absolute zero are needed.

32. $CaCl(OCl) \longrightarrow Ca(ClO_3)_2 + CaCl_2$

33. $2HClO_4 + P_2O_5 \longrightarrow Cl_2O_7 + 2HPO_3$

34. KrF_2 is a F^- donor and form complexes with F^- acceptors where, only cationic species or Kr will be present.

35. XeO_6^{4-} ion is perxenate.

36. Due to electronegativity difference, the stability of interhalogen compounds follows following the order

$$IF_3 > BrF_3 > ClF_3$$

37. Xenon hexafluoride reacts with silica to form $XeOF_4$ as

$$2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$$

The oxidation state of xenon in $XeOF_4$ is calculated as

$$\overset{x}{Xe}\,\overset{-2-1}{OF_4}$$

$$x + (-2) + 4 \times (-1) = 0$$
$$x - 2 - 4 = 0$$
$$x = +6$$

38. The electron affinity (in kJ/mol)

Fluorine = 332.6
Chlorine = 348.5
Bromine = 324.7
Iodine = 295.5

Chlorine has highest electron affinity value.

So, according to question the correct order of electron affinity will be

$$Cl_2 > F_2 > Br_2$$

39. The first ionisation energy of xenon is quite close to that of oxygen and the molecular diameter of xenon and oxygen are almost identical.

Based on the above facts it is suggested that as oxygen combines with PtF_6, so xenon should also form similar compound with PtF_6.

40. MCl_2; oxidation state of $M = +2$

MCl_4; oxidation state of $M = +4$

Higher the oxidation state, smaller the size.

Greater the polarizing power, greater the covalent characteristics.

Hence, MCl_4 is more covalent and MCl_2 is more ionic.

41. $3HOCl \longrightarrow 2HCl + HClO_3$

42. Fluorine exhibits an oxidation state of only –1 because it is most electronegative element. (maximum electronegativity in the Periodic Table).

43. In the yellow region of sun's spectrum, observed D_3 lines are due to He.

44. $$3\overset{0}{Cl_2} + \underset{\substack{\text{(hot and}\\\text{concentrated)}}}{6NaOH} \longrightarrow \underset{\substack{\text{sodium}\\\text{chloride}}}{5Na\overset{-1}{Cl^-}} + \underset{\substack{\text{sodium}\\\text{chlorate}}}{Na\overset{+5}{Cl}O_3} + 3H_2O$$

Hence, oxidation number of chlorine changes from 0 to –1 and 0 to +5.

45. The ionic character of $M—X$ bond decreases as the size of halogen atom increases.

$$MF > MCl > MBr > MI$$

with the increase of size, the bond length increases from F to I. Since, the bond length of fluorine is minimum, its bond dissociation enthalpy should be highest. However, the bond dissociation enthalpy of fluorine is less than Cl—Cl and Br—Br due to the high interelectronic repulsions between non-bonding electrons in the 2*p*-orbitals of fluorine. Hence, the correct order of bond dissociation enthalpy is

$$Cl—Cl > Br—Br > F—F > I—F$$

46. (a) In the presence of moisture, SO_2 liberates nascent hydrogen. Due to which it can bleach delicate articles like silk and straw.

$$SO_2 + H_2O \longrightarrow H_2SO_3 \rightleftharpoons 2H^+ + SO_3^{2-}$$

(b) Geometry of SO_2 molecule is bent.

(c) Its dilute solution is used as disinfectant.

(d) SO_2 is prepared by the reaction of conc. H_2SO_4 with metals.

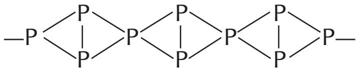
$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + 2H_2O + SO_2$$

47. Concentrated sulphuric acid (H_2SO_4) is hygroscopic, oxidising agent and sulphonating agent. It is not an efflorescent.

48. He_{II} has extremely low viscosity and readily form films only a few hundred atom thick, which flow without friction.

49. When highly conc. HNO_3 (80%) is reacted with iron, it forms a thin protective layer of ferric oxide (Fe_2O_3) over its surface due to which it makes iron passive.

50. Red phosphorus is less volatile than white phosphorus because it exists in linked tetrahedral structures.



51. H—S bond is weaker than H—O bond hence, H_2S is more acidic than H_2O.

52. XeF_2 oxidises HCl to Cl_2 and Ce(III) to Ce(IV). Its oxidation potential is +2.64 V.

53. Zero point energy of helium is so high that it outweighs the weak interatomic forces which are not strong enough to bind the helium atoms into the crystalline state.

54. Bond angle decreases as the electronegativity of the element M in H_2M decreases. It is minimum for H_2Te.

55. Acidic character increases from top to bottom in a group.

56. H_2S has the lowest boiling point whereas H_2O has the highest boiling point.

57. Due to non-availability of *d*-orbitals in case of nitrogen, NCl_5 is not known.

58. $NCl_3 + 3H_2O \longrightarrow 3HOCl + NH_3$

Other halides do not react with H_2O.

59. Due to high electronegativity of F atom, the bonding pairs of electrons are attracted more towards F atoms in NF_3 and N has a decreased tendency to donate its lone pair of electrons.

60. $$\left.\begin{array}{l} N \\ P \\ As \\ Sb \end{array}\right] \begin{array}{l} \text{Group} = 15 \\ \left.\begin{array}{l}\text{Valence} \\ \text{electrons}\end{array}\right] = 5 \end{array}$$

MCl_3 has sp^3 hybridized *M*-element with one lone pair.

Lone pair and bond pair repulsion decreases bond angle. However, the bond pairs of electrons are much farther away from the central atom than they are in PCl_3, $AsCl_3$ and $SbCl_3$. Thus, bond angle decreases from NCl_3 (maximum) to $SbCl_3$ (minimum).

61. (a) $2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2$

(b) $2KClO_3 \xrightarrow{\Delta} 2KCl + 3O_2$

(c) $CaCO_3 \xrightarrow{\Delta} \underset{\text{basic}}{CaO} + \underset{\text{acidic}}{CO_2}$

(d) $NH_4NO_3 \xrightarrow{\Delta} N_2O + H_2O$

62. (a) Thermal stability of the hydrides decreases as we go down the group in Periodic Table for group 15 (N-family)

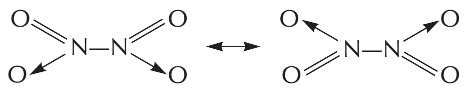
$$BiH_3 < SbH_3 < AsH_3 < PH_3 < NH_3$$

Least stable					
M-H Bond energy kJ mol^{-1}	–	255	247	322	391

(b) Due to absence of *d*-orbital, nitrogen can't from $d\pi$-$d\pi$ bond, thus it is correct.

(c) The N—N bond (BE 160 kJ mol^{-1}) is weaker than P—P bond (BE 209 kJ mol^{-1}). Thus, it is correct.

(d) N_2O_4 can form two resonance structures.



Thus, it is correct.

63. (a) S_2 molecule is paramagnetic due to unpaired electrons in MO configuration and is blue-coloured compound thus true.

(b) The vapour at 200°C consists mostly of S_8 rings, thus correct.

(c) At 600°C, the gas mainly consists of S_2 molecules thus correct.

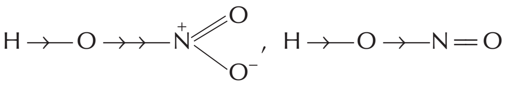
(d) Oxidation states of sulphur are

–2	in	H_2S
0	in	S_8
+2	in	$S_2O_3^{2-}$
+4	in	SO_2
+6	in	SO_3

64. XeF_6 has much tendency to hydrolyse. The reverse reaction is more spontaneous.

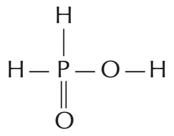
$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

65. Br_2 reacts with hot and strong NaOH to give NaBr, $NaBrO_3$ and H_2O.

66. 

Polarity along O—H in HNO_3 is more in comparison to —O—H in HNO_2.

67. Hypophosphorus acid (H_3PO_2) is a monobasic acid and has only one ionisable H, two H-atoms are directly attached to phosphorous.



68. In Holmes signals of the ship, mixutre of CaC_2 and Ca_3P_2 is used.

69. $2HCl + \frac{1}{2}O_2 \longrightarrow H_2O + Cl_2$

70. Phosphorus (3rd period element) can raise covalency facilitating vacant *d*-orbitals

$$P\,(\text{ground}) = [\text{Ne}]\,3s^2\ \ 3p^3\ \ 3d^0$$
$$P\,(\text{excited}) = [\text{Ne}]\,3s^1\ \ 3p^3\ 3d^1$$

8 The *d*- and *f*-Block Elements

JEE Main MILESTONE

- *d*-Block Elements
- Potassium Dichromate
- Potassium Permanganate
- *f*-Block Elements

8.1 *d*-Block Elements

These are the elements in which the differentiating electron (*i.e.*, the last electron) enters in the *d*-subshell, *e.g.,* elements of group 3 to 12 (*i.e.*, IB to VIIB and VIII). In Periodic Table, they are placed between *s*- and *p*-blocks and have properties in between of them, *i.e.*, their properties are intermediate between those of *s*- and *p*-block elements. That's why, these elements are called **transition elements.**

Zinc, cadmium and mercury, however, because of the presence of completely filled $(n-1)$ *d*-subshell in their elementary as well as in combined state, do not show much resemblance with other *d*-block elements except for their ability to form complexes with ligands such as NH_3, RNH_2 and halides. Nevertheless, these are studied with the *d*-block elements in order to maintain a rational classification of elements. These elements, thus, are called **non-typical transition elements.**

These are the elements having completely filled outermost shell and incomplete inner shall. If last electron enters in penultimate (n-1) d-orbital the elements are called d-block elements and if enters in (n-2) f-orbital, the elements are called f-block elements.

Elements of IIIB group (*i.e.*, Sc, Y, La and Ac) also differ in their properties from rest of the members, *e.g.,* they form compounds only in +3 oxidation state. Unlike the compounds of other members, these are diamagnetic and colourless. Hence, **these elements are also not considered as transition elements.**

Caution Point *All transition elements are d-block elements but all the d-block elements are not transition elements.*

Classification of *d*-Block Elements

These elements make up three complete rows of ten elements and an incomplete fourth row. These rows are named as 3*d*, 4*d*, 5*d* and 6*d* series respectively as shown below

Table 8.1 **Different Series of *d*-Block Elements**

Series name	3 (IIIB)	4 (IVB)	5 (VB)	6 (VIB)	7 (VIIB)	8 (VIII)	9 (VIII)	10 (VIII)	11 (IB)	12 (IIB)
3*d*-series	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
4*d*-series	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
5*d*-series	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg
6*d*-series	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds		

On August 16, 2003 IUPAC approved the name for the element of atomic number 110 as **Darmstadtium** with symbol Ds. It is a super heavy element which was first produced in 1994.

General and Physical Properties

The general and physical properties of *d*-block elements and their trends are discussed

(a) Electronic Configuration

The general electronic configuration of these metals is $(n-1)\, d^{1-10}\, ns^{1-2}$. Here, it is obvious that the electronic configuration of these elements differ only in the number of electrons in their penultimate shell (*i.e.*, in *d*-orbital). Thus, they do not show a regular trend of physical and chemical properties like *s*- and *p*-block elements.

Half and completely filled sets of orbitals are relatively more stable. *e.g.*, $\text{Cr}\,(24) = [\text{Ar}]\, 3d^5\, 4s^1$ and $\text{Cu}(29) = [\text{Ar}]\, 3d^{10}\, 4s^1$.

The electronic configurations of Zn, Cd and Hg are represented by the general formula $(n-1)\, d^{10} ns^2$.

(b) Atomic Radii

In a given series, the atomic radii of these elements generally decreases from group 3 to group 10 and after that increases again towards the end of the series. This is because the nuclear charge increases with increase in atomic number.

Due to this, the electron clouds are attracted more strongly and results in decreased size. However, the decrease in the radii across the period is not uniform, *e.g.,* the radii of elements from Cr to Cu are very close to one another.

This is due to the effective screening of outer *ns*-electrons by the electrons of $(n-1)$ *d* subshell. The reason for the anomalous increase in atomic radii towards the end of the series is predominant repulsion between the added electrons. Presence of completely filled *d*-orbitals also decreases the force of attraction.

On moving downwards in the groups, the atomic radii increases although the increase is not as significant as in the case of *s*- and *p*-block elements.

The members of 4*d* and 5*d* series exhibit near about similar radii which is due to **lanthanide contraction** (filling of 4*f* electrons before 5*d* results in regular decrease of atomic size with increase in atomic number).

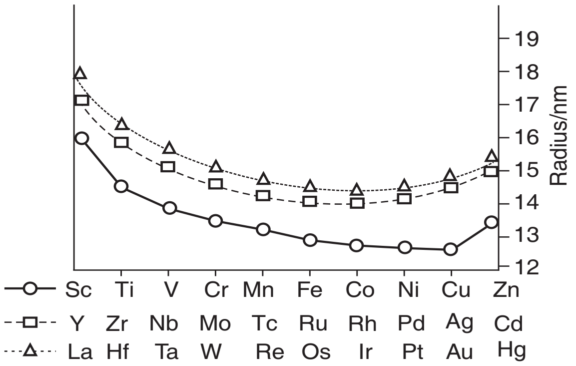


Fig. 8.1 Plot of radii with atomic number of transition elements

Hence, Zr—Hf, Nb—Ta, Mo—W and Tc—Re are called chemical twins. Zr and Hf have very similar physical and chemical properties because of their similar radii (Zr = 160 pm, Hf = 159 pm) which makes their separation difficult.

Sample **Problem 1** *Although zirconium belongs to 4d transition series and hafnium to 5d transition series even then they show similar physical and chemical properties because*

(a) *both belong to d-block*
(b) *both have same number of electrons*
(c) *both have similar atomic radius*
(d) *both belong to the same group of the Periodic Table*

Interpret (c) Because Zr and Hf have the almost same size (Zr = 160, Hf = 159 pm) due to lanthanoid contraction.

(c) Ionic Radii

The ionic radii of these elements follow the same trend as their atomic radii. In case of ions carrying identical charges, the ionic radius decreases slowly with increase in atomic number in a series.

(d) Molar Volume and Density

The molar volumes of *d*-block elements are much lower than those of *s*-and *p*-block elements of neighbouring groups. It is due to the reason that as inner orbitals gets filled, the increased nuclear charge pulls the electrons inward. Due to such decrease in molar volumes, an increase in density is seen. In a series from left to right density increases and attains a maximum value at the middle of the series. On moving down a group,density increases.

Sample Problem 2 *Metallic radii of some transition elements are given below. Which of these elements will have highest density?* **[NCERT Exemplar]**

Elements	Fe	Co	Ni	Cu
Metallic radii/pm	126	125	125	128

(*a*) Fe
(*b*) Ni
(*c*) Co
(*d*) Cu

Interpret (*d*) Copper have the highest density because of low molar volumes.

Elements	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Density ($g\ cm^{-3}$)	3.43	4.1	6.07	7.19	7.21	7.8	8.7	8.8	8.9	7.1

(e) Ionisation Energy

Since, the atoms are smaller in size, their ionisation energies are fairly high. The values in most cases lie in between those of *p*- and *s*-block elements, thus indicating that transition metals are less electropositive than the elements of *s*-block. In a series, the IE increases from left to right but the increase is not so pronounced as in the case of *s-and p*-block elements. *The IE, of 5d series elements is higher than the elements of 4d and 3d series.* This is due to the greater effective nuclear charge acting on outer valence electrons because of the weak shielding of the nucleus by 4*f* electrons.

IE_2 of the first transition series increases almost regularly with increase in atomic number. However, the value for Cr and Cu are sufficiently higher than those of their neighbours. This is due to their stable electronic configurations.

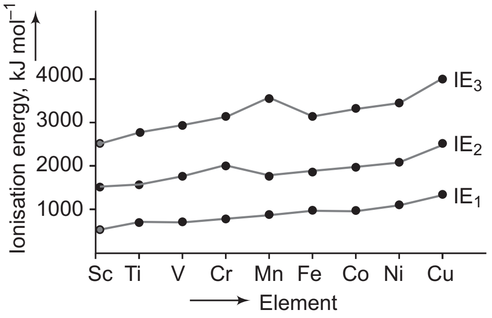


Fig. 8.2 Variation of the IE_1, IE_2 and IE_3 for the first transition metals

The ionisation energy of Zn, Cd and Hg are abnormally higher due to the greater stability of *s*-subshell.

Table 8.2 **Ionisation Energies of *d*-block Elements**

Elements of 3*d*-series	Ionisation energies ($kJ\ mol^{-1}$)	Elements of 4*d*-series	Ionisation energies ($kJ\ mol^{-1}$)	Elements of 5*d*-series	Ionisation energies ($kJ\ mol^{-1}$)
Sc	631	Y	616	La	541
Ti	656	Zr	674	Hf	760
V	650	Nb	664	Ta	760
Cr	653	Mo	685	W	770
Mn	717	Tc	703	Re	759
Fe	762	Ru	711	Os	840
Co	758	Rh	720	Ir	900
Ni	736	Pd	804	Pt	870
Cu	745	Ag	731	Au	889
Zn	906	Cd	876	Hg	1007

The sum of first three ionisation energies for Sc is a little less than the sum for Al. Thus, the properties of Sc are similar in some ways to those of Al.

The magnitude of ionisation energies give an idea about the relative stabilities of various oxidation states of transition elements. *e.g.,* Ni (II) compounds are thermodynamically more stable than platinum (II) while platnium (IV) compounds are relatively more stable than nickle (IV) compounds.

	$IE_1 + IE_2$	$IE_3 + IE_4$	Total
Ni	2.49×10^3	8.80×10^3	11.29×10^3
Pt	2.66×10^3	6.70×10^3	9.36×10^3

Sample Problem 3 *For d-block elements the first ionisation potential is of the order*

(a) Zn > Fe > Cu > Cr

(b) Sc = Ti < V = Cr

(c) Zn < Cu < Ni < Co

(d) V > Cr > Mn > Fe

Interpret (a) The ionisation energies increase with increasing atomic number. The trend is irregular among *d*-block elements.

Zn > Fe > Cu > Cr is correct order.

Sample Problem 4 *First IE of 5d elements are higher than those of 3d and 4d elements. This is due to*

(a) *greater effective nuclear charge acting on outer valence electrons*

(b) *greater effective nuclear charge is experienced because of the weak shielding of the nucleus by 4f electrons*

(c) *Both (a) and (b)*

(d) *None of the above*

Interpret (b) The first ionisation enthalpies of 5*d* elements are higher than those of 3*d* and 4*d* series. This is because of weak shielding of nucleus by 4*f* electrons in the 5*d* series.

(f) Nature of Bond

Unlike alkali and alkaline earth metals, the transition elements have the tendency to form covalent bond also along with the ionic bonds. Generally the compounds in which smaller valency is exercised are ionic while those in which higher valency is exercised are covalent compounds.

(g) Metallic Character

Nearly all transition elements show typical metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity and metallic lusture (except Hg, which is a liquid at room temperature).

With the exception of Zn, Cd and Hg, all the transition elements are much harder and less volatile. Although hardness and brittleness are associated with covalent bonding between metal atoms, the existence of metallic bonding cannot be denied. While the overlapping of unfilled *d*-orbitals of metals causes covalent bonding, the valence *s*-electrons are responsible for metallic bonding. Cu, Ag and Au are particularly outstanding in their thermal and electrical conductivities.

(h) Enthalpy of Atomisation

Since the atoms of transition elements are closely packed and held together by strong metallic bonds because of large number of unpaired electrons in their atoms, they possess high enthalpy of atomisation.

The metals of 2nd and 3rd series have greater enthalpies of atomisation than the corresponding elements of the first series.

(i) Melting and Boiling Points

Their melting and boiling points are high which is attributed to strong interatomic bonding involving participation of *ns* and $(n-1)\,d$ electron, *i.e.,* **metallic bonding is stronger in them.** In any row, the melting points of these metals rise to a maximum at d^5 except for anomalous values of Mn and Tc and fall regularly as the atomic number increases. However, Zn, Cd and Hg due to the presence of completely filled $(n-1)\,d$ orbital are not expected to have covalent bonding, thus their melting and boiling points are relatively low, as compared to the other elements of this block.

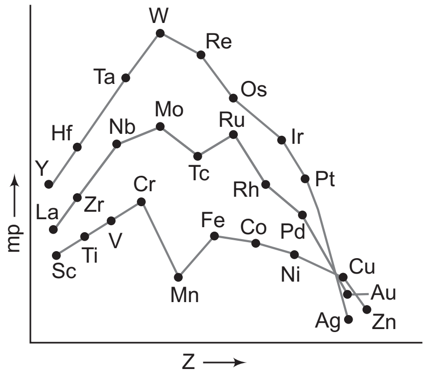


Fig. 8.3 Melting point of 3*d*, 4*d* and 5*d*-series elements (not according to scale)

Hot Spot 1

OXIDATION State

It is an important topic for JEE Main examination. Generally questions are asked from this topic. The level of question vary from easy to average.

Transition elements show a large number of oxidation states differing usually by unit of one. This is due to the fact that $(n-1)$ d electrons may get involved along with ns-electrons in bonding as electrons in $(n-1)$ d-orbitals are in an energy state comparable to ns-electrons. The stability of a given oxidation state depends on the nature of the element with which the transition metal is combined.

The highest oxidation states are found in the compounds of fluorides and oxides because of the most electronegative nature of F and O. The different oxidation states of 3d-series have been given below

Table 8.3 **Oxidation States of First Transition Series**

Elements	Outer electronic configuration	Oxidation states
Sc	$3d^1 4s^2$	+2, +3
Ti	$3d^2 4s^2$	+2, +3, +4
V	$3d^3 4s^2$	+2, +3, +4, +5
Cr	$3d^5 4s^1$	+1, +2, +3, +4, +5, +6
Mn	$3d^5 4s^2$	+2, +3, +4, +5, +6, +7
Fe	$3d^6 4s^2$	+2, +3, +4, +5, +6
Co	$3d^7 4s^2$	+2, +3, +4
Ni	$3d^8 4s^2$	+2, +3, +4
Cu	$3d^{10} 4s^1$	+1, +2
Zn	$3d^{10} 4s^2$	+2

The oxidation states of elements of 2nd and 3rd transition series are

Table 8.4 **Oxidation States of Second Transition Series**

Elements	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Oxidation states									+1	
						+2		+2	(+2)	+2
	+3		+3	+3		+3	+3	(+3)	(+3)	
		+4		+4	+4	+4	+4	(+4)		
			+5	+5		+5				
				+6	(+6)	+6	+6			
					+7	(+7)				
						(+8)				

Table 8.5 **Oxidation States of Third Transition Series**

Elements	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Oxidation states									+1	+1
				(+2)		(+2)	(+2)	+2		+2
	+3			(+3)	(+3)	(+3)	+3	(+3)	+3	
		+4	(+4)	+4	+4	+4	+4	+4		
			+5	+5	+5	+5				
				+6	+6	+6	+6			
					+7					
						+8				

Caution Point *First member of each transition series does not show variable valency. It generally shows only + 3 oxidation state.*

Except scandium, the most common oxidation state of first row transition elements is (+ 2) which arises due to the loss of two 4s electrons.

In (II) and (III) oxidation states, bonds formed are mostly ionic. In the compounds of the higher oxidation states (MnO_4^-), the bonds formed are essentially covalent.

Some transition elements also show an oxidation of zero in their compounds *e.g.*, $[Ni(CO)_4]$ and $[Fe(CO)_5]$.

In general for the first four elements of a transition series, higher oxidation states are more stable than lower oxidation states. For the next five elements lower oxidation states are more stable than higher oxidation states *e.g.*, Cr (III) is more stable than Cr(II) but Mn (II) is more stable than Mn (III).

Among the group of d-block elements, the higher oxidation states are favoured by heavier members (the opposite is true in p-block) *e.g.*, in group 6 Mo (VI) and W (VI) are found to be more stable than Cr (VI). Thus, Cr (VI) In the form of dichromate in acidic medium is a strong oxidising agent whereas MoO_3 and WO_3 are not.

Only Ru and Os show + 8 oxidation states in their compounds.

While solving problems based on oxidation state, always keep in mind

(i) Atomic number of the elements and their electronic configuration

(ii) Minimum oxidation state is generally + 2 but it is + 3 for Sc and Cr and +1 for Cu and Ag.

(iii) For d-block elements up to 7 group, maximum oxidation state $= nse^- + (n-1)\,d$ unpaired e^-

Sample **Problem 5** *The 3d-element that exhibits maximum number of oxidation states is*

(*a*) Sc (*b*) Ti (*c*) Mn (*d*) Zn

Interpret (*c*) Mn exhibits the maximum number of oxidation states Mn(25) = [Ar] $3d^5\ 4s^2$ because of the presence 5 unpaired *d*-electrons and two paired *s*-electrons.

It can show + 2, + 3, + 4, + 5, + 6 and + 7 oxidation states.

Sample **Problem 6** *A transition metal exists in its highest oxidation state. It is expected to behave as*

(*a*) *a chelating agent*
(*b*) *a central metal in a coordination compound*
(*c*) *an oxidising agent*
(*d*) *a reducing agent*

Interpret (*c*) A transition metal ion existing in the highest oxidation state behave as an oxidising agent because in such a condition its further oxidation is not possible but it can be reduced. Thus, it itself undergo reduction and oxidises the other species.

Remember ! All Cu (II) halides are known except the iodide as Cu^{2+} oxidises I^- to I_2. However, many copper (I) compounds are unstable in aqueous solution and undergo disproportionation

$$2Cu^+ \longrightarrow Cu^{2+} + Cu$$

The stability of Cu^{2+} (*aq*) rather than Cu^+(*aq*) is due to much more negative $\Delta H°$ of Cu^{2+} (aq) than Cu^+, which is more than that compensates for the second ionisation enthalpy of Cu.

(j) Standard Electrode Potentials

The $E°$ values of all the transition metals (except Cu) is lower (negative) than that of hydrogen (taken as zero). Thus, all the transition elements, with negative reduction potential, liberate hydrogen from dilute acids.

Table 8.6 ***E°* Values for First Row Transition Metals**

Elements	V	Cr	Mn	Fe	Co	Ni	Cu
$E°(M^{2+}/M)$ in volts	–1.18	– 0.91	–1.18	– 0.44	– 0.28	–0.5	+0.34

Most transition metals are inert towards acids or react slowly with them because of a protective layer of oxide. In case of Cr, despite a negative $E°$, it is quite inert chemically because of the formation of chromium (III) oxide, Cr_2O_3 on its surface.

$E°\ (M^{2+}/M)$ values are not regular for 3*d* series elements. It can be explained from the irregular variation of ionisation enthalpies $(\Delta_i H_1 + \Delta_i H_2)$ and also the sublimation enthalpies which are relatively much less for Mn and V.

Sample **Problem 7** *Which one of the following is a stronger reducing agent?*

(*a*) Cr^{2+}
(*b*) Fe^{2+}
(*c*) Cu
(*d*) *None of the above*

Interpret (*a*) Cr^{2+} is a stronger reducing agent than Fe^{2+} and Cu because $E°$ values for (Cr^{3+}/Cr^{2+}) are more negative than that of $E°$ for Fe^{3+}/Fe^{2+}. Further more, transition $\underset{(3d^4)}{Cr^{2+}} \longrightarrow \underset{(3d^3)}{Cr^{3+}}$ is easier than $\underset{(3d^6)}{Fe^{2+}} \longrightarrow \underset{(3d^5)}{Fe^{3+}}$ because in latter, an electron is removed from the paired orbital.

(k) Reducing Property

All these elements (of 3*d*-series) except Cu has SRP (standard reducing potential) lower than H, hence, all of them (except Cu) are good reducing agents. However, they are not as good reducing agents as the metals of 1st, 2nd and 13th group.

Hot Spot 2

COLOUR and Magnetic Properties

Colour and magnetic properties both are the important topic for JEE Main examination. In general, the level of question is easy, so a small practice can help you in scoring marks.

Colour

Most of the compounds of transition metals are coloured in solid state or solutions. The colour of transition metal ions arises from the excitation of electron from *d*-orbitals of lower energy to *d*-orbitals of higher energy (*d*-*d*) transition. The transition metal ions which have either completely filled *d*-orbitals or completely empty *d*-orbitals are colourless because they are not capable of showing *d*-*d* transition.

The colour of a transition metal complex is dependent on how big the energy difference in between the two *d*-levels. This in turn depends on the nature of the ligand, and the type of the complex formed.

The colour which we see is the colour of the transmitted wavelength and is complimentary colour absorbed by the complex.

In the series Sc^{3+}, Ti^{4+}, V^{5+}, Cr^{6+} and Mn^{7+} all have empty *d*-orbitals, hence, *d*-*d* spectra are impossible and they should be colourless. But VO_2^{2+} (V^{5+}), CrO_4^{2-} (Cr^{6+}) and MnO_4^- (Mn^{7+}) ions in aqueous solution are coloured. The colour arise due to charge transfer.

Sample **Problem 8** *Generally transition elements form coloured salts due to the presence of unpaired electrons. Which of the following compounds will be coloured in solid state ?*

(a) Ag_2SO_4 (b) CuF_2

(c) ZnF_2 (d) Cu_2Cl_2

Interpret (*b*) In Ag_2SO_4, Ag is in + 1 oxidation state ($4d^{10}$), so colourless. In CuF_2, Cu is in + 2 oxidation state ($3d^9$), so it is coloured. In ZnF_2, Zn is in +2 oxidation state ($3d^{10}$) colourless. In Cu_2Cl_2, Cu is in + 1 oxidation state ($3d^{10}$), so it is colourless. The transition metal ions having d^1 to d^9 configuration are coloured whereas the transition metal ions having d^0 and d^{10} configuration are colourless. Thus, among the given only CuF_2 is coloured.

Magnetic Properties

Many of the transition metal ions are paramagnetic due to the presence of unpaired electrons in them. Each such unpaired electron have a magnetic moment associated with its **spin angular momentum and orbital angular momentum.** In transition elements, the orbital motion of unpaired electron is severely disturbed by the electrons of surrounding ligands. Therefore, here the contribution of spin angular momentum becomes much more significant than orbital angular momentum contribution *i.e.*, μ-orbital contribution may be neglected. Thus, effective magnetic moment (μ_{eff}) is given by the expression

$$\mu_{eff} \approx \mu_{spin} \approx \sqrt{n\,(n+2)}$$

where, *n* is the number of unpaired electrons.

Magnetic moment ∝ number of unpaired electrons.

Species having unpaired electrons are paramagnetic whereas the species having all paired electrons are diamagnetic.

Magnetic moment is given in Bohr-magneton (BM) which is given by the expression

$$\text{BM} = \frac{eh}{4\pi mc}$$

where, h = Planck's constant, e = electronic charge

c = velocity of light, m = mass of electron

Sample **Problem 9** *The magnetic nature of elements depends on the presence of unpaired electrons. Identify the configuration of transition element, which shows highest magnetic moment.*

(a) $3d^7$ (b) $3d^5$

(c) $3d^8$ (d) $3d^2$

Interpret (*b*) Magnetic moment increases with the increasing number of unpaired electrons. Hence, $3d^5$ configuration of transition element shows highest magnetic moment.

Sample **Problem 10** *The magnetic moment is associated with its spin angular momentum and orbital angular momentum. Spin only magnetic moment value of* Cr^{3+} *ion is*

(a) 2.87 *BM*

(b) 3.87 *BM*

(c) 3.47 *BM*

(d) 3.57 *BM*

Interpret (*b*) $\mu = \sqrt{n\,(n+2)}$; where n = number of unpaired electrons

$$Cr^{3+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^3, 4s^0;$$

$$\mu = \sqrt{3(3+2)} = 3.872 \text{ BM}$$

(l) Catalytic Property

Most of the transition metals and their compounds have good catalytic properties, *e.g.,* Pt, Fe, V_2O_5, Ni etc. According to modern theory of catalysis, a catalytic substance is capable of forming an unstable intermediate which readily decomposes yielding the product and regenerating the catalyst, *i.e.*,

$$A + B + \text{catalyst} \longrightarrow \underset{\substack{\text{intermediate} \\ \text{(unstable)}}}{AB\,\text{catalyst}} \longrightarrow C + \text{catalyst}$$

Transition elements on account of their variable valency have the ability to form intermediate compounds very readily thus, acting as good catalysts.

Sample Problem 11 *Which one of the following characteristics of the transition metals is associated with their catalytic activity?*

(a) *Colour of hydrated ions*
(b) *Variable oxidation states*
(c) *High enthalpy of atomisation*
(d) *Paramagnetic behaviour*

Interpret (*b*) Catalytic activity of transition elements is due to their ability to adopt multiple oxidation states and to form complexes.

(m) Complex Formation

The transition metals are almost unique in their tendency to form coordination complexes, which is due to following factors

(i) Very small size,
(ii) High positive charge density,
(iii) Vacant orbitals with suitable energy to accept lone pair of electrons.

(n) Alloy Formation

Since, transition elements have almost similar radii, they have a tendency to replace each other from their lattice and form solid solutions over an appreciable composition range. These solid solutions are called alloy. These and are hard, and have high melting point as compared to the host metal, *e.g.,* some important alloys of copper and steel along with their properties and uses are tabulated below.

Table 8.7 **Some Alloys of Copper**

S.N.	Name	Composition	Important properties	Uses
1.	Brass	Cu = 60–80% Zn = 20–40%	Harder, paler and more brittle with more zinc, can be moulded, malleable and ductile, high tensile strength	Domestic utensils, condensers, tubes, casting cartridges.
2.	Bronze	Cu = 75–90% Sn = 10–25%	Hard, brittle, tenacious, durable, resistant to corrosion, takes high polish.	Statues, coins, utensils, bells, machine parts, propellers, blades.
3.	Aluminium bronze	Cu = 90% Al = 10%	Light, strong, tenacious, resistant to corrosion, golden yellow.	Utensils, coins, frames, statues, jewellery, bearings and castings.
4.	Phosphorus bronze	Cu = 85% Sn = 13% P = 2%	Very hard, tough, elastic, resistant to corrosion.	Suspension wire instrument, gears, aerials, ships, propellers.
5.	Silica bronze	Cu = 97% Sn = 2% Si = 1%	Very hard, tensile, tough, non-corrosive, good conductor.	Telephone and telegraph wires, suspension wires.
6.	German silver or nickel silver	Cu = 50% Zn = 30% Ni = 20%	White shining, malleable and ductile, tough, resistance to corrosion.	Utensils, plates, ornaments.
7.	Gun metal	Cu = 88% Sn = 10% Zn = 2%	Strength increases with the increase of the percentage of Sn, very hard and strong, resistant to corrosion.	For making cannons, guns, machine parts.
8.	Monel metal	Cu = 30% Ni = 67% Fe + Mn = 3%	Very resistant to chemical action, high tensile strength.	Alkali industry resistance wires, domestic wires, valves, automobile engine parts.

Table 8.8 **Some Important Alloys of Steels**

S.N.	Name of the alloy (steel)	Metal added	Properties	Uses
1.	Manganese steel	1.2–15% Mn	Hard, tough, resistant to wear	Rock crushing machinery, safes, helmets.
2.	Nickel steel	2.5–5% Ni	Hard, tough, rustless	Armour plate, cables, propeller shafts, automobile parts, heavy guns.
3.	Invar	3.6% Ni	Same coefficient of expansion as glass	Pendulum, measuring tapes, instruments.
4.	Chrome steel	1.5–2% Cr	Extremely hard	Cutting tools, crushing machinery.
5.	Stainless steel	13–14% Cr, 1% Ni	Resists corrosion	Cutlery, food processing machinery.
6.	Tungsten steel	14 –20% W	Hard and strong	High speed tools.
7.	Chrome-vanadium steel	1% Cr, 0.15% V	High tensile strength	For making spring, shafts, axles.

(o) Interstitial Compounds

Transition elements also have some tendency to trap small atoms like H, B, C, N etc., in the interstitial space and thus, forming some interstitial or non-stoichiometric compounds. FeC, Fe_8N are the examples of interstitial compounds and $Fe_{0.98}O$, $Ni_{0.98}O$, $TiH_{1.7}$ are the examples of both interstitial as well as non-stoichiometric compounds.

The principal physical and chemical characteristics of these compounds are as follows :

1. Their melting points are higher than that of pure metals.
2. They are very hard *e.g.*, some borides approach diamond in hardness.
3. They are chemically inert.
4. They retain metallic conductivity.

(p) Reactivity

The transition elements have small tendency to react due to their high heats of sublimation, high ionisation energies and low heats of hydration. They have rather a tendency to remain unreactive or **noble** *e.g.,* Pt, Au etc.

(q) Nature of Oxides and Hydroxides

While moving along a period from Sc and Zn, basic nature decreases and acidic nature increases. Behaviour differs when oxidation states are different. Sc_2O_3, TiO_2, V_2O_5, Cr_2O_3, MnO_2 and ZnO are amphoteric while Fe_2O_3, Co_2O_3, NiO and CuO are basic.

With increase in the oxidation state of a given transition metal, the covalent character of its compound increases and thus, acidic character also increases.

	MnO	Mn_3O_4	Mn_2O_3	MnO_2	MnO_3	Mn_2O_7
Oxidation state of Mn	+2	+8/3	+3	+4	+6	+7
	↑ basic	amphoteric			weakly acidic	strongly acidic

	VO	V_2O_3	VO_2	V_2O_5
Oxidation state of V	+2	+3	+4	+5
	basic		amphoteric	

	CrO	Cr_2O_3	CrO_3
Oxidation state of Cr	+2 basic	+3 amphoteric	+6 acidic

As we move along a given transition series, +2 oxidation state of the metals becomes more and more stable and hence, the tendency of these metals to lose electrons increases hence, reducing nature of the metal oxide increases. VO and CrO are strong reducing agents.

The basic and amphoteric oxides dissolve in non-oxidising acids and form hexaquo ions $[M(H_2O)_6]^{n+}$. The acidic oxides like CrO_3 and Mn_2O_3 dissolve in water to form oxyacids. These oxides also react with bases to form oxosalts.

$$2CrO_3 + H_2O \longrightarrow H_2Cr_2O_7 \quad \text{(dichromic acid)}$$

$$2CrO_3 + 2KOH \longrightarrow K_2Cr_2O_7 + H_2O$$

$$Mn_2O_7 + H_2O \longrightarrow 2HMnO_4 \quad \text{(permanganic acid)}$$

$$Mn_2O_7 + 2KOH \longrightarrow 2KMnO_4 + H_2O$$

Caution Point *Mercury can't from any hydroxide, because alkali, dilute non-oxidising acids and water or steam have no effect on mercury.*

Sample Problem 12 *Which oxide of* Mn *is acidic in nature ?*

(*a*) MnO (*b*) Mn_2O_7 (*c*) Mn_2O_3 (*d*) MnO_2

Interpret (*b*) Transition metal oxide in higher oxidation states are acidic in nature. Thus, Mn_2O_7 is most acidic among the given.

(r) Halides of 3*d* Series of Transition Elements

The reactivity order for halogen for a given transition metal is $F_2 > Cl_2 > Br_2 > I_2$. Metals usually posses maximum oxidation state in their fluorides. Fluorides of all transition metals are ionic. The ionic character of halides decreases in the order : fluorides > chlorides > bromides > iodides.

To make the trihalides of the *d*-block elements, direct reaction of the element with the halogen is needed. The dihalides are obtained by reacting the element with hydrogen halides.

Sample Problem 13 *Transition elements form binary compounds with halogens. Which of the following elements will form MF_3 type compounds ?* [**NCERT** Exemplar]

(*a*) Cr (*b*) Co

(*c*) Cu (*d*) Ni

Interpret (*a,b*) The +3 oxidation state is more stable only for Cr and Co. Cu exhibits only +1 and +2 oxidation states. Ni generally exhibits +2 oxidation state. This is the reason for the fact that Cr and Co form MF_3 (where, M = Cr and Co) whrereas Cu and Ni do not.

Check Point 1

1. Zinc, cadmium and mercury are not regarded as transition elements, why ?
2. Zn^{2+} salts are white whereas Cu^{2+} salts are blue. Explain.
3. Why do transition metals generally form alloy ?
4. Why IE_1 of Cr is lower than that of Zn? [**NCERT** Exemplar]
5. Although fluorine is more electronegative than oxygen, but the ability of oxygen to stabilise higher oxidation states exceeds that of fluorine, why ?
6. Although Zr belongs to 4*d* and Hf belongs to 5*d* -series but it is quite difficult to separate them, Why ?

8.2 Potassium Dichromate

Its chemical formula is $K_2Cr_2O_7$. It contains ionic as well as covalent bonds.

Methods of Preparation

$K_2Cr_2O_7$ is manufactured from chromite ore, $FeO \cdot Cr_2O_3$ by a method which consists of four steps *viz*

Step I Concentration of the chromite ore by wilfley table method.

Step II Conversion of the concentrated chromite ore into Na_2CrO_4 (roasting of the concentrated ore). Concentrated chromite ore is fused with molten Na_2CO_3 in the presence of air when Na_2CrO_4 and Fe_2O_3 are formed.

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \xrightarrow{1100^\circ C} \underset{\text{water soluble}}{8Na_2CrO_4} + \underset{\text{water insoluble}}{2Fe_2O_3} + 8CO_2\uparrow$$

Step III Conversion of Na_2CrO_4 into $Na_2Cr_2O_7$.

Aqueous solution of Na_2CrO_4 is acidified to obtain $Na_2Cr_2O_7$.

$$2Na_2CrO_4 + \underset{\text{dil.}}{H_2SO_4} \longrightarrow Na_2Cr_2O_7 + H_2O.$$

Step IV Conversion of $Na_2Cr_2O_7$ to $K_2Cr_2O_7$. Hot solution of $Na_2Cr_2O_7$ obtained as above in step (III) is treated with the calculated quantity of KCl whereby less soluble $K_2Cr_2O_7$ separates out from the solution on crystallisation.

$$Na_2Cr_2O_7 + 2KCl \longrightarrow \underset{\substack{\text{more}\\\text{soluble}}}{2NaCl} + \underset{\substack{\text{less}\\\text{soluble}}}{K_2Cr_2O_7}$$

Physical and Chemical Properties

General poperties exhibited by $K_2Cr_2O_7$ *are as follows*:

1. $K_2Cr_2O_7$ forms orange-red prismatic crystals which melt at 396°C.
2. It is moderately soluble in cold water and freely soluble in hot water.
3. When heated to a white heat, it decomposes to give potassium chromate, K_2CrO_4 and O_2 gas is evolved.
$$4K_2Cr_2O_7 \xrightarrow{\Delta} 4K_2CrO_4 + 2Cr_2O_3 + 3O_2\uparrow$$
4. $K_2Cr_2O_7$ is a powerful oxidising agent. In the presence of dil H_2SO_4, one molecule of this compound gives three atoms of oxygen as shown below
$$\underset{\text{orange}}{K_2Cr_2O_7} + 4H_2SO_4\,(\text{dil.}) \longrightarrow K_2SO_4 + \underset{\text{green}}{Cr_2(SO_4)_3} + 4H_2O + 3O$$
Thus, in presence of dil H_2SO_4, it liberates I_2 from KI solution, oxidises Fe(+2) salts to Fe(+3) salts, H_2S to S, SO_2 to H_2SO_4 as
$$K_2Cr_2O_7 + 7H_2SO_4 + 6KI \longrightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$$
$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3Fe_2(SO_4)_3$$
$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$$
$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$
5. With cold H_2SO_4, red crystals of chromium trioxide, CrO_3 are formed. When $K_2Cr_2O_7$ is heated with H_2SO_4, O_2 gas is evolved.
$$K_2Cr_2O_7 + H_2SO_4(\text{cold}) \longrightarrow \underset{\text{red crystals}}{2CrO_3} + K_2SO_4 + H_2O$$
$$2K_2Cr_2O_7 + 8H_2SO_4 \xrightarrow{\Delta} 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2$$
6. **Chromyl chloride test** When solid $K_2Cr_2O_7$ is heated with conc. H_2SO_4 and a soluble chloride like NaCl, deep red vapours of chromyl chloride, CrO_2Cl_2 are produced.

$$K_2Cr_2O_7 + 4NaCl + 3H_2SO_4 \text{ (concentrated)} \xrightarrow{\Delta} \underset{\text{red vapours}}{2CrO_2Cl_2} + K_2SO_4 + 2Na_2SO_4 + 3H_2O$$

When vapours of chromyl chloride are passed into aqueous NaOH solution, yellow colour solution of Na_2CrO_4 is obtained which is on reaction with acetic acid and lead acetate gives yellow ppt of $PbCrO_4$. This test is called chromyl chloride test. It is used to identify Cl^- in inorganic salt analysis.

7. When $K_2Cr_2O_7$ is heated with conc. HCl, Cl_2 is given off and chromic chloride $(CrCl_3)$ is obtained.

$$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2\uparrow$$

When Zn metal is added to the above solution, nascent hydrogen is evolved which reduces $CrCl_3$ to blue chromous chloride, $CrCl_2$.

$$CrCl_3 + H(\text{from Zn / HCl}) \longrightarrow CrCl_2 + HCl$$

When a saturated solution of CH_3COONa is added to the blue solution of $CrCl_2$ obtained as above, a red precipitate of chromous acetate, $(CH_3COO)_2Cr$ is obtained.

$$CrCl_2 + 2CH_3COONa \longrightarrow \underset{\text{red ppt.}}{(CH_3COO)_2Cr\downarrow} + 2NaCl$$

8. When an alkali is added to an orange-red solution of $K_2Cr_2O_7$, a yellow solution results.

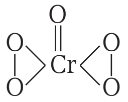
$$\underset{\text{orange-red}}{K_2Cr_2O_7} + 2KOH \longrightarrow \underset{\text{yellow}}{2K_2CrO_4} + H_2O$$

$$\underset{\text{orange-red}}{K_2Cr_2O_7} + 2NaOH \longrightarrow \underset{\text{yellow}}{K_2CrO_4} + H_2O + Na_2CrO_4$$

9. When H_2O_2 is added to an acidified solution of a dichromate, a complicated reaction occurs. The products depend on the pH and concentration of Cr(VI) ion.

$$Cr_2O_7^{2-} + 2H^+ + 4H_2O_2 \longrightarrow \underset{\substack{\text{chromic peroxide}\\\text{(deep blue-violet)}}}{2CrO(O_2)_2} + 5H_2O$$

A deep blue-violet coloured chromic peroxide is formed which is decomposed rapidly in aqueous solution into Cr^{3+} and oxygen.



chromic peroxide
(Oxidation state + 6 due to the presence of two peroxide linkages)

Uses

1. Potassium dichromate finds extensive use in dyeing, calico-printing and chrome-tanning.
2. It is used as an oxidising agent and in the preparation of various chromium compounds like Cr_2O_3, CrO_3 $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$, CrO_2Cl_2, K_2CrO_4, $CrCl_3$, $Cr(CH_3COO)_2$ etc.
3. It is also used in photography.
4. A mixture of $K_2Cr_2O_7$ and conc. H_2SO_4, usually known as chromic acid mixture, has strong oxidising properties and is used as a cleaning agent for glassware etc.
5. It is also used in leather industry (chrome tanning).

Interconversion of K_2CrO_4 and $K_2Cr_2O_7$

On acidifying, the yellow colour of K_2CrO_4 again changes to orange-red due to the reformation of $K_2Cr_2O_7$.

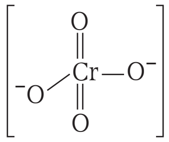
$$\underset{\text{yellow}}{2K_2CrO_4} + H_2SO_4 \longrightarrow \underset{\text{orangered}}{K_2Cr_2O_7} + K_2SO_4 + H_2O$$

This interconversion is explained on the basis of the fact that in $K_2Cr_2O_7$ solution, orange-red $Cr_2O_7^{2-}$ ions are in equilibrium with yellow CrO_4^{2-} ions.

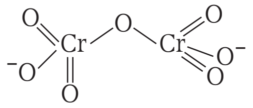
$$\underset{\text{orange-red}}{Cr_2O_7^{2-}} + H_2O \rightleftharpoons \underset{\text{yellow}}{2CrO_4^{2-}} + 2H^+$$

On adding an alkali, the concentration of H^+ ions decreases and hence, the above reaction proceeds in the forward direction producing yellow solution containing CrO_4^{2-} ions. On the other hand, when an acid is added, the concentration of H^+ ions increases and hence, the above reaction proceeds in the backward direction producing the orange solution containing $Cr_2O_7^{2-}$ ions.

Structures of Chromate and Dichromate Ions



tetrahedral
(chromate ion)



(dichromate ion)

In $Cr_2O_7^{2-}$ two CrO_3 units have been joined by O.

The above description makes it evident that since both $Cr_2O_7^{2-}$ and CrO_4^{2-} ions are present in a dichromate solution, $K_2Cr_2O_7$ will precipitate a salt of lower solubility product with Pb^{2+} or Ba^{2+} ions. Thus, when $K_2Cr_2O_7$ is treated with $Pb(NO_3)_2$, $PbCrO_4$ and not $PbCr_2O_7$ is precipitated. This is because of the fact that $PbCrO_4$ has less solubility product than $PbCr_2O_7$.

$$K_2Cr_2O_7 + 2Pb(NO_3)_2 + H_2O \longrightarrow 2PbCrO_4 + 2KNO_3 + 2HNO_3$$

Caution Point *In less acidic solution* $K_2Cr_2O_7$ *and* H_2O_2 *give violet coloured diamagnetic salt* $[CrO(O_2)(OH)]^-$. *In alkaline solution with* 30% H_2O_2, *a red brown compound* K_3CrO_8 *is formed.*

Estimation of $Cr_2O_7^{2-}$

$K_2Cr_2O_7$ can be estimated volumetrically by iodometric titration. Acidified $K_2Cr_2O_7$ is treated with KI and liberated I_2 is titrated using hypo ($Na_2S_2O_3$ solution) with starch indicator.

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 7H_2O + 3I_2$$

$$I_2 + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I^-$$

$$Cr_2O_7^{2-} \equiv 3I_2 \equiv 6I^- \equiv 6e^-$$

$$\text{Equivalent weight of } K_2Cr_2O_7 = \frac{\text{molecular wt.}}{6} = \frac{294}{6}$$

$$2S_2O_3^{2-} \equiv I_2 \equiv 2I^- \equiv 2e^-$$

$$\text{Equivalent weight of } Na_2S_2O_3 \cdot 5H_2O = \frac{248}{1}$$

Sample **Problem 14** *When acidified* $K_2Cr_2O_7$ *solution is added to* Sn^{2+} *salts then* Sn^{2+} *changes to* **[NCERT** Exemplar]

(*a*) Sn (*b*) Sn^{3+} (*c*) Sn^{4+} (*d*) Sn^+

Interpret (*c*)

$$Cr_2O_7^{2-} + 14H^+ + 3Sn^{2+} \longrightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O$$

Sample **Problem 15** *In the reduction of dichromate by* Fe *(II), the number of electrons involved per chromium atom is*

(*a*) 2 (*b*) 3 (*c*) 4 (*d*) 1

Interpret (*b*) $Cr_2O_7^{2-} + 6e^- + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$

Electron per Cr atom = 3

8.3 Potassium Permanganate

Its formula is $KMnO_4$. It is the salt of permanganic acid, $HMnO_4$ which is an unstable acid and exists only in solution.

Methods of Preparation

1. It may be prepared by acidifying the solution of potassium manganate, K_2MnO_4 by H_2SO_4.

$$3K_2MnO_4 + 2H_2SO_4 \longrightarrow 2K_2SO_4 + 2KMnO_4 + MnO_2\downarrow + 2H_2O$$

2. On a large scale, it is prepared from the mineral **pyrolusite,** MnO_2. The finely powdered pyrolusite mineral is fused with KOH in presence of air or an oxidising agent like KNO_3, $KClO_3$, etc. This treatment gives us fused green coloured potassium manganate, K_2MnO_4.

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$

$$MnO_2 + 2KOH + KNO_3 \longrightarrow K_2MnO_4 + KNO_2 + H_2O$$

$$3MnO_2 + 6KOH + KClO_3 \longrightarrow 3K_2MnO_4 + KCl + 3H_2O$$

The fused K_2MnO_4 obtained as above is extracted with water and the solution, after filtration, is converted into potassium permanganate ($KMnO_4$) by any of the following methods

(i) In **Stadeler's process** Cl_2 is passed through the green solution of K_2MnO_4 until it becomes purple due to the formation of $KMnO_4$. Here, Cl_2 oxidises K_2MnO_4 into $KMnO_4$.

$$2K_2MnO_4 + Cl_2 \longrightarrow 2KCl + 2KMnO_4$$

(ii) By passing CO_2 or O_3 through the green solution of K_2MnO_4 until it becomes purple.

$$\underset{\text{green}}{3K_2MnO_4} + 2H_2O + 4CO_2 \rightarrow \underset{\text{purple}}{2KMnO_4} + MnO_2 + 4KHCO_3$$

$$2K_2MnO_4 + H_2O + O_3 \longrightarrow \underset{\text{purple}}{2KMnO_4} + 2KOH + O_2$$

(iii) Now-a-days the conversion of K_2MnO_4 into $KMnO_4$ is done by **the electrolytic oxidation process** in alkaline medium.

$$K_2MnO_4 \longrightarrow 2K^+ + MnO_4^{2-}$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$\text{At anode} \quad MnO_4^{2-} \longrightarrow MnO_4^- + e^-$$

$$\text{At cathode} \quad 2H + 2e^- \longrightarrow H_2\uparrow$$

Physical and Chemical Properties

1. Potassium permanganate forms dark purple lustrous crystals giving deep pink colour in solution.
2. It is isomorphous with potassium perchlorate, $KClO_4$.
3. Its solubility in water at 20°C is only about 7% while it dissolves more at higher temperature (25% at 63°C).
4. It gives off O_2 at 200°C.

$$2KMnO_4 \xrightarrow[200°C]{\Delta} K_2MnO_4 + MnO_2 + O_2$$

At red heat, K_2MnO_4 formed as above is decomposed into permanganite, K_2MnO_3 and O_2.

$$2K_2MnO_4 \rightleftharpoons 2K_2MnO_3 + O_2$$

5. When an alkaline solution of $KMnO_4$ is heated, O_2 is evolved.

$$4KMnO_4 + 4KOH \xrightarrow{\Delta} 4K_2MnO_4 + 2H_2O + O_2$$

6. With well cooled conc. H_2SO_4, it gives Mn_2O_7 which decomposes on warming.

$$2KMnO_4 + 2H_2SO_4 \longrightarrow Mn_2O_7 + 2KHSO_4 + H_2O$$

$$2Mn_2O_7 \xrightarrow{\Delta} 4MnO_2 + 3O_2$$

With warmed conc. H_2SO_4, oxygen gas is evolved.

$$4KMnO_4 + 6H_2SO_4 \longrightarrow 2K_2SO_4 + 4MnSO_4 + 6H_2O + 5O_2$$

7. When heated in a current of H_2, solid $KMnO_4$ gives KOH, MnO and steam.

$$2KMnO_4 + 5H_2 \longrightarrow 2KOH + 2MnO + 4H_2O$$

8. A mixture of $KMnO_4$ with sulphur and charcoal burns when heated, and explodes like a gun powder when rubbed.
9. A well-powdered mixture of $KMnO_4$ and oxalic acid catches fire spontaneously in a few seconds.

Hot Spot 3

OXIDISING Nature of $KMnO_4$

$KMnO_4$ as an oxidising agent is another important topic for JEE Main examination. The level of question vary from easy to average.

$KMnO_4$ is a powerful oxidising agent. The course of reaction depends on whether the oxidation takes place in alkaline, neutral or acid solution.

(i) In alkaline solution, MnO_4^- ion (Mn = +7) is first reduced to MnO_4^{2-} ion (Mn = +6) and then to insoluble MnO_2 (Mn = +4). The solution first changes from purple (due to MnO_4^-) to green (due to MnO_4^{2-}) and finally it becomes colourless (MnO_2).

$$\underset{\substack{\text{purple}\\(\text{Mn} = +7)}}{2KMnO_4} + 2KOH \longrightarrow \underset{\substack{\text{green}\\(\text{Mn} = +6)}}{2K_2MnO_4} + H_2O + O \quad \text{...(i)}$$

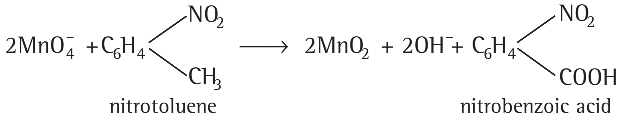
$$\underset{\substack{\text{green}\\(\text{Mn} = +6)}}{2K_2MnO_4} + 2H_2O \longrightarrow \underset{\substack{\text{colourless}\\(\text{Mn} = +4)}}{2MnO_2} + 4KOH + 2O \quad \text{...(ii)}$$

$$\underset{\substack{\text{purple}\\(\text{Mn} = +7)}}{2KMnO_4} + H_2O \longrightarrow \underset{\substack{\text{colourless}\\(\text{Mn} = +4)}}{2MnO_2} + 2KOH + 3O \quad (1)$$

Change in oxidation number of Mn = 3

In alkaline medium, $KMnO_4$ oxidises iodides (I^-) to iodates (IO_3^-), NH_3 to N_2 and nitrotoluene to nitrobenzoic acid as

$$2MnO_4^- + H_2O + I^- \xrightarrow{\text{Alkali}} 2MnO_2 + 2OH^- + IO_3^-$$



$$2MnO_4^- + C_6H_4\begin{cases} NO_2 \\ CH_3 \end{cases} \longrightarrow 2MnO_2 + 2OH^- + C_6H_4\begin{cases} NO_2 \\ COOH \end{cases}$$

nitrotoluene　　nitrobenzoic acid

$$2MnO_4^- + 2NH_3 \longrightarrow 2MnO_2 + 2OH^- + N_2 + 2H_2O$$

(ii) In neutral solution, $KMnO_4$ is directly reduced to MnO_2.

$$2K\overset{+7}{M}nO_4 + H_2O \longrightarrow 2KOH + 2\overset{+4}{Mn}O_2 + 3O \quad (2)$$

Change in oxidation number (Mn) = 3

In neutral medium, $KMnO_4$ oxidises Mn^{2+} salt to MnO_2, $Na_2S_2O_3$ to Na_2SO_4, H_2S to S as

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \longrightarrow 5MnO_2 + 4H^+$$

$$8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$$

$$2MnO_4^- + 4H_2S \longrightarrow 2MnS + S + SO_4^{2-} + 4H_2O$$

(iii) In acidic medium (dil H_2SO_4), MnO_4^- ion is reduced to Mn^{2+} ion and five O-atoms are rendered available from two MnO_4^- ions as :

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O \quad (3)$$

In acidic medium, $KMnO_4$ oxidises Fe (II) salts to Fe (III) salts, oxalic acid to CO_2, H_2S to S, SO_2 to H_2SO_4, sulphites to sulphates, KI to I_2, H_2O_2 to O_2, halogen acids to halogens as

$$MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

$$2MnO_4^- + 16H^+ + 5S^{2-} \longrightarrow 2Mn^{2+} + 5S + 8H_2O$$

$$2MnO_4^- + 2H_2O + 5SO_2 \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+$$

$$2MnO_4^- + 6H^+ + 5SO_3^{2-} \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$$

$$2MnO_4^- + 16H^+ + 10I^- \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O$$

$$2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 5O_2 + 8H_2O$$

$$2MnO_4^- + 16H^+ + 10X^- \longrightarrow 2Mn^{2+} + 5X_2 + 8H_2O$$

Equivalent Weight of $KMnO_4$

In different mediums, equivalent weight of $KMnO_4$ *is different.*

(a) In Alkaline Medium

From the equation (1), it is evident that two molecules of $KMnO_4$ in alkaline solution give three oxygen atoms (*i.e.*, six equivalents) and, therefore, the equivalent weight of $KMnO_4$ as an oxidising agent in alkaline solution is one-third of its molecular weight.

$$\text{Eq. wt. of } KMnO_4 = \frac{\text{mol. wt.}}{3} = \frac{158}{3} = 52.67$$

(Change in oxidation no = 3)

(b) In Neutral Medium

Equation (2) is the same as for alkaline medium. Evidently, in neutral medium as well, the equivalent weight of $KMnO_4$ is one-third of its molecular weight.

$$\text{Eq. wt. of } KMnO_4 = \frac{\text{mol. wt.}}{3} = \frac{158}{3} = 52.67$$

(Change in oxidation number = 3)

(c) In Acidic Medium

It is obvious that in acid solution, the equivalent weight of $KMnO_4$ is one-fifth of its molecular weight.

$$\text{Eq. wt. of } KMnO_4 = \frac{\text{mol. wt.}}{5} = \frac{158}{5} = 31.6$$

(Change in oxidation number of Mn = 5)

Sample Problem 16 $KMnO_4$ *acts as an oxidising agent in acidic medium. The number of moles of* $KMnO_4$ *that will be needed to react with one mole of sulphide ions in acidic solution is* **[NCERT Exemplar]**

(a) $\frac{2}{5}$ (b) $\frac{3}{5}$ (c) $\frac{4}{5}$ (d) $\frac{1}{5}$

Interpret (a) $2MnO_4^- + 16H^+ + 5S^{2-} \longrightarrow 2Mn^{2+} + 5S + 8H_2O$

5 moles of S^{2-} ions react with 2 moles of $KMnO_4$

So, 1 mole of S^{2-} ion will react with $\frac{2}{5}$ mole of $KMnO_4$.

Sample **Problem 17** $KMnO_4$ *acts as an oxidising agent in alkaline medium. When alkaline* $KMnO_4$ *is treated with* KI, *iodide ion is oxidised to*

(*a*) I_2

(*b*) IO^-

(*c*) IO_3^-

(*d*) IO_4^-

Interpret (c) $2MnO_4^- + H_2O + I^- \xrightarrow{\text{Alkali}} 2MnO_2 + 2OH^- + IO_3^-$

Sample **Problem 18** MnO_4^{2-} *changes to* MnO_2 *and* MnO_4^- *in acidic medium. The equivalent wt. of* MnO_4^{2-} *will be*

(*a*) $\frac{M}{2}$ (*b*) $\frac{2M}{3}$ (*c*) $\frac{3M}{2}$ (*d*) $\frac{M}{5}$

Interpret (c) $3\overset{+6}{Mn}O_4^{2-} + 4H^+ \longrightarrow \overset{+4}{Mn}O_2 + 2\overset{+7}{Mn}O_4^- + 2H_2O$

(disproportionation reaction) Eq. wt. of the species undergoing disproportionation = eq. wt. (in oxidation) + eq. wt. (in reduction)

$$\overset{+6}{Mn}O_4^{2-} \longrightarrow \overset{+4}{Mn}O_2; \quad \text{eq. wt. (reduction)} = \frac{M}{2}$$

$$\overset{+6}{Mn}O_4^{2-} \longrightarrow \overset{+7}{Mn}O_4^-; \quad \text{eq. wt. (oxidation)} = \frac{M}{1}$$

$$\therefore \text{ Eq. wt. of } MnO_4^{2-} = \frac{M}{2} + \frac{M}{1} = \frac{3M}{2}$$

Uses

It is used

1. as an oxidising agent in the laboratory as well as in industry.
2. in volumetric estimations of ferrous salts, oxalic acid, H_2O_2 etc.
3. as a disinfectant and a germicide on account of its oxidising property.
4. in qualitative analysis for detecting halides and oxalates.
5. in the manufacture of saccharin, benzoic acid, acetaldehyde etc.
6. for bleaching waxes.
7. for the detection of double bond in organic compounds. (For this purpose alkaline $KMnO_4$ solution under the name Baeyer's reagent is used.)
8. as a source of reactive form of MnO_2 which is used in place of pyrolusite in the manufacture of dry cells.

8.4 *f*-Block Elements

The elements in which last electron enters into *f*-orbitals of the anti-penultimate (inner to the penultimate shell), *i.e.,* $(n-2)$ shell, are called ***f*-block elements.** Since, they constitute transition series within transition series and the last electron occupies the antipenultimate shell, they are named as **inner-transition elements.** They all belong to III-B group (3 group) of Periodic Table. In these elements, both the *d* and *f* subshells are incomplete. The general outer electronic configuration of these elements is $(n-2)f^{1-14}$, $(n-1)d^{10}ns^2$. Depending upon the nature of *f*-orbital of the antipenultimate shell in which the differentiating electron enters, they are divided into two series, *viz*, 4*f* and 5*f* series.

4*f*-Series or First Inner-Transition Series

In this series, the last electron occupies the 4*f* orbital. This series includes next fourteen elements after lanthanum $(Z = 57)$, *i.e.,* from cerium $(Z = 58)$ to lutetium $(Z = 71)$. These are commonly called **lanthanides** or **lanthanons** or **rare earths.** The name lanthanides or lanthanons was given because they are closely related with lanthanum ($_{57}$La) in their properties. However, the name rare earth was given because these elements were difficult to obtain. But now this term is obsolete.

The general characteristics of lanthanoids are as follows

(a) Electronic Configuration

General electronic configuration of these elements is $[Xe]\ 4f^{1-14}, 5d^{0-1}, 6s^2$.

Table 8.9 **Electronic Configuration of Lanthanides**

Name	Symbol	Atomic no.	Configuration
Cerium	Ce	58	[Xe] $4f^2 5d^0 6s^2$
Praseodymium	Pr	59	[Xe] $4f^3 5d^0 6s^2$
Neodymium	Nd	60	[Xe] $4f^4 5d^0 6s^2$
Promethium	Pm	61	[Xe] $4f^5 5d^0 6s^2$
Samarium	Sm	62	[Xe] $4f^6 5d^0 6s^2$
Europium	Eu	63	[Xe] $4f^7 5d^0 6s^2$
Gadolinium	Gd	64	[Xe] $4f^7 5d^1 6s^2$
Terbium	Tb	65	[Xe] $4f^9 5d^0 6s^2$
Dysprosium	Dy	66	[Xe] $4f^{10} 5d^0 6s^2$
Holmium	Ho	67	[Xe] $4f^{11} 5d^0 6s^2$
Erbium	Er	68	[Xe] $4f^{12} 5d^0 6s^2$
Thulium	Tm	69	[Xe] $4f^{13} 5d^0 6s^2$
Ytterbium	Yb	70	[Xe] $4f^{14} 5d^0 6s^2$
Lutetium	Lu	71	[Xe] $4f^{14} 5d^1 6s^2$

(b) Physical State

All of them are silvery white soft metals with high density and melting point. These get tarnish readily in air. The hardness of these metals increases with rise in atomic number.

(c) Atomic and Ionic Radii

In 4*f* series, as the atomic number increases from La to Lu, the atomic and ionic radii decreases gradually. This decrease in atomic and ionic size from lanthanum (at. no. 57) to lutetium (at. no. 71) is a unique feature and is known as **lanthanide contraction.** This contraction is attributed to imperfect shielding of electrons of *f*-orbital. It is even less than the shielding shown by *d*-electron.

As a result of lanthanide contraction, the normal increase in size from Sc → Y → La disappears after the lanthanide and the pairs of elements such as Zr—Hf, Nb—Ta and Mo—W have nearly same size. The properties of these elements are very similar.

The similarities in properties within these pairs make their separation very difficult.

Due to lanthanide contraction, the elements of 5*d* and 4*d* series resemble each other much more closely than do the elements of 4*d* and 3*d* series.

Sample **Problem 19** *The radius of* La^{3+} *(atomic number of* La= 57) *is* 1.06 Å. *Which one of the following given values will be closest to the radius of* Lu^{3+}?
(Atomic number of Lu = 71)

(*a*) 1.60 Å (*b*) 1.40 Å
(*c*) 1.06 Å (*d*) 0.85 Å

Interpret (*d*) Due to lanthanoid contraction there occurs net decrease in size. Only one 0.85 Å is smaller one.

(d) Oxidation State

All of them show variable valency or oxidation state. However, +3 oxidation state is most stable. Some of these elements also exhibit +2 and +4 oxidation states along with +3 oxidation state. Higher oxidation states are not possible because there is a large energy gap beween 4*f* and 5*d* subshells.

Following stable ions also exist as

$$4f^0 = La^{3+}$$
$$4f^7 = Eu^{2+}, Gd^{3+}, Tb^{4+}$$
$$4f^{14} = Yb^{2+}, Lu^{3+}$$

Stability of these ions depend on

(i) ionisation energy (ii) sublimation energy
(iii) lattice energy

(e) Colour

Many trivalent lanthanide ions are coloured in both solid state as well as aqueous solutions (not shown by La^+, Ce^{3+}, Gd^{3+}, Yb^{3+} and Lu^{3+}). The colour of these ions is because of *f*-*f* transition due to the presence of partly filled *f*-orbitals.

Ce^{4+} is orange red ($4f^0$, isoelectronmic of La^{3+}) and Yb^{2+} is yellow ($4f^{14}$ isoelectronic of Lu^{3+}).

(f) Magnetic Properties

Except Lu^{3+}, Yb^{3+} and Ce^{4+}, all other lanthanoid ions are paramagnetic. However, the point of difference from transition elements is that here, both spin as well as orbital moments give contribution and the μ_{eff} is calculated as

$$\mu_{eff} = \sqrt{4S(S+1) + L(L+1)} \text{ BM}$$

The paramagnetism increases to maximum in neodymium (Nd) (atomic number 60).

(g) Ionisation Energy

These elements have low ionisation energy and thus, have high electropositive character.

(h) Complex Formation

Because of their low charge density lanthanoids have very less tendency to form complexes. They form complexes with strong chelating agents like EDTA oxime but not with π-bonding ligands.

(i) Alloy Formation

They form alloy with other metals like iron, *e.g.,* misch metal which consists of lanthanoid metal (~ 95%), iron (~ 5%) and traces of S, C, Ca, Al, etc.

(j) Reactivity

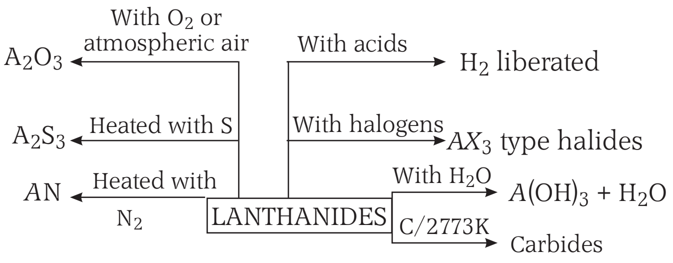
As far as their chemical behaviour is concerned, their earlier members are quite reactive (similar in behaviour to Ca) but with increasing atomic number they behave more like Al.

These elements easily combine with hydrogen forming hydrides.

The carbides (with C) of the type A_2C, A_2C_3 and AC_2 are reported where, A = lanthanide.

They liberate H_2 with dilute acids and form halides with halogens.

Their oxides (M_2O_3) and hydroxides [$M(OH)_3$] are stable. The hydroxides are ionic and basic. They are less basic than $Ca(OH)_2$ but more basic than amphoteric $Al(OH)_3$. The basic strength decreases from $Ce(OH)_3$ to $Lu(OH)_3$. Their generalised reactions can be summarised as



Here, A = lanthanides

Carbonyls are not formed by lanthanides due to non-availability of d-electrons for π-bonding. However, an unstable $Nd(CO)_6$ has been prepared.

Ce and Tb give CeF_4 and TbF_4 instead of CeF_3 and TbF_3 respectively.

Eu and Yb dissolve in liquid ammonia and form blue solution (which give spectra characteristic of M^{2+} and ammoniated electrons). The solution decolourises slowly but the concentrated solution appear golden.

Sample Problem 20 *Match the property given in Column I with the element given in Column II.*

	Column I (Property)		**Column II** (Element)
(I)	Lanthanoid which shows +4 oxidation state	(A)	Pm
(II)	Lanthanoid which can show +2 oxidation state	(B)	Ce
(III)	Radioactive lanthanoid	(C)	Lu
(IV)	Lanthanoid which has $4f^7$ electronic configuration in +3 oxidation state	(D)	Eu
(V)	Lanthanoid which has $4f^{14}$ electronic configuration in +3 oxidation state	(E)	Gd
		(F)	Dy

(*a*) I-B, II-D, III-A, IV-E, V-C
(*b*) I-B, II-C, III-E, IV-A, V-D
(*c*) I-E, II-F, III-C, IV-A, V-D
(*d*) I-F, II-A, III-B, IV-C, V-D

Interpret (*a*) Ce = + 4 oxidation state, Eu = + 2 oxidation state

Pm = radioactive lanthanoid, $Gd^{3+} = 4f^7$

$Lu^{3+} = 4f^{14}$

5*f*-Series or Second Inner-Transition Series

If the last electron (*i.e.,* the differentiating electron) occupies $5f$ orbital, the element is said to belong **5*f*-series**. This series also includes fourteen elements but here, the elements are after actinium, Ac ($Z = 89$) *i.e.,* from thorium ($Z = 90$) to lawrencium ($Z = 103$). These are called **actinides** or **actinones** because of their close resemblance in properties with actinium.

Except thorium, protactinium and uranium, all other actinides are synthetic elements (*i.e.,* man made elements) These all are radioactive.

Important characteristics of actinides include

(a) Electronic Configuration

Their general electronic configuration is $[Rn]\,5f^{1-14}6d^{0-1}7s^2$. These elements along with their electronic configuration are tabulated below

Table 8.10 **Electronic Configuration of Actinides**

Name	Symbol	Atomic no.	Configuration
Thorium	Th	90	$[Rn]\,5f^0 6d^2 7s^2$
Protactinium	Pa	91	$[Rn]\,5f^2 6d^1 7s^2$
Uranium	U	92	$[Rn]\,5f^3 6d^1 7s^2$
Neptunium	Np	93	$[Rn]\,5f^4 6d^1 7s^2$
Plutonium	Pu	94	$[Rn]\,5f^6 6d^0 7s^2$
Americium	Am	95	$[Rn]\,5f^7 6d^0 7s^2$
Curium	Cm	96	$[Rn]\,5f^7 6d^1 7s^2$
Berkelium	Bk	97	$[Rn]\,5f^8 6d^1 7s^2$
Californium	Cf	98	$[Rn]\,5f^{10} 6d^0 7s^2$
Einsteinium	Es	99	$[Rn]\,5f^{11} 6d^0 7s^2$
Fermium	Fm	100	$[Rn]\,5f^{11} 6d' 7s^2$
Mendelevium	Md	101	$[Rn]\,5f^{13} 6d^0 7s^2$
Nobelium	No	102	$[Rn]\,5f^{14} 6d^0 7s^2$
Lawrencium	Lr	103	$[Rn]\,5f^{14} 6d^1 7s^2$

Sample Problem 21 *General electronic configuration of actinoids is $(n-2)f^{1-14}(n-1)d^{0-2}\,ns^2$. Which of the following actinoids have one electron in 6d orbital?* [**NCERT** Exemplar]

(*a*) U (Atomic no. 92)
(*b*) Np (Atomic no. 93)
(*c*) Pu (Atomic no. 94)
(*d*) Am (Atomic no. 95)

Interpret (*a, b*) $U = 5f^3, 6d^1, 7s^2$

$Np = 5f^4, 6d^1, 7s^2$

(b) Physical State

These metals are silvery white in appearance and display a variety of structures. Except thorium and americium, all actinides have high density.

(c) Oxidation State

For them, there is a greater range of oxidation states (*i.e.*, +4, +5, +6 along with +3) seen which in part attributed to the fact that the $5f$, $6d$ and $7s$ levels are of comparable energy. The maximum oxidation state increases from + 4 in Th to + 5 in Pa, + 6 in U and + 7 in Np and Pu and then decreases in succeding elements. However, here also the predominant oxidation state is +3, which is more stable in case of heavier elements.

(d) Atomic and Ionic Radii

There is seen a gradual decrease in the size of atoms or ions (actinide contraction) which is like lanthanide contraction but less prone. The contraction is infact attributed to the shielding effect of $5f$ electrons.

(e) Magnetic Property

The magnetic properties of them are even more complex than those of lanthanides. These are also paramagnetic in nature due to unpaired $5f$ electrons.

(f) Colour

Actinides are also coloured because of *f*-*f* transition, from the *f*-orbital of lower energy to the *f*-orbital of higher energy. The ions having $5f^0$, $5f^7$ and $5f^{14}$ are colourless. The colour of some other ions are as

$$U^{3+}\ (5f^3) : \text{Red};\quad Np^{3+}\ (5f^4) : \text{Bluish}$$
$$Pu^{3+}\ (5f^5) : \text{Blue};\quad Am^{3+}\ (5f^6) : \text{Pink}$$

(g) Ionisation Energies

Their ionisation energies are very low and thus, they have high electropositive character and behave as strong reducing agents.

In actinoids $5f$ electrons are more effectively shielded from the nuclear charge than $4f$ electrons of corresponding lanthanoids. Hence, outer electrons are less firmly held and they are available for bonding in the actinoids.

(h) Complex Formation

Because of their higher nuclear charge and small size, these elements form complex.

(i) Reactivity

Actinoids metals are reactive. Their reactivity increase with increase in atomic number. They tarnish rapidly. Protective covering is formed only in case of Th. Conc. HCl reacts rapidly with these metals but conc. HNO_3 makes Th, U and Pu passive.

Check Point 2

1. Actinoid contraction is greater from element to element than lanthanoid contraction. why?
2. Explain, why among the lanthanides, Ce(III) can be easily oxidised to Ce(IV)? (Ce = 50)
3. Ionisation energy of Ce, Pr, Nd are higher than Th, Pa and U. Why? **[NCERT Exemplar]**
4. The magnetic properties of actinides are more complex than those of lanthanides. Explain it.

WORKED OUT
Examples

Example 1 *Which one of the following arrangement of ions in order of increasing strength as a reducing agent is correct?*

(a) $Cr_2O_7^{2-} < Cr^{3+} < Cr^{2+}$
(b) $Cr_2O_7^{2-} < Cr^{2+} < Cr^{3+}$
(c) $Cr^{3+} < Cr^{2+} < Cr_2O_7^{2-}$
(d) $Cr^{2+} < Cr^{3+} < Cr_2O_7^{2-}$

Solution (a) $Cr_2O_7^{2-} < Cr^{3+} < Cr^{2+}$

Smaller the oxidation state of element in the ion, greater the reducing nature.

Example 2 *The magnetic moment of* Mn *in* MnO_4^- *is*

(a) *zero BM*
(b) $\sqrt{3}$ *BM*
(c) $\sqrt{8}$ *BM*
(d) $\sqrt{15}$ *BM*

Solution (b) Oxidation number of Mn in $MnO_4^- = +7$

So, it should have [Ar] configuration and it should be colourless and diamagnetic. But one electron is transferred to Mn from oxygen and thus Mn in MnO_4^- has one unpaired electron making it paramagnetic.

$$\text{Magnetic moment} = \sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3}\ \text{BM}$$

Example 3 *Black coloured solid (A)* $\xrightarrow[\Delta]{KNO_3\ +\ KOH}$ *green colour solution (B)* $\xrightarrow{CO_2} \underset{\text{pink}}{(C)} + (A)$

Pink compound (C) is decolourised by Fe^{2+}. *The compound A, B and C are*

(a) MnO_2, K_2MnO_4, $KMnO_4$
(b) MnO_2, $KMnO_4$, K_2MnO_4
(c) $KMnO_4$, MnO_2, K_2MnO_4
(d) K_2MnO_4, MnO_4, $KMnO_4$

Solution (c) Black colour compound is $MnO_2(A)$.

When it is fused with KOH and KNO_3, potassium manganate (K_2MnO_4) is formed. It is indicated by its green colour.

In acidic medium, K_2MnO_4 is unstable and disproportionates

$$\underset{(A)}{MnO_2} + KOH + O_2(KNO_3) \xrightarrow{\Delta} \underset{\text{green colour }(B)}{K_2MnO_4}$$

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$3MnO_4^{2-} + 4H^+ \longrightarrow MnO_2 + 2MnO_4^- + 2H_2O$$

(disproportionation reaction)

Example 4 *Possible oxidation state of last element in the series of the actinoids will be* **[NCERT]**

(a) $+2$
(b) $+3$
(c) $+4$
(d) $+5$

Solution (b) Actinoids = ${}_{89}Ac$ to ${}_{103}Lr$

Lawrencium (Lr; $Z = 103$) is the last element of actinoids series.

Electronic configuration of ${}_{103}Lr = [Rn]\,5f^{14}6d^17s^2$

Its possible oxidations state = $+3$

Because after losing three electrons lawrencium acquire stable configuration $5f^{14}$.

Example 5 *Which one of the following species is the most stable in aqueous solution?* **[NCERT]**

(a) Mn^{3+}
(b) Cr^{3+}
(c) V^{3+}
(d) Ti^{3+}

Solution (a) $Mn^{3+}(Z = 25) = [Ar]\,3d^4$; $Cr^{3+}(Z = 24) = [Ar]\,3d^3$
$V^{3+}(Z = 23) = [Ar]\,3d^2$; $Ti^{3+}(Z = 22) = [Ar]\,3d^1$

Out of these species, Cr^{3+} is most stable in aqueous solution due to its tendency of complex formation.

Example 6 *Transition metals form alloys easily. The reason for this is*

(a) *their occurrence*
(b) *similar size*
(c) *magnetic nature*
(d) *do not form easily*

Solution (b) Transition metals are quite similar in atomic size. Therefore, the atoms of one metal can substitute the atoms of other metal in its crystal lattice. Thus, on cooling a mixture, solution of two or more transition metals, *i.e.*, smooth solid alloy, is formed.

Example 7 *The correct statement about ionisation energies of* Cu *and* Zn *is/are*

(a) IE_1 *of* Cu *is less than that of* Zn
(b) IE_2 *of* Cu *is more than that of* Zn
(c) IE_2 *of* Zn *is more than that of* Cu
(d) *Both* (a) *and* (b)

Solution (d) IE_1 of Cu ($3d^{10}4s^1$) is less than that of Zn ($3d^{10}4s^2$) because it is easy to remove an electron from a half-filled *s*-orbital as compared to fully-filled *s*-orbital. However, in case of IE_2, the electron is lost from 3*d* orbital of Cu and 4*s* orbital of Zn and loss of electron from 4*s* orbital is easier as compared to fully-filled 3*d* orbital.

Start Practice for JEE Main

Round I (Topically Divided Problems)

Characteristics of Transition Elements

1. Which of the following is amphoteric oxide?

Mn_2O_7, CrO_3, Cr_2O_3, CrO, V_2O_5, V_2O_4 **[NCERT Exemplar]**

(a) V_2O_5, Cr_2O_3 (b) Mn_2O_7, CrO_3
(c) CrO, V_2O_5 (d) V_2O_5, V_2O_4

2. Which of the following statements is not correct? **[NCERT Exemplar]**

(a) Copper liberates hydrogen from acids
(b) In its higher oxidation states, manganese forms stable compounds with oxygen and fluorine
(c) Mn^{3+} and Co^{3+} are oxidising agents in aqueous solution
(d) Ti^{2+} and Cr^{2+} are reducing agents in aqueous solution

3. Paramagnetism is given by the relation $\mu = 2\sqrt{s(s+1)}$ magnetons where 's' is the total spin. On this basis, the paramagnetism of Cu^+ ion is

(a) 3.88 magnetons (b) 2.83 magnetons
(c) 1.41 magnetons (d) zero

4. Ti^{2+} is purple whereas Ti^{4+} is colourless, because

(a) there is no crystal field effect in Ti^{4+}
(b) Ti^{2+} has $3d^2$ configuration
(c) Ti^{4+} has $3d^2$ configuration
(d) Ti^{4+} is a very small cation when compared to Ti^{2+} and hence, does not absorb any radiation

5. Magnetic moment of $Cr(Z = 24)$, $Mn^+(Z = 25)$ and $Fe^{2+}(Z = 26)$ are x, y, z. They are in order

(a) $x < y < z$ (b) $x = y < z$
(c) $z < x = y$ (d) $x = y = z$

6. VO_2 is an amphoteric oxide and in acidic medium it forms

(a) VO^{2+} (b) VO_2^+
(c) V^{3+} (d) VO_2^{2+}

7. Which of the following is most stable among Cu^+, Fe^+, Fe^{2+} and Fe^{3+}?

(a) Cu^+ (b) Fe^+
(c) Fe^{2+} (d) Fe^{3+}

8. Select the incorrect statement about transition elements.

(a) The last electron enters in the *d*-orbital
(b) Their properties are in between *s* and *p*-block elements
(c) Scandium is the transition element with smallest atomic radii
(d) Their common oxidation state is +3

9. Transition elements exhibit variable valencies because they release electrons from the following orbits

(a) *ns* (b) *ns* and *np*
(c) $(n-1)d$ and *ns* (d) $(n-1)\,d$

10. The transition elements are more metallic than the representative elements because they have

(a) electron pairs in *d*-orbitals
(b) availability of *d*-orbitals for bonding
(c) the electron in *d*-orbitals
(d) unpaired electron in metallic orbitals

11. Which of the following is not a property of transition elements?

(a) Fixed valency
(b) Catalytic property
(c) Paramagnetism
(d) Colour

12. Coinage metals show the properties of

(a) inert elements
(b) normal elements
(c) typical elements
(d) transition elements

13. The valence shell electronic configuration of Cr^{2+} ion is

(a) $4s^0, 3d^4$ (b) $3p^6, 4s^2$

(c) $4s^2, 3d^2$ (d) $4s^2, 3d^0$

14. Zinc does not show variable valency like *d*-block elements because

(a) it is low melting

(b) *d*-orbital is complete

(c) it is a soft metal

(d) two electrons are present in the outermost orbit

15. The catalytic activity of the transition metals and their compounds is ascribed to their

(a) magnetic behaviour

(b) chemical reactivity

(c) ability to adopt multiple oxidation states and their complexing ability

(d) unfilled *d*-orbitals

16. Transition elements are coloured

(a) due to unpaired *d*-electrons

(b) due to small size

(c) due to metallic nature

(d) All of the above

17. Which of the following has the maximum number of unpaired *d*-electrons?

(a) Fe^{2+} (b) Cu^+ (c) Zn (d) Ni^{3+}

18. Cuprous ion is colourless, while cupric ion is coloured because

(a) both have half-filled *p* and *d*-orbitals

(b) cuprous ion has a completed *d*-orbital and cupric ion has incomplete *d*-orbital

(c) cuprous ion has incomplete *d*-orbital and cupric ion has a complete *d*-orbital

(d) both have unpaired electrons in *d*-orbital

19. Of the ions Zn^{2+}, Ni^{2+} and Cr^{3+},
(atomic number of $Zn = 30, Ni = 28, Cr = 24$)

(a) all three are coloured

(b) all three are colourless

(c) only Zn^{2+} is colourless and Ni^{2+} and Cr^{3+} are coloured

(d) only Ni^{2+} is coloured and Zn^{2+} and Cr^{3+} are colourless

20. Which of the following ionic species will impart colour to an aqueous solution?

(a) Cu^+ (b) Zn^{2+}

(c) Cr^{3+} (d) Ti^{4+}

21. In which of the following metallic bond is strongest?

(a) V (b) Fe

(c) Cr (d) Sc

22. Which of the following ions has the highest magnetic moment?

(a) Ti^{3+} (b) Sc^{3+}

(c) Mn^{2+} (d) Zn^{2+}

23. Which of the following is the correct sequence of atomic weights of given elements?

(a) Co > Ni > Fe (b) Fe > Co > Ni

(c) Fe > Ni > Co (d) Ni > Co > Fe

24. Which of the following elements has the maximum first ionisation potential?

(a) V (b) Ti

(c) Mn (d) Cr

25. Which oxide of manganese is amphoteric?

(a) MnO (b) MnO_2

(c) Mn_2O_7 (d) Mn_2O_3

26. Which of the following is correct?

(a) Duralumin : Al + Cu + Mg + Ag

(b) German silver : Cu + Zn +C

(c) Gun metal : Cu + Zn + Sn

(d) Solder : Pb + Al

27. Which one of the following is a diamagnetic ion?

(a) Co^{2+} (b) Cu^{2+}

(c) Mn^{2+} (d) Sc^{3+}

Compounds of Transition Elements

28. $K_2Cr_2O_7 \xrightarrow{\Delta} K_2CrO_4 + O_2 + X$. In the above reaction X is

(a) CrO_3 (b) Cr_2O_7

(c) Cr_2O_3 (d) CrO_5

29. One of the product formed when $K_2Cr_2O_7$ reacts with conc. H_2SO_4 in cold is

(a) CrO_3 (b) $Cr_2(SO_4)_3$

(c) Cr_2O_3 (d) CrO_4Cl_2

30. The reaction of $K_2Cr_2O_7$ with NaCl and conc. H_2SO_4 gives

(a) CrO_2Cl_2 (b) Cr_2O_3

(c) $CrCl_3$ (d) $CrOCl_2$

31. Why is HCl not used to make the medium acidic in oxidation reactions of $KMnO_4$ in acidic medium? **[NCERT Exemplar]**

(a) Both HCl and $KMnO_4$ act as oxidising agents.

(b) $KMnO_4$ oxidises HCl into Cl_2 which is also an oxidising agent.

(c) $KMnO_4$ is a weaker oxidising agent that HCl.

(d) $KMnO_4$ acts as a reducing agent in the presence of HCl.

32. $Cr_2O_7^{2-} \xrightarrow{pH = x} CrO_4^{2-} \xrightarrow{pH = y} Cr_2O_7^{2-}$ pH values x and y can be

(a) 4 and 5
(b) 4 and 8
(c) 8 and 4
(d) 8 and 9

33. In dilute alkaline solution, MnO_4^- changes to

(a) MnO_4^{2-}
(b) MnO_2
(c) Mn_2O_3
(d) MnO

34. What are the species A and B in the following

$$CrO_3 + H_2O \longrightarrow A \xrightarrow{OH^-} B$$

(a) H_2CrO_4, $H_2Cr_2O_7$
(b) $H_2Cr_2O_7$, Cr_2O_3
(c) CrO_4^{2-}, $Cr_2O_7^{2-}$
(d) H_2CrO_4, CrO_4^{2-}

35. Which statement is not correct?

(a) Potassium dichromate oxidises a secondary alcohol into a ketone
(b) Potassium permanganate is a weaker oxidising substance than potassium dichromate
(c) Potassium permanganate is a stronger oxidising substance
(d) All of the above statements are correct

Inner-Transition Elements

36. Lanthanum is grouped with f-block elements because

(a) it has partially filled f-orbitals
(b) it has both partially filled f and d-orbitals
(c) the properties of lanthanum are very similar to the elements of 4*f*-block
(d) it is just before Ce in the Periodic Table

37. Cerium ($Z = 58$) is an important member of the lanthanides. Which of the following statements about cerium is incorrect?

(a) The common oxidation states of cerium are +3 and +4
(b) Cerium (IV) acts as an oxidising agent
(c) The +4 oxidation state of cerium is not known in solutions
(d) The +3 oxidation state of cerium is more stable than the +4 oxidation state

38. Which one of the following acts as an oxidising agent?

(a) Np^{4+}
(b) Sm^{2+}
(c) Eu^{2+}
(d) Yb^{2+}

39. Gadolinium belongs to $4f$ series. atomic number is 64. Which of the following is the correct electronic configuration of gadolinium? **[NCERT** Exemplar**]**

(a) $[Xe]4f^7 5d^1 6s^2$
(b) $[Xe]4f^6 5d^2 6s^2$
(c) $[Xe]4f^8 6d^2$
(d) $[Xe]4f^9 5s^1$

40. Which of the following oxidation state is common for all lanthanoids? **[NCERT** Exemplar**]**

(a) +2
(b) +3
(c) +4
(d) +5

41. There are 14 elements in actionoid series. Which of the following elements does not belong to this series? **[NCERT** Exemplar**]**

(a) U
(b) Np
(c) Tm
(d) Fm

42. Lanthanide for which +2 and +3 oxidation states are common is

(a) La
(b) Nd
(c) Ce
(d) Eu

43. Which pair of lanthanides is used in glass, blowers, goggles?

(a) Np, Pu
(b) Pu, Gd
(c) Fm, Ho
(d) Pr, Ho

44. Which of the following trivalent ion has the largest atomic radii in the lanthanide series?

(a) Ce
(b) Pm
(c) La
(d) Lu

45. Across the lanthanide series, the basicity of lanthanide hydroxides

(a) increases
(b) decreases
(c) first increases and then decreases
(d) first decreases and then increases

46. The +3 ion of which one of the following has half-filled $4f$ subshell?

(a) La
(b) Lu
(c) Gd
(d) Ce

47. Actinides

(a) have variable valency
(b) include 12 elements
(c) are all synthetic elements
(d) have only short lived isotopes

48. Actinides and lanthanides resemble in

(a) formation of complexes
(b) oxidation state
(c) ionisation energy
(d) electronic configuration

49. Lanthanide contraction occurs because

(a) *f*-orbitals are incompletely filled
(b) *f*-orbital electrons are easily lost
(c) *f*-orbital do not come out on the surface of atom and are buried inside
(d) *f*-orbital electrons are poor shielders of nuclear charge

50. Which of the following ion is diamagnetic?
(a) Nd^{3+} (b) La^{3+} (c) Tb^{3+} (d) Er^{3+}

51. The colour of $_{62}Sm^{3+}$ is yellow. The expected colour of $_{66}Dy^{3+}$ is
(a) yellow (b) red
(c) blue (d) green

52. The actinoids showing +7 oxidation state are
(a) U, Np (b) Pu, Am
(c) Np, Pu (d) Am, Cm

53. The lanthanoids contraction relates to
(a) atomic radii
(b) atomic as well as M^{3+} radii
(c) valence electrons
(d) oxidation states

54. In aqueous solution Eu^{2+} ion acts as
(a) an oxidising agent (b) a reducing agent
(c) an acid (d) All of these

55. A reduction in atomic size with increase in atomic number is a characteristic of elements of
(a) *f*-block (b) *d*-block
(c) high atomic masses (d) radioactive series

56. Which of the following statement is not correct?
(a) $La(OH)_3$ is less basic than $Lu(OH)_3$
(b) In lanthanide series ionic radius of Ln^{3+} ions decreases
(c) Zn, Cd, Hg are colourless and are diamagnetic
(d) Mn shows maximum oxidation state +7

57. Misch metal is
(a) an alloy of lanthanoid and copper
(b) an alloy of lanthanoid and nickel
(c) an alloy of lanthanoid, iron and carbon
(d) an alloy of actinoid and copper

58. Uranium reacts with conc. HNO_3
(a) to give $U(NO_3)_4$ and H_2
(b) to give $U(NO_3)_2$ and NO_2
(c) $UO_2(NO_3)_2$ and H_2
(d) to make metal passive

59. Select the correct statements.
(a) Pu^{4+} disproportionates to Pu^{3+} and PuO_2^{2+} in strongly acidic medium
(b) Maximum oxidation state of Np is +7
(c) UO_2^{2+} is stable
(d) All of the above are correct statements

60. Which one of the following elements shows maximum number of different oxidation states in its compounds?
(a) Eu
(b) La
(c) Gd
(d) Am

Round II (Mixed Bag)

Only One Correct Option

1. Transition metal with low oxidation number will act as
(a) an oxidising agent (b) a base
(c) an acid (d) None of these

2. Which of the following pair will have effective magnetic moment equal?
(a) Ti^{2+} and V^{2+} (b) Cr^{2+} and Fe^{2+}
(c) Cr^{3+} and Mn^{2+} (d) V^{2+} and Sc^{3+}

3. Consider the following statements.
(I) $La(OH)_3$ is the least basic among hydroxides of lanthanides.
(II) Zr^{4+} and Hf^{4+} possess almost the same ionic radii.
(III) Ce^{4+} can act as an oxidizing agent.

Which of the above is/are true?
(a) I and III (b) II and III
(c) II only (d) I and II
(e) I only

4. Most basic hydroxide among the following is
(a) $Lu(OH)_3$ (b) $Eu(OH)_3$
(c) $Yb(OH)_3$ (d) $Ce(OH)_3$

5. Arrange Ce^{3+}, La^{3+}, Pm^{3+} and Yb^{3+} in increasing order of their ionic radii.
(a) $Yb^{3+} < Pm^{3+} < Ce^{3+} < La^{3+}$
(b) $Ce^{3+} < Yb^{3+} < Pm^{3+} < La^{3+}$
(c) $Yb^{3+} < Pm^{3+} < La^{3+} < Ce^{3+}$
(d) $Pm^{3+} < La^{3+} < Ce^{3+} < Yb^{3+}$

6. The basic character of the transition metal monoxide follows the order
(At. no. of Ti = 22, V = 23, Cr = 24, Fe = 26)
(a) TiO > VO > CrO > FeO (b) VO > CrO > TiO > FeO
(c) CrO > VO > FeO > TiO (d) TiO > FeO > VO > CrO

7. When MnO_2 is fused with KOH, a coloured compound is formed. The product and its colour is
(a) K_2MnO_4, purple colour (b) Mn_2O_3, brown
(c) Mn_2O_4, black (d) $KMnO_4$, purple

8. Which of the following weighs less when weighted in magnetic field?

(a) $ScCl_3$
(b) $FeCl_3$
(c) $TiCl_3$
(d) VCl_3

9. An element is in M^{3+} form. Its electronic configuration is $[Ar]3d^1$, the ion is

(a) Ca^{2+} (b) Sc^+ (c) Ti^{4+} (d) Ti^{3+}

10. Transuranic elements begins with

(a) Np (b) Cm (c) Pu (d) U

11. Which among the following metals does not dissolve in aqua regia?

(a) Pt (b) Pd (c) Au (d) Ir

12. If M is element of actinoids series, the degree of complex formation decreases in the order

(a) $M^{4+} > M^{3+} > MO_2^{2+} > MO_2^+$
(b) $MO_2^+ > MO_2^{2+} > M^{3+} > M^{4+}$
(c) $M^{4+} > MO_2^{2+} > M^{3+} > MO_2^+$
(d) $MO_2^{2+} > MO_2^+ > M^{4+} > M^{3+}$

13. The electronic configuration of actinoids cannot be assigned with degree of certainty because of

(a) overlapping of inner orbitals
(b) free movement of electrons over all the orbitals
(c) small energy difference between $5f$ and $6d$ levels
(d) None of the above

14. Which lanthanoid compound is used as a most powerful liquid lasers after dissolving it in selenium oxychloride?

(a) Cerium oxide
(b) Neodymium oxide
(c) Promethium sulphate
(d) Ceric sulphate

More than One Correct Option

15. Generally transition elements and their salts are coloured due to the presence of unpaired electrons in metal ions. Which of the following compounds are coloured? **[NCERT Exemplar]**

(a) $KMnO_4$
(b) $Ce(SO_4)_2$
(c) $TiCl_4$
(d) Cu_2Cl_2

16. Which of the following will not act as oxidising agents? **[NCERT Exemplar]**

(a) CrO_3 (b) MoO_3 (c) WO_3 (d) CrO_4^{2-}

17. Although +3 is the characteristic oxidation state for lanthanoids but cerium also shows +4 oxidation state because **[NCERT Exemplar]**

(a) it has variable ionisation enthalpy
(b) it has a tendency to attain noble gas configuration
(c) it has a tendency to attain f^0 configuration
(d) it resembles Pb^{4+}

18. Transition elements show magnetic moment due to spin and orbital motion of electrons. Which of the following metallic ions have almost same spin only magnetic moment? **[NCERT Exemplar]**

(a) Co^{2+}
(b) Cr^{2+}
(c) Mn^{2+}
(d) Cr^{3+}

19. In the form of dichromate, Cr (VI) is a strong oxidising agent in acidic medium but Mo (VI) in MoO_3 and W (VI) in WO_3 are not because **[NCERT Exemplar]**

(a) Cr (VI) is more stable than Mo(VI) and W(VI).
(b) Mo(VI) and W(VI) are more stable than Cr(VI).
(c) Higher oxidation states of heavier members of group-6 of transition series are more stable.
(d) Lower oxidation states of heavier members of group-6 of transition series are more stable.

Assertion and Reason

Directions (Q. Nos. 20 to 24) *Each of these questions contains two statements : Statement* I *(Assertion) and Statement* II *(Reason). Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes* (*a*), (*b*) (*c*), (*d*) *given below :*

(a) Statement I is true; Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true; Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

20. **Statement I** Cu^{2+} iodide is not known.

Statement II Cu^{2+} oxidises I^- to iodine. **[NCERT Exemplar]**

21. **Statement I** Separation of Zr and Hf is difficult.

Statement II Zr and Hf lie in the same group of the Periodic Table. **[NCERT Exemplar]**

22. **Statement I** Actinoids form relatively less stable complexes as compared to lanthanoids.

Statement II Actinoids can utilise their $5f$ orbitals along with $6d$ orbitals in bonding but lanthanoids do not use their $4f$ orbital for bonding. **[NCERT Exemplar]**

23. **Statement I** Cu cannot liberate hydrogen from acids.

Statement II It has positive electrode potential. **[NCERT Exemplar]**

24. **Statement I** The highest oxidation state of osmium is +8.

Statement II Osmium is a $5d$-block element. **[NCERT Exemplar]**

Comprehension Type Questions

Directions (Q. Nos. 25 to 27) A characteristic property of the *d*-transition metals is the ability to exhibit several oxidation states. The stability of a given oxidation state depends on the nature of the element with which the transition metal is combined. The highest oxidation states are found in the compounds of fluorides and oxides because of the most electronegative nature of F and O (oxygen).

25. Nickel also shows zero (0) oxidation state. This oxidation state is in

(a) nitriles
(b) carbonyls
(c) cyclopentadienyl
(d) All of these

26. In which case there is a change in oxidation number?

(a) Aqueous solution of CrO_4^{2-} is acidified
(b) SO_2 gas is passed into $Cr_2O_7^{2-}/H^+$
(c) $Cr_2O_7^{2-}$ solution is made alkaline
(d) CrO_2Cl_2 is dissolved in NaOH

27. Most transition metals are inert towards acids or react slowly with them because of

(a) negative standard reduction potential
(b) protective layer of oxide
(c) Both (a) and (b)
(d) None of the above

Directions (Q. Nos. 28 to 29) Many ionic and covalent compounds of transition elements and also inner-transition elements are coloured. Colour may arise from an entirely different cause in ions with incomplete *d*-or *f* shells. In a free isolated gaseous ion, the five-*d*-orbitals are degenerate, that is they are identical in energy. The surrounding groups, which can be solvent molecules in solution or ligands in a complex or other ions in a crystal lattice, affect the energy of some *d*-orbitals more than others.

28. Consider the following statements

I. Colour of a transition metal complex is dependent on energy difference between two *d*-levels.
II. Colour of the complex is dependent on the nature of the ligand and the type of complex formed.
III. $ZnSO_4$ and TiO_2 are white as in both *d*-*d* spectra are impossible.

Select the correct statements.

(a) I, II, III
(b) I, II
(c) II, III
(d) I, III

29. MnO_4^- is of intense pink colour, though Mn is in (+7) oxidation state. It is due to

(a) oxygen gives colour to it
(b) charge transfer when oxygen gives its electron to Mn making it Mn (+ VI) hence, coloured
(c) charge transfer when Mn gives its electron to oxygen
(d) None of the above is correct

Previous Years' Questions

30. Iron exhibits +2 and +3 oxidation states. Which of the following statements about iron is incorrect? [AIEEE 2012]

(a) Ferrous oxide is more basic in nature than the ferric oxide
(b) Ferrous compounds are relatively more ionic than the corresponding ferric compounds
(c) Ferrous compounds are less volatile than the corresponding ferric compounds
(d) Ferrous compounds are more easily hydrolysed than the corresponding ferric compounds

31. In the context of lanthanoids, which of the following statements is not correct? [AIEEE 2011]

(a) There is a gradual decrease in the radii of the members with increasing atomic number in the series
(b) All the members exhibit +3 oxidation state
(c) Because of similar properties the separation of lanthanoids is not easy
(d) Availability of 4*f*-electrons results in the formation of compounds in +4 state for all members of the series

32. Larger number of oxidation states are exhibited by the actinoides than those by the lanthanoides, the main reason being [AIEEE 2008]

(a) 4*f* orbitals are more diffused than the 5*f* orbitals
(b) lesser energy difference between 5*f* and 6*d* than between 4*f* and 5*d* orbitals
(c) more energy difference between 5*f* and 6*d* than between 4*f* and 5*d* orbitals
(d) more reactive nature of the actinoids than the lanthanoids

33. Identify the incorrect statement among the following. [AIEEE 2007]

(a) *d*-block elements show irregular and erratic chemical properties among themselves
(b) La and Lu have partially filled *d* orbitals and no other partially filled orbitals
(c) The chemistry of various lanthanoids is very similar
(d) 4*f* and 5*f* orbitals are equally shielded

34. The actinoids exhibit more number of oxidation states in general than the lanthanoids. This is because [AIEEE 2007]

(a) the 5*f* orbitals are more buried than the 4*f* orbitals
(b) there is a similarity between 4*f* and 5*f* orbitals in their angular part of the wave function
(c) the actinoids are more reactive than the lanthanoids
(d) the 5*f* orbitals extend farther from the nucleus than the 4*f* orbitals

35. The 'spin-only' magnetic moment [in units of Bohr magneton, (μ_β)], of Ni^{2+} in aqueous solution would be (Atomic number of Ni = 28) [AIEEE 2006]

(a) 2.84 (b) 4.90 (c) 0 (d) 1.73

36. Lanthanoid contraction is caused due to [AIEEE 2006]

(a) the appreciable shielding on outer electrons by 4*f* electrons from the nuclear charge
(b) the appreciable shielding on outer electrons by 5*d* electrons from the nuclear charge
(c) the same effective nuclear charge from Ce to Lu
(d) the imperfect shielding on outer electrons by 4*f* electrons from the nuclear charge

37. Which of the following factors may be regarded as the main cause of lanthanide contraction? [AIEEE 2005]

(a) Greater shielding of 5*d* electron by 4*f* electrons
(b) Poor shielding of 5*d* electron by 4*f* electrons
(c) Effective shielding of one of 4*f* electrons by another in the sub shell
(d) Poor shielding of one of 4*f* electron by another in the sub-shell

38. The lanthanide contraction is responsible for the fact that [AIEEE 2003, 05]

(a) Zr and Zn have the same oxidation state
(b) Zr and Hf have about the same radius
(c) Zr and Nb have similar oxidation state
(d) Zr and Y have about the same radius

39. The oxidation state of chromium in the final product formed by the reaction between KI and acidified potassium dichromate solution is [AIEEE 2005]

(a) +3
(b) +2
(c) +6
(d) +4

Answers

Round I

1. (a)	**2.** (a)	**3.** (d)	**4.** (b)	**5.** (c)	**6.** (a)	**7.** (a)	**8.** (c)	**9.** (c)	**10.** (b)
11. (a)	**12.** (d)	**13.** (a)	**14.** (b)	**15.** (c)	**16.** (a)	**17.** (a)	**18.** (b)	**19.** (c)	**20.** (c)
21. (c)	**22.** (c)	**23.** (a)	**24.** (c)	**25.** (b)	**26.** (c)	**27.** (d)	**28.** (c)	**29.** (a)	**30.** (a)
31. (b)	**32.** (c)	**33.** (a)	**34.** (d)	**35.** (b)	**36.** (c)	**37.** (b)	**38.** (a)	**39.** (a)	**40.** (b)
41. (c)	**42.** (d)	**43.** (b)	**44.** (c)	**45.** (b)	**46.** (c)	**47.** (a)	**48.** (d)	**49.** (d)	**50.** (b)
51. (a)	**52.** (c)	**53.** (b)	**54.** (b)	**55.** (a)	**56.** (a)	**57.** (c)	**58.** (d)	**59.** (d)	**60.** (d)

Round II

1. (b)	**2.** (b)	**3.** (b)	**4.** (d)	**5.** (a)	**6.** (a)	**7.** (a)	**8.** (a)	**9.** (d)	**10.** (a)
11. (d)	**12.** (c)	**13.** (c)	**14.** (b)	**15.** (a,b)	**16.** (b,c)	**17.** (b,c)	**18.** (a,d)	**19.** (b,c)	**20.** (a)
21. (b)	**22.** (d)	**23.** (a)	**24.** (b)	**25.** (b)	**26.** (b)	**27.** (b)	**28.** (a)	**29.** (b)	**30.** (d)
31. (d)	**32.** (b)	**33.** (d)	**34.** (d)	**35.** (a)	**36.** (d)	**37.** (d)	**38.** (b)	**39.** (a)	

the Guidance

Round I

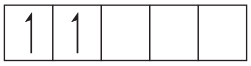
1. V_2O_5 and Cr_2O_3 are amphoteric because both react with alkalies as well as acids. (In lower oxides, the basic character is predominant while in higher oxides, the acidic character is predominant).

2. Copper does not liberate hydrogen from acids because it has positive $E°$.

3. $Cu^+ = [Ar]3d^{10}$

No unpaired electron, thus $s = 0$. Paramagnetism of ion is also zero.

4. $Ti(22) = [Ar]4s^2 3d^2$



$Ti^{2+} = [Ar]3d^2$

$Ti^{4+} = [Ar]3d^0$

Ti^{2+} has two unpaired electrons in $3d$ and thus d-d transition is possible due to absorption of light in visible region.

5. Magnetic moment, $\mu = \sqrt{N(N+2)}$ BM

where, N = unpaired electrons

$Cr(24) = [Ar]3d^5, 4s^1$; $N = 6, \mu = \sqrt{48}$ BM $= x$

$Mn^+ = [Ar]3d^5\ 4s^1$; $N = 6, \mu = \sqrt{48}$ BM $= y$

$Fe^{2+} = [Ar]3d^6$; $N = 4, \mu = \sqrt{24}$ BM $= z$

Thus, $z < x = y$

6. $VO_2 + 2H^+ \longrightarrow VO^{2+} + H_2O$

7. $Cu^+ = [Ar]3d^{10}; Fe^+ = [Ar]3d^5$

9. Variable valency is due to the participation of electron from $(n-1)d$ and ns levels in bond formation.

10. Transition elements are more metallic than representative elements due to the availability of d-orbitals for bonding.

12. Coinage metals (Cu, Ag, Au) shows the properties of transition elements as in their common oxidation states they possess partially filled d-subshells.

14. ${}_{30}Zn \longrightarrow [Ar]\ 3d^{10}4s^2$

$\because$ Its d-orbital is complete.

$\therefore$ It does not show variable valency.

15. The ability of transition elements to adopt multiple oxidation states and complexing ascribed their catalytic activity.

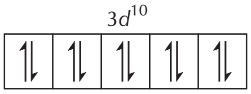
17. $Fe^{2+} = [Ar]\ 3d^6 4s^0 \Rightarrow$ 4 unpaired electrons

$Cu^+ = [Ar]\ 3d^{10}4s^0 \Rightarrow$ 0 unpaired electron

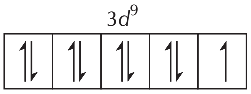
$Zn = [Ar]\ 3d^{10}4s^2 \Rightarrow$ 0 unpaired electron

$Ni^{3+} = [Ar]\ 3d^7 4s^0 \Rightarrow$ 3 unpaired electrons

18. Cuprous ion (Cu^+) $3d^{10}$ (completely filled d-subshell)



Cupric ion (Cu^{2+}) $3d^9$ (one unpaired electron)



19. Ni^{2+} and Cr^{3+} are coloured due to the presence of unpaired electrons. But Zn^{2+} is colourless because of the absence of unpaired electrons.

21. Strength of metallic bond depends upon number of unpaired electrons. As number of unpaired electrons increases, the bond strength increases. So, Cr, Mo, W show stronger bonding due to maximum number of unpaired electrons.

22. $Ti^{3+} \longrightarrow 3d^1, 4s^0$

$Sc^{3+} \longrightarrow 3d^0$

$Mn^{2+} \longrightarrow 3d^5, 4s^0$

$Zn^{2+} \longrightarrow 3d^{10}, 4s^0$

In Mn^{2+} number of unpaired electrons = 5. So, it has maximum magnetic moment according to the formula

$$\mu = \sqrt{n(n+2)}\ \text{BM}$$

23. The atomic weight of, Co, Ni and Fe are 59.90, 58.60, 55.85 respectively. Therefore, Co > Ni > Fe is the correct sequence of atomic weights.

24. Among the given, manganese has the most stable electronic configuration, thus it is very hard to remove an electron from its outer shell. Hence, a large amount of energy is required. Therefore, manganese has the maximum first ionisation potential.

25. MnO_2 forms amphoteric oxide due to intermediate oxidation state.

28. Potassium dichromate on heating gives oxygen and chromic oxide (Cr_2O_3).

$$4K_2Cr_2O_7 \xrightarrow{\Delta} 4K_2CrO_4 + 3O_2 + 2Cr_2O_3$$

29. $K_2Cr_2O_7 + 2H_2SO_4 \xrightarrow{\text{Cold}} 2CrO_3 + 2KHSO_4 + H_2O$

CrO_3 is highly acidic and oxidising and is called chromic acid.

30. $4NaCl + 3H_2SO_4 + K_2Cr_2O_7 \longrightarrow \underset{\text{chromyl chloride}}{2CrO_2Cl_2} + K_2SO_4 + 2Na_2SO_4 + 3H_2O$

31. Because hydrochloric acid is oxidised to chlorine.

32. $Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$ pH > 7(x > 7)

$2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$ pH < 7 (y < 7)

33. $MnO_4^- + e^- \longrightarrow MnO_4^{2-}$

34. $CrO_3 + H_2O \longrightarrow \underset{(A)}{H_2CrO_4} \xrightarrow{OH^-} \underset{(B)}{CrO_4^{2-}}$

35. In acidic medium, $KMnO_4$ gives 5 oxygen while, acidic $K_2Cr_2O_7$ gives 3 oxygen.

38. All those inner-transition elements having +2 oxidation state, changes to +3, and act as reducing agents. While those having +4 oxidation state tend to change to +3 oxidation state and act as oxidising agents. Therefore, Np^{4+} acts as an oxidising agent.

39. Gadolinium, $Gd = 4f^7\,5d^1\,6s^2$

41. Tm (thulium) does not belong to actinoids.

45. Basicity of lanthanide hydroxides decreases along the lanthanides series from left to right.

46. $Gd = [Xe]\,4f^7 5d^1 6s^2$,

$Gd^{3+} = [Xe]\,4f^7$ (half-filled)

47. Actinides have variable valency due to very small difference in energies of $5f$, $6d$ and $7s$ orbitals.

49. The size of lanthanides are smaller than expected. This is associated with the filling up of 4*f* orbitals which must be filled before the 5*d* orbitals. The electrons in *f*-orbitals are not effective in screening other electrons from the nuclear charge.

50. Paramagnetism is shown by the positive ions of lanthanides except $La^{3+}(4f^0)$ and $Lu^{3+}(4f^{14})$. These ions are diamagnetic.

51. The electronic configuration of ${}_{62}Sm^{3+}$ is $4f^4$ and that of ${}_{66}Dy^{3+}$ is $4f^9$. The colour of f^n and f^{14-n} are often identical.

52. Np and Pu in NpO_3^+ and PuO_3^+ oxocations show +7 oxidation state which are not so stable.

53. Lanthanide contraction relates to decrease in atomic as well as ionic size of M^{3+} ions.

55. A reduction in atomic size with increase in atomic number is a characteristics of elements of *f*-block. This is due to lanthanide contraction.

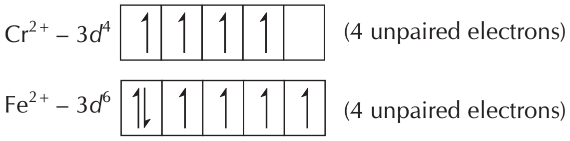
56. $La(OH)_3$ is more basic than $Lu(OH)_3$. This is because ionic size of La^{3+} ion is more than Lu^{3+} ion.

60. Oxidation states of Americium are +3, +4, +5 and +6.

Round II

1. Transition metal which have low oxidation number acts as reducing agent because of greater tendency to lose the electron. Moreover, they behave like a base.

2. Cr^{2+} and Fe^{2+}



$Cr^{2+} - 3d^4$ (4 unpaired electrons)

$Fe^{2+} - 3d^6$ (4 unpaired electrons)

3. (a) The basic character of hydroxides decreases from $La(OH)_3$ to $Lu(OH)_3$. Due to smaller size of Lu, The Lu—OH bond attains more covalent character. $La(OH)_3$ is the most basic among hydroxides of lanthanoids. Statement II and III are true.

4. Due to lanthanide contraction, the size of M^{3+} ions [*i.e.*, Lu^{3+}, Eu^{3+}, Yb^{3+} and Ce^{3+}] decreases and thus, the basic strength of their hydroxides decreases.

The order of size of given M^{3+} ions is

$$Ce^{3+} > Eu^{3+} > Yb^{3+} > Lu^{3+}$$

∴ The order of basic strength of hydroxides is

$$\underset{\text{(most basic)}}{Ce(OH)_3} > Eu(OH)_3 > Yb(OH)_3 > Lu(OH)_3$$

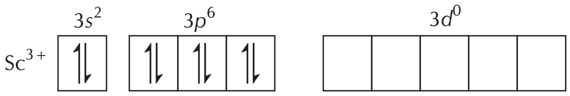
5. Due to lanthanoid contraction order will be

$$Yb^{3+} < Pm^{3+} < Ce^{3+} < La^{3+}$$

6. Basic character of oxides decreases from left to right in a period of Periodic Table.

7. $2MnO_2 + 4KOH + O_2 \longrightarrow \underset{\text{purple green}}{2K_2MnO_4} + 2H_2O$

8. $ScCl_3 \longrightarrow Sc^{3+} + 3Cl^-$



No unpaired electron, so will show diamagnetic character so, will weigh less in magnetic field.

9. $[Ar]\,3s^1$, + 3 = Ti, it means M^{3+} from Ti^{3+} ion.

10. Transuranic elements start after uranium and begin with Np (Neptunium).

11. Ir does not dissolve in aqua-regia as it is much more noble than Au and Pt.

12. The higher the charge on the metal ion, smaller is the ionic size and more is the complex forming ability. Thus, the degree of complex formation decreases in the order

$$M^{4+} > MO_2^{2+} > M^{3+} > MO_2^+$$

The higher tendency of complex formation of MO_2^{2+} as compared to M^{3+} is due to high concentration of charge on metal atom *M* in MO_2^{2+}.

13. There is very small difference in energies of $5f$, $6d$ and $7s$ orbitals of actinoids, therefore their electronic configuration cannot assigned with a degree of certainty.

14. Neodymium oxide (Nd_2O_3) dissolved in selenium oxychloride is one of the most powerful liquid lasers known so far.

15. $KMnO_4$ and $Ce(SO_4)_2$ are coloured due to charge transfer spectra.

16. In group 6, Mo (VI) and W (VI) are found to be more stable than Cr (VI). (Higher oxidation state is more stable in heavier members, the opposite is true in *p*-block.) Thus, Cr (VI) in the form of dichromate in acidic medium is a strong oxidising agent, whereas MoO_3 and WO_3 are not.

17. $Ce = [Xe]\,4f^1\,5d^1\,6s^2$

$Ce^{4+} = [Xe]\,4f^0$

Ce also shows + 4 oxidation state because it has the tendency to attain noble gas configuration and $4f^0$ configuration.

18. $Co^{2+} = 3d^7$, $Cr^{2+} = 3d^4$, $Mn^{2+} = 3d^5$ and $Cr^{3+} = 3d^3$

Co^{2+} and Cr^{3+} have same number of unpaired electrons *i.e.*, 3 therefore these ions have almost same spin only magnetic moment.

29. In the form of dichromate, Cr (VI) is a strong oxidising agent in acidic medium but Mo (VI) in MoO_3 and W (VI) in WO_3 are not because Mo (VI) and W (VI) are more stable than Cr (VI). Further more, in heavier members of group-6 higher oxidation states are more stable.

20. Cu^{2+} iodide is not known because Cu^{2+} oxidises I^- to iodine.

$$2Cu^{2+} + 4I^- \longrightarrow Cu_2I_2 + I_2$$

21. Separation of Zr and Hf is difficult because both have very similar physical and chemical properties. Both the elements have almost similar atomic radii (Zr = 160 pm) and (Hf = 159 pm) due to lanthanoid contraction.

22. Actinoids possess greater tendency for complexion and form more stable complexes as compared to lanthanoids.

23. Statement II is the correct explanation for statement I.

24. Higher oxidation state in heavier members among the groups of *d*-block elements are found to be more stable. Hence, highest oxidation state shown by Os is + 8.

25. Nickel shows zero oxidation state in carbonyls.

26. (a) $2\overset{+6}{Cr}O_4^{2-} + 2H^+ \longrightarrow \overset{+6}{Cr_2}O_7^{2-} + H_2O$

(No change in oxidation state of Cr.)

(b) $\overset{+6}{Cr_2}O_7^{2-} + 2H^+ + 3SO_2 \longrightarrow 2Cr^{3+} + H_2O + 3SO_4^{2-}$

(Oxidation state of Cr changes from + 6 to + 3 in this reaction.)

(c) $\overset{+6}{Cr_2}O_7^{2-} + 2OH^- \longrightarrow 2\overset{+6}{Cr}O_4^{2-} + H_2O$

(No change in oxidation state of Cr)

(d) $\overset{+6}{Cr}O_2Cl_2 + 2NaOH \longrightarrow Na_2\overset{+6}{Cr}O_4 + 2HCl$

(No change in oxidation state of Cr)

27. Most transition metals are inert towards acids or react slowly with them because of a protective layer of oxide.

28. The colour of a transition metal complex is dependent on how big the energy difference in between the two *d*-levels. This in turn depends on the nature of the ligands and the type of the complex formed. The colour which we see is the colour of the transmitted wavelength.

$ZnSO_4$ and TiO_2 are white. $Zn^{2+} = 3d^{10}$, $Ti^{4+} = 3d^0$.

d-d spectra are impossible in those ions which have d^0 or d^{10} configuration.

29. The colour arise by charge transfer. In MnO_4^-, an electron is momentarily transferred from oxygen to the metal and thus oxygen changes from O^{2-} to O^- and Mn from (+ 7) to (+ 6).

30. (a) $FeO > Fe_2O_3$ (basic) thus, true.

(b) $FeCl_2 > FeCl_3$ (ionic), larger the charge, greater the polarizing power and thus greater the covalent nature. Thus, true.

(c) Fe^{2+} salts are more ionic thus less volatile than Fe^{3+} salts. Thus, true.

(d) Greater the covalent nature, more easily they are hydrolyzed. Thus, $FeCl_3$ is more hydrolyzed than $FeCl_2$. Thus, statement (d) is incorrect.

31. Formation of + 4 state requires very high energy, thus incorrect.

32. Lanthanoides : $[Xe]4f^{1-14}5d^{0-1}6s^2$

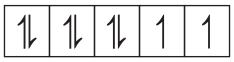
Actinoides : $[Rn]\,5f^{1-14}6d^{0-1}7s^2$

Lathanoides and actinoides use core *d* and *f* orbitals also to show higher oxidation state. As actinoides have comparatively low energy difference between *f* and *d* orbitals, they show more oxidation states.

33. $4f$ and $5f$ belong to different shell, thus experience different amount of shielding.

34. The actinoid ($5f$-elements) exhibit more number of oxidation states in general than the lanthanoid because $5f$-orbitals extend farther from the nucleus than the $4f$-orbitals.

35. $Ni^{2+} = [Ar]\,3d^8$



Number of unpaired electrons = 2

Hence, magnetic moment = $\sqrt{n(n+2)} = \sqrt{8} = 2.84$

36. Lanthanoid contraction is due to ineffective shielding produced by larger *f*-subshell.

37. Lanthanide contraction is due to poor shielding of one of $4f$ electron by another in the sub-shell.

38. Lanthanide contraction, cancels almost exactly the normal size increase on descending a group of transition elements, thus Nb and Ta and, Zr and Hf have same covalent and ionic radii.

39. $Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 7H_2O + 3I_2$

$Cr_2O_7^{2-}$ is reduced to Cr^{3+}.

Thus, final state of Cr is + 3.

9 Coordination Compounds

JEE Main MILESTONE

- Molecular or Addition Compounds
- Terminology Used in Coordination Compounds
- Werner's Theory
- IUPAC Nomenclature of Mononuclear Coordination Compounds
- Isomerism
- Bonding in Coordination Compounds
- Stability of Complexes
- Importance of Coordination Compounds

9.1 Molecular or Addition Compounds

When solutions containing two or more stable salts in simple molecular (stoichiometric) proportions, are evaporated, crystals of new compounds may separate out. These new compounds are called **molecular** or **addition compounds.**

e.g., $K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \longrightarrow \underset{\text{potash alum crystals}}{K_2SO_4Al_2(SO_4)_3 \cdot 24H_2O}$

$$AgCN + KCN \longrightarrow \underset{\text{potassium argentocyanide}}{K[Ag(CN)_2]}$$

$$Fe(CN)_2 + 4KCN \longrightarrow \underset{\text{potassium ferrocyanide}}{K_4[Fe(CN)_6]}$$

The addition compounds can be divided into two classes

(a) Those which Loose their Identity in Solution *i.e.,* Double Salts

In aqueous solution these addition compounds break down into simpler ions, thus, exhibit the properties of their constituent ions. *e.g.*, an aqueous solution of carnallite $KCl \cdot MgCl_2 \cdot 6H_2O$ shows the properties of K^+, Mg^{2+} and Cl^- simpler ions. Such addition compounds, which loose their identity in solution, are called **'double salts.'** They only exist in the crystalline state. Some other examples of double salts are potash alum $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ and Mohr salt $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$

Coordination compounds are those compounds in which a central metal atom or ion is attached with a fixed number of groups or molecules (ligands) through coordinate bonds. In other words, these compounds contain complex ions. These are generally formed by transition elements because of their small radii.

(b) Those which Retain their Identity in Solution *i.e.,* Complex Compounds

In aqueous solution, these addition compounds do not furnish all simple ions but instead give more complex ions having complicated structure *e.g.,* potassium ferrocyanide does not give properties of simple

K^+, Fe^{2+} and CN^- ions but gives the properties of K^+ ions and complex ferrocyanide ions, $[Fe(CN)_6]^{4-}$. In other words, in these compounds, the **complex ions** retains their identity in the solution. Other example of coordination compounds are $[Co(NH_3)_6]Cl_3$, $K_2[PtCl_6]$, etc.

Actually complexes or coordination compounds are the result of acceptance of lone pair of electrons of ligands by the empty orbitals of the metal atom or ion.

9.2 Terminology Used in Coordination Compounds

The important terms used to define a complex completely are as follows

1. Complex Ions

A complex ion may be defined as an electrically charged radical which is formed by the combination of a simple cation with one or more neutral molecules or one or more simple anions or in some cases positive groups also. It exists as a single entity and is usually indicated within square bracket, *i.e.,* [ ]

e.g., $[Cu(NH_3)_4]^{2+}$ is a complex ion, which is formed by the combination of four neutral molecules of ammonia with a simple Cu^{2+} cation. Similarly, $[Fe(CN)_6]^{4-}$ is a complex ion formed by the combination of six CN^- anions with a simple Fe^{2+} cation. In nitroprusside ion, $[Fe(CN)_5NO]^{2+}$, five CN^- ions and one NO^+ (a positively charged ligand) ion are coordinated to Fe^{2+} ion.

The complex ion carrying a positive charge *e.g.,*, $[Cu(NH_3)_4]^{2+}$, is called **cationic complex,** the one with a negative charge *e.g.,* $[Fe(CN)_6]^{4-}$ is called **anionic complex** and the one with no charge *e.g.,* $[PtCl_2(NH_3)_2]$ is called a **neutral complex.**

Complex ions do not give tests of their constituent ions. *e.g.,* $[Cu(NH_3)_4]^{2+}$ does not give test of Cu^{2+} or NH_3.

Homoleptic complex have only one type of ligands linked to the central metal atom/ion. *e.g.,* $[Co(NH_3)_6]^{3+}$ whereas **heteroleptic complex** have more than one type of ligands linked to the central metal atom/ion. *e.g.,* $[Co(NH_3)_4Cl_2]$

Sample **Problem 1** *Which of the following complexes are homoleptic?* **[NCERT Exemplar]**

(*a*) $[Co(NH_3)_6]^{3+}$
(*b*) $[Co(NH_3)_4Cl_2]^+$
(*c*) $[Ni(CN)_4]^{2-}$
(*d*) $[Ni(NH_3)_4Cl_2]$

Interpret (*a,c*) Homoleptic complexes have ligands of only one kind. e.g., $[Co(NH_3)_6]^{3+}$, $[Ni(CN)_4]^{2-}$

2. Central Metal Atom or Ion

Every complex ion contains a metal atom or ion to which one or more neutral molecules or ions are attached. This is known as the **central metal atom** or **ion.** It is sometimes known as the **nuclear atom.** In a complex, the central metal atom or ion behaves as the **electron pair acceptor** or **Lewis acid.**

3. Ligands

The central metal ion is surrounded by a number of the anions or the neutral molecules or sometimes positively charged ions possessing at least one lone pair. These surrounded ions are called **ligands.** The ligands are attached to the central metal ion or atom through coordinate bonds or dative linkage. In the formation of coordination complexes, the ligands act as the **electron-pair donors** or **Lewis bases.**

e.g., in the complex ions $[Cu(NH_3)_4]^{2+}$ and $[Fe(CN)_6]^{4-}$, NH_3 and CN^- are the ligands. Ligands invariably contain one or more atoms (called **donor atoms**) having lone pairs of electrons.

The number of donor groups, from a given ligand, attached to the same central atom, is called the **denticity of the ligand.** Ligands like NH_3, CH_3NH_2, PH_3 can form only one coordinate bond with the central metal ion. So, their denticity is one. $H_2N—CH_2—CH_2—NH_2$, $NH_2CH_2COO^-$ have two donor atoms in each molecule or ion and each can form two coordinate bonds with the central metal ion and hence, their denticity is two.

Depending upon the number of donor atoms (or sites), the ligands may be classified into various categories as follows

(a) Unidentate or Monodentate Ligands

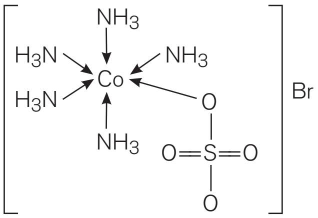
These ligands contain only one donor atom (or site) which is capable of donating an electron pair and thus, attach to the central metal ion only at one point *e.g.,* CN^-, F^-, Cl^-, Br^-, OH^-, H_2O, NH_3, NO_2^-, C_2H_5N (pyridine) etc.

(b) Polydentate or Multidentate Ligands

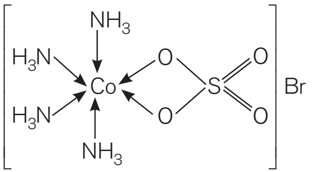
Ligands which contain two or more such atoms which can simultaneously serve as donor atoms are called **polydentate or multidentate ligands.** Such ligands attach to the central metal ion at more than one point. Polydentate ligands with two donor sites are called bidentate, and with three, four, five and six donor sites are called tri (or ter), tetra (or quadri), penta and hexa-(or sexi) dentate ligands respectively.

Certain polydentate ligands have flexi dentate character, *i.e.,* they do not use all the donor atoms to form a complex *e.g.,* EDTA is a hexadentate ligand but it can also act as a pentadentate or a tetradentate ligand.

Caution Point *Some ligands like* SO_4^{2-} *ion etc., can act both as a monodentate as well as a bidentate ligand. This is clear from the following examples.*



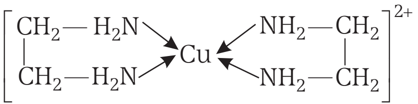
SO_4^{2-} as monodentate



SO_4^{2-} as bidentate

(c) Chelating Ligands

Polydentate ligands, the structures of which permeates the attachment of two or more donor sites at the terminals of a chain to the same metal ion simultaneously, thus, closing one or more rings are called **chelating ligands** and the compounds formed are known as **chelate compounds.** Thus, a chelate may be defined as a ring structure formed by the combination of a polydentate ligand having two or more donor atoms at the terminals with a metal ion forming part of the ring. The process of formation of chelates is called **chelation.**



Chelate formation

Chelate complexes are more stable than ordinary complexes in which the ligand is monodentate. This increased stability of the compound due to chelation is called the chelate effect.

Generally the chelate complexes with five or six membered rings are more stable. Out of these, five membered rings are very stable when they involve saturated ligands, *e.g.,* ethylene diamine contains only single bonds and forms five membered stable ring structures.

On the other hand, six membered ring structures acquire maximum stability when they involve unsaturated ligands containing conjugate double bonds. This is due to the resonance effects involving metal *d*-orbitals and ligand π-orbital electrons. The stability of the chelate complex is explained on the basis of **entropy effect.** When one end of en (ethylene diamine) is coordinated, the probability of the coordination of the other end is high because this end is bound to stay close to the cation. This shows that it is easier to form a chelate ring than coordinate to two independent molecules. Thermodynamically, the increased stability due to chelation can be attributed to an increase in the degree of freedom of the system. A large entropy change but only small heat of reaction generally accompany the chelation process.

The complex compound having maximum number of rings formed with the ligands, is most stable. A complex $[M(en)_3]^{3+}$ is less stable than a complex $[M(EDTA)]^-$ because in the former there are three rings while, the latter involves five rings.

Sample Problem 2 *The stabilisation of coordination compounds due to chelation is called the chelate effect. Which of the following is the most stable complex species?*

[NCERT Exemplar]

(*a*) $[Fe(CO)_5]$ (*b*) $[Fe(CN)_6]^{3-}$

(*c*) $[Fe(C_2O_4)_3]^{3-}$ (*d*) $[Fe(H_2O)_6]^{3+}$

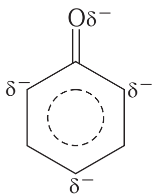
Interpret (*c*) $(C_2O_4)^{2-}$ is a chelating agent $\begin{bmatrix} COO^- \\ | \\ COO^- \end{bmatrix}$, so its complex is more stable than the other given due to chelation.

(d) Ambidentate Ligands

There are certain ligands, which have two or more donor atoms but in forming complexes only one donor atom is attached to metal ion. Such ligands are called ambidentate ligands. Some examples of such ligands are

$M \leftarrow NO_2$ (Nitro)	$M \leftarrow ONO$ (Nitrito)
$M \leftarrow CN$ (Cyano)	$M \leftarrow NC$ (Isocyano)
$M \leftarrow SCN$ (Thiocyano)	$M \leftarrow NCS$ (Isothiocyano)

Phenoxide ion also serves as an ambidentate ligand due to resonance. *o*- and *p*- positions of the benzene ring in the phenoxide ion also become electron donors.



phenoxide ion

4. Coordination Sphere

The central atom and ligands which are directly attached to it, are enclosed in square brackets, called the coordination sphere. *The ligands and the metal atom shown inside the square bracket actually behave as a single constituent unit.* The bonding between the central metal ion/atom, and the ligands in its coordination sphere is non-ionisable.

5. Coordination Number

The total number of ligands attached to the central metal ion through coordinate bond is called the **coordination number** (CN) of the metal ion, *e.g.,* in the complex ion $[Cu(NH_3)_4]^{2+}$, the coordination number of Cu^{2+} is 4 and that of Fe^{2+} ion in $[Fe(CN)_6]^{4-}$ is 6. The coordination numbers of most common metals are 4 and 6. Ag^+, Pt^{2+}, Cr^{3+}, Fe^{2+}, Fe^{3+}, Co^{3+} and Pt^{4+} ions show only one coordination number, *e.g.,* Ag^+ shows CN = 2, Pt^{2+} CN = 4 and Cr^{3+} Fe^{2+}, Fe^{3+}, Co^{3+} and Pt^{4+} show CN = 6 only.

In case of polydentate ligands,

Coordination number = No. of ligand × its denticity

e.g., in $[CoBr_2(en)_2]^+$. CN *wrt* Br = 2

CN *wrt* en = 2 × 2 = 4

Total CN = 2 + 4 = 6

6. Oxidation Number or Oxidation State

It is a number that represents an electric charge in which a metal atom or ion has or appears to have when combined with ligands, *e.g.,* oxidation number of copper in $[Cu(NH_3)_4]^{2+}$ is +2 but its coordination number is 4. Similarly, the oxidation number of Fe in $[Fe(CN)_6]^{3-}$ is +3 but its coordination number is 6.

7. Charge on the Complex Ions

The charge carried by a complex ion is the algebraic sum of the charges carried by central metal ion and the ligands coordinated to the central metal ion, *e.g.,* in the complex ion, $[Ag(CN)_2]^-$, Ag^+ ion carries a charge of +1. Therefore, the net charge on the complex ion $[Ag(CN)_2]$ is + 1 – 2 = – 1. Similarly, in the complex ion, $[Cu(NH_3)_4]^{2+}$, Cu ion carries charge equal to +2 and as NH_3 molecules are neutral, therefore, the net charge on the complex is +2.

8. Representation of a Complex Ion

The terms ligand, central metal, charge on complex ion and coordination number can be illustrated as

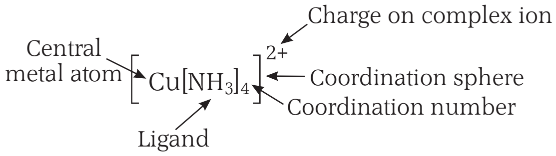


Fig. 9.1 A complex Ion

9. Effective Atomic Number [EAN]

In order to explain the stability of the complex **Sidgwick** proposed effective atomic number abbreviated as EAN, which is defined as the *resultant number of electrons with the metal atom or ion after gaining electrons from the donor atoms of the ligand. The effective atomic number* (EAN) generally coincides with the atomic number of next inert gas except in some cases.

Calculation of EAN EAN can be calculated by the following relation

EAN = *Z* (atomic number of the metal) – number of electrons lost in the ion formation + number of electrons gained from the donor atoms of the ligands

The EAN's of various metals in their respective complexes is tabulated below

Table 9.1 **EAN of Some Species**

Complex	Oxidation state of metal ion	Atomic number of metal (*Z*)	Coordination number	Effective atomic number
$[Co(NH_3)_6]Cl_3$	+3	27	6	(27 – 3) + (6 × 2) = 36 (Kr)
$K_4[Fe(CN)_6]$	2	26	6	(26 – 2) + (6 × 2) = 36 (Kr)
$Ni[CO]_4$	0	28	4	(28 – 0) + (4 × 2) = 36 (Kr)
$K_2[PtCl_6]$	+4	78	6	(78 – 4) + (6 × 2) = 86 (Rn)
$K_3[Fe(CN)_6]$	+3	26	6	(26 – 3) + (6 × 2) = 35

Sample **Problem 4** *Using the EAN rule predict the value of x in* $Cr(CO)_x$.

(*a*) 4 (*b*) 5

(*c*) 6 (*d*) 8

Interpret (c) EAN = 24 – 0 + 2*x* = 36

$2x = 12$ [*i.e.,* atomic number of nearest noble gas]

$x = 6$

Therefore, the formula of the compound is $Cr(CO)_6$.

9.3 Werner's Theory

Werner proposed a theory called **Werner's coordination theory** for which he was awarded Nobel prize in 1913. It was the first successful theory, which explained the properties of complexes.

The main postulates of this theory are

1. Metals possess two types of linkages (valencies)
   (i) primary or principal linkage and
   (ii) secondary linkage
2. **Primary linkages** (valencies) **are ionisable** and are exhibited by a metal in the formation of its simple salts such as $CoCl_3$, $CuSO_4$ and AgCl. In these salts, the primary valencies of Co, Cu and Ag are 3, 2 and 1 respectively. Now a days, **primary valency** is referred to as **oxidation state** of the metal ion.
3. **Secondary linkages** (valencies) **are non-ionisable** and are exhibited by a metal in the formation of its complex ions such as $[Co(NH_3)_6]^{3+}$, $[Cu(NH_3)_4]^{2+}$ and $[Ag(NH_3)_2]^+$. In these complexes, the secondary valencies of Co^{3+}, Cu^{2+} and Ag^+ are 6, 4 and 2 respectively. The secondary valency is also referred to as **coordination number** (CN) of the metal cation.
4. **Primary linkages** (valencies) *are satisfied by negative ions while, secondary linkages (valencies) can be satisfied by neutral molecules or negative ions or in some cases positive ions* (ligands) **also.** This happens in case of mixed complexes.
5. *Every metal atom or ion has a fixed number of secondary linkages. In other words, the coordination number of the metal atom is fixed.* Thus, the coordination number gives the total number of neutral molecules of negative or positive groups, which may be directly linked to the metal cation in the formation of its complexes.
6. *Every metal has a tendency to satisfy both its primary and secondary linkages (valencies).* The ligands satisfying secondary linkages (valencies) are always directed towards fixed positions in space about the central metal atom or ion. Thus, the coordination compounds have a definite geometry (structure or shape).

Werner's Representation

Consider the case of $CoCl_3 \cdot xNH_3$

where maximum value of x = CN of Co(III) = 6

and minimum value of x = CN − ON = 3

Various structures are summarized in Table 9.3.

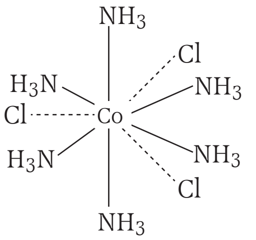
Table 9.2 **Werner's Coordination Compounds**

Werner complex	Modern notation	Ionisation	Secondary valency satisfied by	Primary valency satisfied by
(A) $CoCl_3 \cdot 6NH_3$	$[Co(NH_3)_6]Cl_3$	$[Co(NH_3)_6]^{3+} + 3Cl^-$	six (NH_3)	three (Cl^-)
(B) $CoCl_3 \cdot 5NH_3$	$[Co(NH_3)_5Cl]Cl_2$	$[Co(NH_3)_5Cl]^{2+} + 2Cl^-$	five (NH_3) and one (Cl^-)	three (Cl^-) including one (Cl^-) with **dual nature**
(C) $CoCl_3 \cdot 4NH_3$	$[Co(NH_3)_4Cl_2]Cl$	$[Co(NH_3)_4Cl_2]^+ + Cl^-$	four (NH_3) and two (Cl^-)	three (Cl^-) including two (Cl^-) with **dual nature**
(D) $CoCl_3 \cdot 3NH_3$	$[Co(NH_3)_3Cl_3]$	$[Co(NH_3)_3Cl_3]$ (single species)	three (NH_3) and three (Cl^-)	three (Cl^-) all with **dual nature**

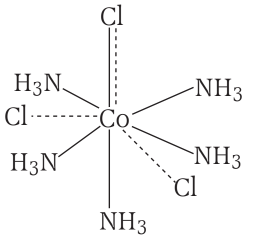
From the Table 9.3, it is clear that conduction of the complexes which depends on the number of ions will be in order: *D* < *C* < *B* < *A*

They are represented as :

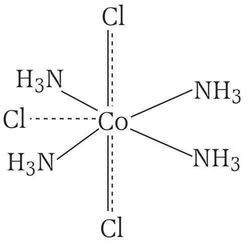
[only Cl^- ions joined by (........) will ionise].



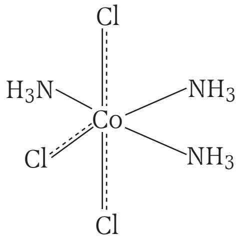
(*A*)



(*B*)



(*C*)



(*D*)

Sample Problem 5 *When* 0.1 *mole* $CoCl_3(NH_3)_5$ *is treated with excess of* $AgNO_3$, 0.2 *mole of* AgCl *are obtained. The conductivity of solution will correspond to*

[NCERT Exemplar]

(*a*) 1 : 3 *electrolyte* (*b*) 1 : 2 *electrolyte*
(*c*) 1 : 1 *electrolyte* (*d*) 3 : 1 *electrolyte*

Interpret (*b*) Formation of 0.2 mole of AgCl, from 0.1 mole complex suggest the presence of two Cl^- outside the coordination sphere. Thus, the formula of the complex should be $[Co(NH_3)_5Cl]Cl_2$.

This complex ionises as

$$[Co(NH_3)_5Cl]Cl_2 \longrightarrow \underset{1}{[Co(NH_3)_5Cl]^{2+}} + \underset{2}{2Cl^-}$$

Hence, it is 1 : 2 electrolyte.

Sample **Problem 6** *Arrange the following complexes in the increasing order of conductivity of their solution :*

I. $[Co(NH_3)_3Cl_3]$ *II.* $[Co(NH_3)_4Cl_2]Cl$, *III.* $[Co(NH_3)_6]Cl_3$,
IV. $[Cr(NH_3)_5Cl]Cl_2$ **[NCERT Exemplar]**

(*a*) $I < II < III < IV$
(*b*) $II < I < IV < III$
(*c*) $I < II < IV < III$
(*d*) $II < I < III < IV$

Interpret (*c*) Ions or molecules present outside the coordination sphere are ionisable. A complex which gives more ions on dissolution, is more conducting.

$$\underset{\substack{\text{(1 ion)}\\ \text{(I)}}}{[Co(NH_3)_3Cl_3]} < \underset{\substack{\text{(2 ions)}\\ \text{(II)}}}{[Co(NH_3)_4Cl_2]Cl} < \underset{\substack{\text{(3 ions)}\\ \text{(IV)}}}{[Cr(NH_3)_5Cl]Cl_2} < \underset{\substack{\text{(4 ions)}\\ \text{(III)}}}{[Co(NH_3)_6]Cl_3}$$

Check Point 1

1. Why does NH_4^+ ion not form complexes?
2. A freshly prepared aqueous solution of $Pd(NH_3)_2Cl_2$ does not conduct electricity. Is this compound is regarded as a weak electrolyte?
3. $CuSO_4$ on mixing with NH_3 (ratio 1: 4) does not give test for Cu^{2+} ions but gives test for SO_4^{2-} ions; why?
4. Why is $K_4[Fe(CN)_6]$ more conducting as compared to $[Cr(NH_3)_6]Cl_3$?

9.4 IUPAC Nomenclature of Mononuclear Coordination Compounds

The various rules are applied in naming the coordination compounds according to the IUPAC (International Union of Pure and Applied Chemistry) system are

Order of Naming Ions

If the complex compound is ionic, the positive ion (cation) whether simple or complex, is named first followed by the negative ion (anion). *e.g.,* $K[BF_4]$ ionises to K^+ and BF_4^- ions. Here cation (K^+) is simple and it is named first followed by anionic part. Thus, $K[BF_4]$ is named as potassium tetrafluoroborate (III). The complex $[Ag(NH_3)_2]Cl$ ionises as

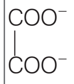
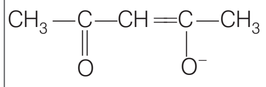
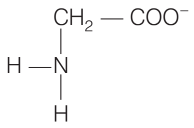
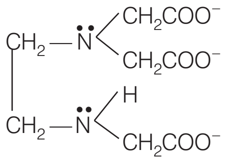
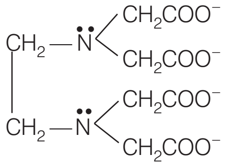
$$[Ag(NH_3)_2]Cl \longrightarrow [Ag(NH_3)_2]^+ + Cl^-$$

Here, the cation $[Ag(NH_3)_2]^+$ is not a simple one but a complex. Therefore, it is named first and then the anionic part. Thus, $[Ag(NH_3)_2]Cl$ is named as diamminesilver (I) chloride. But one word name is given to non-ionic and molecular complexes.

Naming Ligands

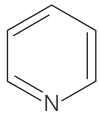
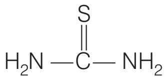
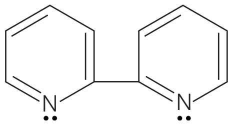
1. The number of each kind of ligand is specified using the Greek **prefixes** like di, tri, tetra, penta, and hexa. The term mono is generally not mentioned. If the name of ligand itself is complex, *i.e.,* it includes a numerical prefix, *e.g.,* in case of organic molecules such as dipyridyl or ethylenediamine, then the terms **bis** (for two), **tris** (for three), **tetrakis** (for four), **pentakis** (for five), etc., are used followed by the name of the ligand placed without brackets. *e.g.,* $[Cu(NH_3)_4]^{2+}$ is named as tetramminecopper (II) ion and $[Co(en)_3]^{3+}$ is named as tris (ethylenediamine) cobalt (III) ion.
2. **Negative ligands** are normally end in –o, *e.g.,*

Table 9.3 **Different Negative Ligands, Their Charge and Donor Atoms**

	Name	Formula	Charge	Name of ligand in the complex	Donor atom/ atoms
Monodenate ligands with one unit negative charge	Halide ion	(X = Cl, Br, I)	– 1	Halo or halido	X
	Hydroxide ion	$:OH^-$	– 1	Hydroxo	O
	Cyanide ion	$-C\equiv N$	– 1	Cyano	C
	Isocyanide	$N^+\equiv C^-$	– 1	Isocyano	N
	Nitro ion	NO_2^-	– 1	Nitro	N
	Nitrito ion	ONO^-	– 1	Nitrito	O
	Thiocyanate ion	SCN^-	– 1	Thiocyanato	S
	Isothiocyanate ion	NCS^-	– 1	Isothiocyanato	N
	Hydride ion	H^-	– 1	Hydrido	H
	Amide ion	NH_2^-	– 1	Amido	N
	Acetate ion	CH_3COO^-	– 1	Acetato	O
	Nitrate ion	NO_3^-	– 1	Nitrato	O
	Cyanate	ONC^-	– 1	Cyanato	O
	Isocyanate	NCO^-	– 1	Isocyanato	N
Monodentate ligands with two negative charges	Sulphate ion	SO_4^{2-}	–2	Sulphato	O
	Oxide ion	O^{2-}	–2	Oxo	O
	Peroxide ion	O_2^{2-}	–2	Peroxo	O
	Carbonate ion	CO_3^{2-}	–2	Carbonato	O
	Sulphite ion	SO_3^{2-}	–2	Sulphito	O
	Sulphide ion	S^{2-}	–2	Sulphido	S
	Thiosulphate ion	$S_2O_3^{2-}$	–2	Thiosulphato	S
	Imide ion	NH^{2-}	–2	Imido	N
Bidentate ligands with one/two negative charges	Oxalate ion (o*x)	 $\begin{array}{l}COO^-\\ \vert\\ COO^-\end{array}$	– 2	Oxalato	Two O-atoms
	Acetyl acetonate (a*cac)	 $CH_3-\underset{\overset{\Vert}{O}}{C}-CH=\underset{\overset{\vert}{O^-}}{C}-CH_3$	– 1	Acetyl acetonato	Two O-atoms
	Glycinate ion (g*ly)		– 1	Glycinato	One N-atom and one O-atom
	* Symbol used				
Polydentate ligands with high negative charges	Ethylenediamine triacetate ion (a pentadentate ligand)		–3	$EDTA^{3-}$	Two N-atoms and three O-atoms
	Ethylenediamine tetra-acetate ion (a hexadentate ligand)		–4	$EDTA^{4-}$	Two N-atoms and four O-atoms

3. **Neutral ligands** have no special ending *e.g.,*

Table 9.4 **Neutral Ligands**

	Name and symbol of ligand	Formula	Charge	Name of ligand on the complex	Donor atom
Neutral monodentate ligands	Ammonia	NH_3	Zero	Ammine	N
	Water	H_2O	Zero	Aqua	O
	Phosphine	PH_3	Zero	Phosphine	P
	Nitrogen oxide	NO	Zero	Nitrosyl	N
	Carbon monoxide	CO	Zero	Carbonyl	C
	Pyridine (py)	C_6H_5N or 	Zero	Pyridine	N
	Thiourea (tu)	 $H_2N-\overset{\overset{S}{\|}}{C}-NH_2$	Zero	Thiourea	S
	Triphenyl phosphine	$(C_6H_5)_3P$	Zero	Triphenyl phosphone	P
	Thiocarbonyl	CS	Zero	Thiocarbonyl	S
Neutral polydentate ligands	Ethylenediamine (en) (a bidentate ligand)	$NH_2CH_2CH_2NH_2$	Zero	Ethylene diamine	Two N-atoms
	2,2-dipyridyl (dipy) (a bidentate ligand)		Zero	Dipyridyl	Two N-atoms
	Diethylene triamine (dien) (a tridentate ligand)	$NH_2CH_2CH_2NHCH_2CH_2NH_2$	Zero	Diethylene triamine	Three N-atoms
	Triethylene tetramine (trien) (a tetradentate ligand)	$NH_2(CH_2)_2NH(CH_2)_2$ $-NH-(CH_2)_2NH_2$	Zero	Triethylene tetramine	Four N-atoms

Caution Point *In old system, word aquo was used.*

4. **Positive ligands** (which are very few) end in -ium *e.g.,*

Table 9.5 **Positive Ligands**

Name and symbol of ligand	Formula	Charge	Name given in the complex	Donor atom
Nitronium ion	NO_2^+	+ 1	Nitronium	N
Nitrosonium ion	NO^+	+ 1	Nitrosonium	N
Hydrazinium ion	$NH_2NH_3^+$	+ 1	Hydrazinium	N

5. The order of the preference of the ligands in the complexes according to the old system was as

   (i) Negative ligands; (ii) Neutral ligands;

   (iii) Positive ligands

   There should be no hyphen in between. In case, there are more than one negative or positive ligands, they are listed alphabetically. Thus, Cl^-, NO_2^- are written in the order as chloro, nitro etc.

IUPAC rules 1991 recommended that all ligands whether anions, neutral or positive be arranged alphabetically without any preference order. But the old system has also been retained. Some examples are as

Formula of the complex	Old IUPAC Name	Latest IUPAC Name
$[PtCl(NO_2)(NH_3)_4]SO_4$	Chloronitrotetrammine platinum (IV) sulphate	Tetramminechloridonitro platinum (IV) sulphate
$[CoCl(NH_3)_4(H_2O)]Cl_2$	Chloroaquotetrammine cobalt (III) chloride	Tetrammineaquachloridocobalt (III) chloride

Note Always follows latest IUPAC conventions.

6. Certain ligands like NO can act as a neutral as well as unipositive (NO^+) ligand. In such case, it is very difficult to find the oxidation state and the charge on the ligand from the given formula of the complex.

Hot Spot 1

NAMING of the Complex Ion

It is an important topic for JEE Main examination. The level of questions is generally easy so a small practice can help you to solve the problems based on naming and formula writing.

While naming the complex ion, number and name of the ligands are given first, then the central metal atom followed by its oxidation state indicated by Roman numeral in parenthesis.

(i) **If the complex ion is a cation,** the name of the central metal ion is given as such followed by its oxidation state indicated by numerals (such as II, III, IV) in the parenthesis at the end of the name of the complex without a space between the two. Some examples are as follows

[Ni(DMG)$_2$]	Bisdimethylglyoximatonickel (II)
[Pt(NH$_3$)$_2$Cl$_4$]	Diamminetetrachloridoplatinum (IV)

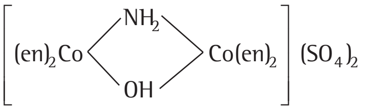
(ii) **If the complex ion is an anion,** the name of the central atom, is made to end in –ate followed by the oxidation number in brackets without any space between them, *e.g.,*

Na$_3$[AlF$_6$]	Sodium hexafluoridoaluminate (III)
[Ag(CN)$_2$]$^-$	Dicyanoargentate (I) ion
[Pb(OH)$_4$]$^{2-}$	Tetrahydroxoplumbate (II) ion

For an acid we have a characteristic ending (ic) *e.g.,*

H$_4$[Pt(CN)$_6$] Hexacyanoplatinic (II) acid.

If the complex contains two or more metal ions, it is termed as polynuclear complex. The ligands, which link the two metal atoms, are called bridge groups and are separated from the rest complex by hyphens and denoted by the prefix μ placed before their names, *e.g.*,



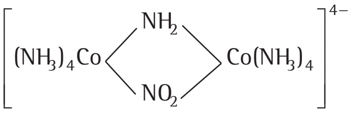
$$\left[(en)_2Co\overset{NH_2}{\underset{OH}{\diamond}}Co(en)_2\right](SO_4)_2$$

is named as

bis (ethylenediamine) cobalt (III) -μ - amido -μ - hydroxo bis (ethylenediamine) cobalt (III) sulphate

[It can also be named as tetrakis (ethylenediamine) μ-amido-μ-hydroxocobalt (III) sulphate.]

Similarly,



$$\left[(NH_3)_4Co\overset{NH_2}{\underset{NO_2}{\diamond}}Co(NH_3)_4\right]^{4-}$$

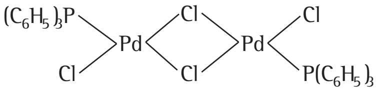
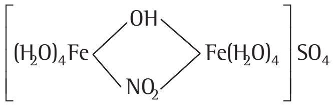
is named as octaammine-μ-amido-μ-nitrodicobalt (III) ion

It can also be named as

[tetramminecobalt (III)-μ-amido-μ-nitrotetrammine cobalt (III) ion].

The following examples illustrate the nomenclature of complexes

1.	[Cr(H$_2$O)$_4$Cl$_2$]Cl	Tetraaquadichloridochromium (III) chloride
2.	[Co(NH$_3$)$_5$CO$_3$]Cl	Pentaamminecarbonatocobalt (III) chloride
3.	[Ag(NH$_3$)$_2$]Cl	Diamminesilver (I) chloride
4.	[Co(en)$_2$Cl$_2$]$_2$SO$_4$	Dichloridobis (ethylenediamine) cobalt (III) sulphate
5.	[Co(NH$_3$)$_4$(NO$_2$)Cl]NO$_3$	Tetraamminechloridonitrocobalt (III) nitrate
6.	[Co(NH$_3$)$_3$(NO$_2$)$_3$]	Triamminetrinitrocobalt (III)
7.	[Pt(NH$_3$)$_6$]Cl$_4$	Hexaammineplatinum (IV) chloride
8.	[Cr(H$_2$O)$_3$(NH$_3$)$_3$]Cl$_3$	Triamminetriaquachromium (III) chloride
9.	[CoF$_2$(en)$_2$]ClO$_4$	Bis (ethylenediammine) difluoridocobalt (III) perchlorate
10.	Na$_2$[SiF$_6$]	Sodium hexafluoridosilicate (IV)
11.	Fe$_4$[Fe(CN)$_6$]$_3$	Iron (III) hexacyanoferrate (II) or ferric hexacyanoferrate (II)
12.	Na$_2$[CrF$_4$O]	Sodium tetrafluoridooxochromate (IV)
13.	K[BF$_4$]	Potassium tetrafluoridoborate (III)
14.	K$_2$[OsCl$_5$N]	Potassium pentachloridonitridoosmate (VI)
15.	Ni(CO)$_4$	Tetracarbonyl nickel (0)
16.	K$_4$[Ni(CN)$_4$]	Potassium tetracyanonickelate (0)
17.	[Ni(dmg)$_2$]	Bis (dimethylglyoximato) nickel (II)
18.	[Pt(NH$_3$)$_2$Cl$_2$]	Diamminedichloridoplatinum (II)

19.	$[Cr(PPh_3)(CO)_5]$	Pentacarbonyltriphenylphosphinechromium (0)
20.	$[Co(NH_3)_4Cl_2]_3[Cr(CN)_6]$	Tetraamminedichloridocobalt (III) hexacyanochromate (III)
21.	$[Pt(NH_3)_4Cl_2][PtCl_4]$	Tetraammine dichloridoplatinum (IV) tetrachloridoplatinate (II)
22.	$[(NH_3)_5Cr-OH-Cr(NH_3)_5]Cl_5$	Pentaamminechridomium (III)-μ-hydroxopentaamminechromium (III) chloride
23.		Chloridotriphenylphosphinepalladium (II)-μ-dichloro chloridotriphenylphoshinepalladium (II)
24.	$[(NH_3)_5Co-NH_2-Co(NH_3)_5](NO_3)_5$	Decammine-μ-amidodicobalt (III) nitrate
25.		Octaaqua-μ-hydroxo-μ-nitrodiiron (III) sulphate
26.	$[Mn_3(CO)_{12}]$	Dodecacarbonyltrimanganese (0)
27.	$[Fe(C_5H_5)_2]$	Bis(cyclopentadienyl)iron (II) or ferrocene
28.	$[PtBrClI(NO_2)(NH_3)(Py)]$	Amminebromidochloridoiodidonitropyridineplatinum (IV)
29.	$[VO(acac)_2]$	Bis(acetylacetonato)oxovanadium (IV)
30.	$Na_3[Ag(S_2O_3)_2]$	Sodium bis(thiosulphato) argentate (I)
31.	$Na_2[Ni(EDTA)]$	Sodium ethylenediaminetetraacetatonickelate (II)
32.	$Hg[Co(SCN)_4]$	Mercuric tetrathiocyanatocobaltate (II)

Sample Problem 7 *Select the incorrect match(s) of IUPAC names with the following coordination compounds :*

(i) $[Co(NH_3)_6]Cl_3$	*Hexaaminocobalt (III) chloride*
(ii) $[Co(NH_3)_5Cl]Cl_2$	*Pentaamminechloridocobalt (III) chloride*
(iii) $K_3[Fe(CN)_6]$	*Potassium hexacyanoferrate (III)*
(iv) $K_3[Fe(C_2O_4)_3]$	*Potassium trioxalatoferrate (III)*
(v) $K_2[PdCl_4]$	*Potassium tetrachlorido palladate (II)*
(vi) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$	*Diamminechlorido (methylamine) platinum (II) chloride* **[NCERT]**

(a) *(i) only* (b) *(i), (v) and (vi)*
(c) *(i), (ii) and (iii) only* (d) *(v) only*

Interpret *(a)*

(i) To write the name of cationic complex, the general formula is

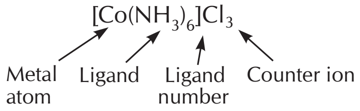
ligand number + ligand names (alphabetically) + metal name + metal oxidation state in parenthesis + counter ion name (counter ion is present outside the coordination sphere.)

(ii) To write the name of anionic complex, the general formula is

counter ion + number of ligands + ligand names (alphabetically) + metal name + 'ate' + (oxidation state of metal).

So write, the name according to above formula

(i)



$[Co(NH_3)_6]Cl_3$

Let the oxidation state of Co be x.

$$x + (0)6 + (-1) \times 3 = 0$$
$$x + 0 - 3 = 0$$
$$x = +3$$

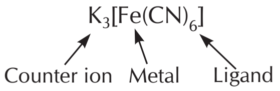
So, the name of this complex is hexaamminecobalt (III) chloride.

(ii) $[Co(NH_3)_5Cl]Cl_2$

$$x + (0) \times 5 + (-1) \times 1 + (-1) \times 2 = 0$$
$$x + 0 - 3 = 0$$
$$x = +3$$

So, the name of the complex is pentaamminechloridocobalt (III) chloride.

(iii)



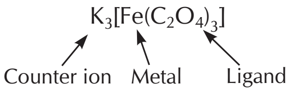
$K_3[Fe(CN)_6]$

Let the oxidation state of Fe is x.

$$(+1)3 + x + (-1)6 = 0$$
$$+3 + x - 6 = 0$$
$$x = +3$$

So, the name of the complex is potassium hexacyanoferrate (III).

(iv)



$K_3[Fe(C_2O_4)_3]$

Let the oxidation state of Fe is x.

$$(+1)3 + x + (-2)3 = 0$$

[∵ Oxalate ion ($C_2O_4^{2-}$) bears – 2 charge.]

$$3 + x - 6 = 0$$
$$x = +3$$

So, the name of the complex is potassium trioxalatoferrate (III).

(v) $\underset{\text{Counter ion}}{K_2}[\underset{\text{Metal atom}}{Pd}\underset{\text{Ligand}}{Cl_4}]$

Let the oxidation state of Pd is x.

$$\begin{aligned}(+1)\,2 + x + (-1)\,4 &= 0\\ 2 + x - 4 &= 0\\ x &= +2\end{aligned}$$

So, the name of the complex is potassium tetrachloridopalladate (II).

(vi) $[\underset{\text{Metal}}{Pt}\ \underset{\text{Ligands}}{\underbrace{(NH_3)_2Cl(NH_2CH_3)}}]\underset{\text{Counter ion}}{Cl}$

Let the oxidation state of Pt is x.

$$\begin{aligned}x + (0)\,2 + (-1)\times 1 + 0 + (-1)\times 1 &= 0\\ x + 0 - 1 + 0 - 1 &= 0\\ x - 2 &= 0\\ x &= +2\end{aligned}$$

So, the name of the complex is diamminechlorido (methylamine) platinum (II) chloride.

Exceptions

Common names in place of IUPAC are used when

(i) Structure of the complex is not certain, *e.g.*, zincate ion $[ZnO_2]^{2-}$

(ii) They are more convenient than the IUPAC names *e.g.*, ferrocyanide rather than hexacyanoferrate for $[Fe(CN)_6]^{4-}$; similarly ferricyanide in place of hexacyanoferrate (III) for $[Fe(CN)_6]^{3-}$; cobaltinitrite in place of hexanitrocobaltate (III) ion for $[Co(NO_2)_6]^{3-}$.

Caution Point *During naming of ligands, when organic free radicals act as ligands, the ligands are named as usual, e.g.,* CH_3 *as methyl,* C_2H_5 *as ethyl etc.*

Formula Writing of Complexes

From the IUPAC name for writing the formula of complexes, following rules may be observed

1. Cation whether simple or complex is written first followed by the anion.
2. The order of formulating a complex ion is reverse to that adopted in naming *i.e.*, the central metal atom is written first followed by the ligand.
3. When there are more than one type of ligands present, they are arranged in the reverse order to that adopted in naming the complexes. *i.e.*,, they are written in the order as anionic ligands first, then neutral and then cationic ligands in the last. For example, $[PdCl_2(H_2O)(N_2H_5)]^+$ where, $N_2H_5^+$ is a cationic ligand. Cl^- is an anionic ligand. This order of ligands in the formula is not yet being fully followed. If there are a number of anionic ligands, they are written alphabetically according to the first symbol of their formulae. Same principle is followed for neutral ligands or positive ligands.
4. Whole of the complex ion is enclosed in a square bracket.
5. The charge on the complex species is equal to the charge on the central metal atom *i.e.*, its oxidation state plus the total charge carried by all the ligands coordinated to the metal atom thus the formula of tetraamminecopper (II) chloride is $[Cu(NH_3)_4]Cl_2$.

Sample Problem 8 *Select the match of formulae for the following coordination compounds :*

(i) Tetraamminediaquacobalt (III) chloride $[Co(NH_3)_4(H_2O)_2]Cl_2$

(ii) Potassium tetracyanonickelate (II) $K_2[Ni(CN)_4]$

(iii) Tris(ethane-1,2-diamine) chromium (III) chloride $[Cr(en)_3]Cl_2$

(iv) Amminebromidochloridonitrito-N-platinate (II) $[Pt(NH_3)_2BrCl(NO_2)]^-$

(v) Dichloridobis-(ethane-1,2-diamine) platinum (IV) nitrate $[PtCl_2(en)_2]NO_3$

(vi) Iron (III) hexacyanoferrate (II) $Fe_3[Fe(CN)_6]$ **[NCERT]**

(a) *(ii) only* (b) *(i), (ii) and (iii) only*

(c) *(ii), (iii), (iv), (v) only* (d) *All the given*

Interpret (a) If complex name starts with metal, it is an anionic complex and if starts with ligand name or number, the complex is cationic.

I. The formula of the cationic complex is written as [metal symbol + ligand (with their number as subscript)] counter ion satisfying the valency of metal or oxidation state of complex.

II. The formula of the anionic complex is written as counter ion satisfying valency of metal [metal symbol + ligand (with their number as subscript)]

(i) $\underset{\text{Ligand}}{\underline{\text{Tetraamminediaqua}}}\ \underset{\text{Metal}}{\underline{\text{Cobalt(III)}}}\ \underset{\text{Counter ion}}{\underline{\text{Chloride}}}$

$$\overset{III}{[Co(NH_3)_4(H_2O)_2]Cl_x}$$

To find the value of x, we have to find the charge on the complex.

$$\overset{III}{[Co(NH_3)_4(H_2O)_2]^{x+}}$$

$$\begin{aligned}+3 + 4\times 0 + 2\times 0 &= x\\ x &= +3\end{aligned}$$

So, the formula of the complex is $[Co(NH_3)_4(H_2O)_2]Cl_3$.

(ii) $\underset{\text{Counter ion}}{\underline{\text{Potassium}}}\ \underset{\text{Ligand}}{\underline{\text{Tetracyano}}}\ \underset{\text{Metal}}{\underline{\text{Nickelate (II)}}}$

$$K_x[\overset{II}{Ni}(CN)_4]$$

To find the value of x, find the charge on the complex.

$$[Ni(CN)_4]^{x-} \quad (\text{as } K^+ \text{ is positive})$$

$$\begin{aligned}+2 + (-1)\times 4 &= -x\\ -x = -2 \text{ or } x &= +2\end{aligned}$$

So, the formula of the complex is $K_2[Ni(CN)_4]$.

Similarly

(iii) $[Cr(en)_3]Cl_3$ (iv) $[Pt(NH_3)\ BrCl(NO_2)]^-$

(v) $[PtCl_2(en)_2]\ (NO_3)_2$ (vi) $Fe_4[Fe(CN)_6]_3$

9.5 Isomerism

It is a phenomenon, in which compounds have the same molecular formula but different physical and chemical properties on account of different structures. These compounds are called **isomers.** The complexes in which ligands undergo rapid displacement by other ligands, cannot exhibit isomerism as the arrangement is not stable. Such complexes are known as **labile complexes.**

There are two main types of isomerism as seen in coordination compound namely :

(i) Structural isomerism, (ii) Space or stereoisomerism

Structural Isomerism

Structural isomerism is mainly of the following types

(a) Ionisation Isomerism

Ionisation isomers yield different ions in solution although they have same composition. This type of isomerism is due to the exchange of groups between the complex ion and the ions outside it, *e.g.,* $[Co(NH_3)_5Br]SO_4$ is red-violet and in solution gives a precipitate of $BaSO_4$ with $BaCl_2$ confirming the presence of SO_4^{2-} ion. On the other hand, $[Co(NH_3)_5SO_4]Br$ is red, and does not give test for sulphate ion in the solution, but instead gives a precipitate of AgBr with $AgNO_3$. Other examples are

(i) $[Pt(NH_3)_4(OH)_2]SO_4$ and $[Pt(NH_3)_4SO_4](OH)_2$
(ii) $[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$
(iii) $[Co(NH_3)_5NO_3]SO_4$ and $[Co(NH_3)_5SO_4]NO_3$

(b) Hydrate Isomerism

Since, water is one of the most effective coordinating agents, therefore the number of water molecules, which may enter into the coordination sphere, may vary resulting in the formation of hydrate isomers, *e.g.,* there are three different hexa-hydrates of chromic chloride with an empirical formula of $CrCl_3 \cdot 6H_2O$. One of these hydrates is violet and the other two are green in colour. All the three differ in the number of molecules of water in the coordination sphere. The formulae, which have been assigned to these hydrate isomers, are

$[Cr(H_2O)_6]Cl_3$
Violet (three ionic chlorine)

$[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$
Bluish green (two ionic chlorine)

$[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$
Dark green (one ionic chlorine)

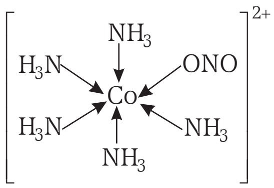
Similarly, other compounds in which hydrate isomerism is observed are

(i) $[Co(NH_3)_4(H_2O)Cl]Cl_2$ and $[Co(NH_3)_4Cl_2]Cl \cdot H_2O$
(ii) $[Co(NH_3)_4(H_2O)Cl]Br_2$ and $[Co(NH_3)_4Cl \cdot Br]Br \cdot H_2O$

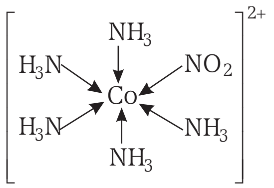
(c) Linkage Isomerism

Isomerism of this type occurs when two or more atoms in a monodentate ligand may function as a donor *i.e.,* when an ambidentate ligand is present. For example, in the case of NO_2^- ion either a nitrogen or an oxygen atom may act as donor giving two different isomers. Thus, two different isomers with molecular formula $[Co(NO_2)(NH_3)_5]^{2+}$ have been prepared. One isomer has N-atom of NO_2 group linked to cobalt atom and the other has O-atom linked to cobalt.

This behaviour is analogous to the behaviour of organic nitrites *R*—ONO and nitro compounds *R*— NO_2. The two isomers are represented below



pentaamminenitritocobalt (III) ion



pentaamminenitrocobalt (III) ion

Other example is

$[Cr(H_2O)_5SCN]^{2+}$ and $[Cr(H_2O)_5NCS]^{2+}$

(d) Coordination Isomerism

This type of isomerism is possible when both positive and negative ions of a salt are complex ions. The two isomers differ in the **distribution of ligands** in the cation and the anion.

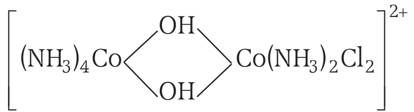
Some important examples are

(i) $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$
(ii) $[Cr(NH_3)_6][Co(C_2O_4)_3]$ and $[Co(NH_3)_6][Cr(C_2O_4)_3]$

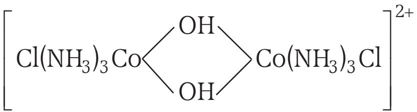
This type of isomerism may be caused by **interchange of ligand between the two complex ions.**

(e) Coordination Position Isomerism

This type of isomerism is due to the difference in the distribution of ligands in two coordination centres. Generally, the bridged complexes involving different ligands show this isomerism *e.g.,*



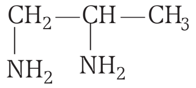
unsymmetrical



symmetrical

(f) Ligand Isomerism

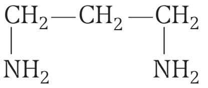
This isomerism arises in those complexes in which the two ligands are isomers themselves *e.g.,*



$CH_2(NH_2)—CH(NH_2)—CH_3$

1,2-diamino propane

and



$CH_2(NH_2)—CH_2—CH_2(NH_2)$

1,3-diamino propane

When these form the complexes, we get ligand isomers. *e.g.,* $[Co(1,2\text{-diaminopropane})_2 Cl_2]^+$ $[Co(1,3\text{-diaminopropane})_2Cl_2]^+$. This type of isomerism is quite rare.

Stereoisomerism

This is due to the different relative positions of the ligands. *It is of two types*

(a) Geometrical isomerism,

(b) Optical isomerism

Out of these two, the most thoroughly investigated is the geometrical isomerism.

(a) Geometrical Isomerism

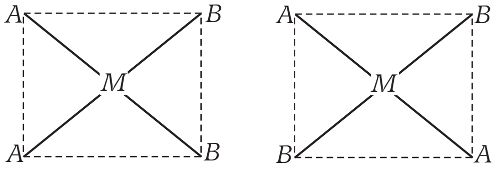
Geometrical isomers differ in the spatial distribution of atoms or groups about the central atom or atom in polynuclear compounds. Those complexes in which the two same ligands occupy adjacent positions to each other or opposite to each other (cis or *trans* respectively) are able to show this isomerism.

This isomerism cannot be exhibited by coordination compounds having 2 or 3 coordination number as it is not possible to have more than a single arrangement of ligands in space around the central ion in these cases. Geometrical isomerism with respect to the metal has also not been found among **tetrahedral** complexes of type MA_4 or MA_3B or MA_2B_2 because all the four ligands are equidistant from each other.

Only square planar and octahedral complexes show this type of isomerism.

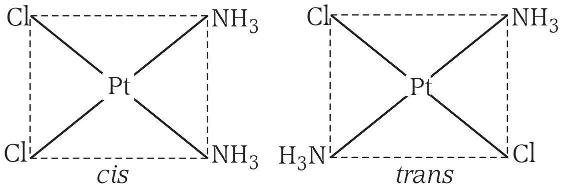
1. ***cis-trans* isomerism in square planar complexes is of various types**

   (i) Any complex of the type MA_2B_2 can exist in *cis-trans* form.



cis *trans*

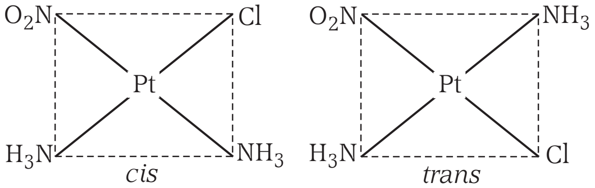
e.g., cis-platin or dichlorodiammineplatinum (II), $[Pt(NH_3)_2Cl_2]$ can exist as under



cis *trans*

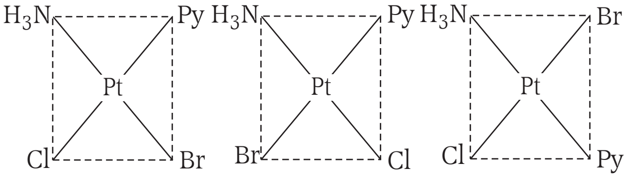
Caution Point *Square planar complexes of the type $[M(AA)_2]$, MA_4, MA_3B and MAB_3 do not show this isomerism since, all possible spatial arrangements for any of these complexes are identical.*

(ii) In a complex of the type MA_2BC, also there are *cis*- and *trans*-isomers, *e.g.,* $[Pt(NH_3)_2ClNO_2]$ can exist as

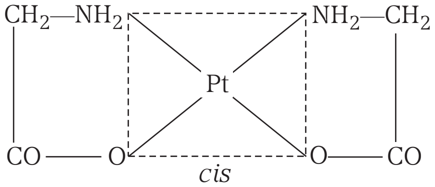


cis *trans*

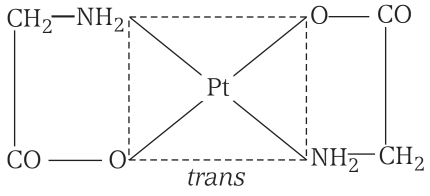
(iii) For a complex of the type *MABCD*, three geometrical isomers are possible, *e.g.,* $[Pt(Py)(NH_3)BrCl]$ can exist as



(iv) The geometrical isomerism can also occur in square planar complexes if the chelate group is not symmetrical, *e.g.,* complex of glycine (NH_2CH_2COOH) and platinum *i.e.,* $[Pt(gly)_2]$

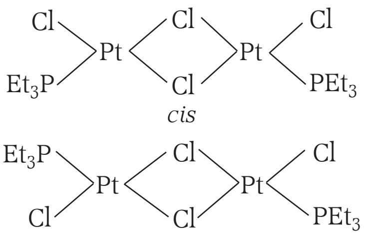


cis



trans

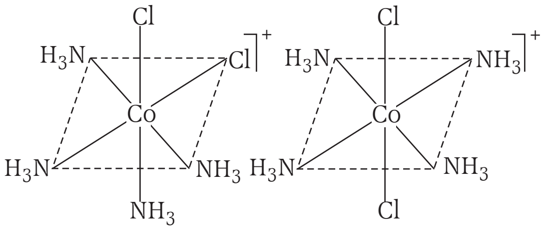
(v) Geometrical isomerism is also shown by **bridged binuclear** planar complexes of the type, $M_2A_4X_2$, *e.g.,* $[PtCl_2PEt_3]_2$



cis

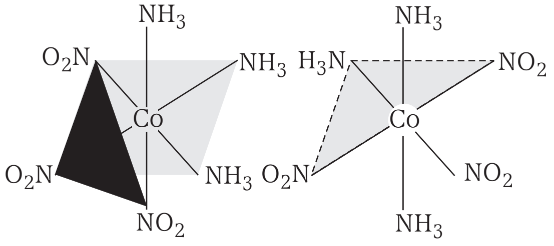
trans

2. Various octahedral complexes that show geometrical isomerism are as follows
   (i) Octahedral complexes of MA_4B_2 type show *cis-trans* isomerism, *e.g.,* dichlorotetramminecobalt (III) complex ion, $[Co(NH_3)_4Cl_2]^+$ shows *cis-trans* isomerism as



cis (violet) *trans* (green)

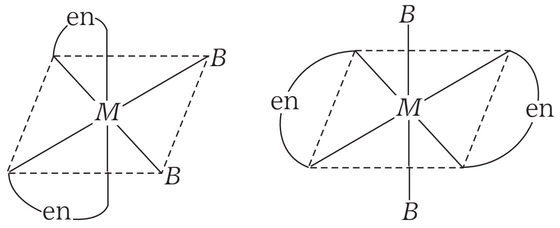
   (ii) An another type of geometrical isomerism called by *fac*-and *mer*-isomerism also occurs in octahedral coordination entities of the type $[Ma_3b_3]$ like $[Co(NH_3)_3(NO_2)_3]$. If three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, we have the **facial** (fac) **isomer.** When the positions are around the meridian of the octahedron, we get **meridional** (mer) **isomer.**



fac- *mer-*

Fig. 9.2 The facial (*fac*) and meridional (*mer*) isomers of $[Co(NH_3)_3(NO_2)_3]$

   (iii) Even $M(AA)_2B_2$ type octahedral complexes also show *cis* and *trans* isomerism where, $A–A$ can be any symmetrical bidentate ligand like ethylenediamine (en) and B can be any anionic ligand, such as Cl^-, CN^-, NO_2^- etc.



cis *trans*

An example of this type is $[Pt(en)_2Cl_2]$.

Octahedral complexes of $[MA_5B]$ or $M(AA)_3$ (where, AA = symmetrical bidentate ligand) do not exhibit geometrical isomerism.

   (iv) Complexes having six different ligands $[M(ABCDEF)]$ shall exhibit geometrical isomerism. Theoretically, fifteen different isomers should be possible. In practice, three isomers of the complex $[Pt(C_5H_5N)(NH_3)(NO_2)(Cl)(Br)(I)]$ have actually been isolated.

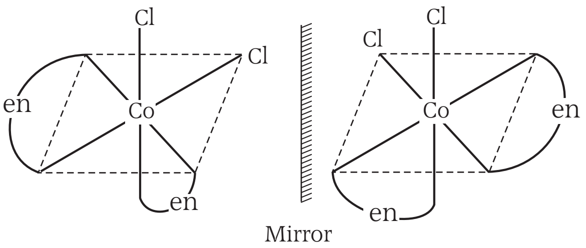
   (v) As was observed in square planar complexes, unsymmetrical bidentate ligands also give rise to geometrical isomerism in octahedral complexes of the type $[M(AB)_3]$.

(b) Optical Isomerism

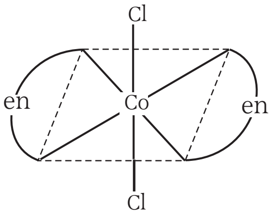
Optical isomerism arises when a compound can be represented by two asymmetrical structures (known as optical isomers). The two isomers are structurally the mirror images of each other (just as in the organic chemistry). Further, it has been found that these mirror image compounds are non-superimposable on each other and they do not possess the plane of symmetry.

Optical isomerism is common in octahedral complexes involving 2 or 3 symmetrical bidentate groups (*i.e.,* a group attached to the central atom by two coordinate bonds of the type $[M(AA)_2X_2]$ and $[M(AA)_3]$ where, AA = bidentate ligand. This is illustrated as under :

   (i) **Example of $M(AA)_2X_2$ type** *cis*-dichloridobis (ethylenediamine) cobalt (III) ion, $[Co(en)_2Cl_2]^+$, the *cis*-form of this complex is optically active and exists in *d* and *l*-forms. Its *trans* form is optically inactive due to the presence of a plane of symmetry as shown below.



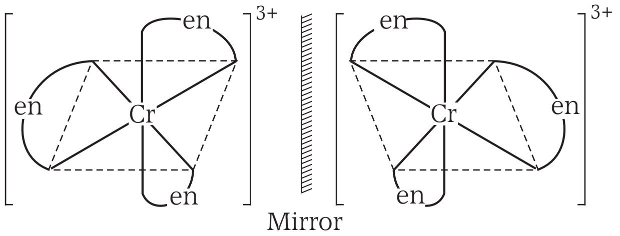
(a) optically active forms



(b) Optically inactive form

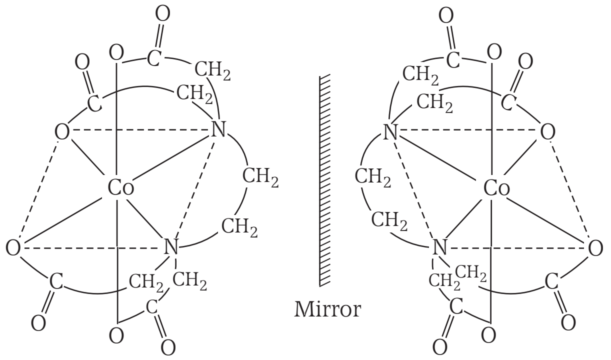
Fig. 9.3 (a) *cis*-dichloro bis(ethylenediamine) cobalt (III) ion
(b) *trans*-dichloro bis (ethylenediamine) cobalt (III) ion

(ii) **Example of $M(AA)_3$ type** octahedral complexes $[Cr(en)_3]^{3+}$, *tris* (ethylenediamine) chromium (III) ion and $[Cr(C_2O_4)_3]^{3-}$, trioxalatochromate (III) ion etc.

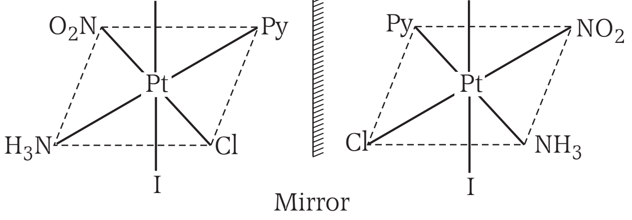


(iii) **Examples of $[M(AA)B_2X_2]$ type** $[CoCl_2(NH_3)_2(en)]^+$,

(iv) **Complexes containing hexadentate ligand** (*e.g.*, ethylenediaminetetraacetic acid) show optical activity, *e.g.*, the anion $[Co(EDTA)]^-$ exists in two forms.

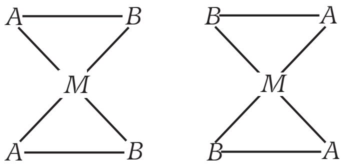


(v) **Example of $ML_aL_bL_cL_dL_eL_f$ type** is $[Pt(Py)(NH_3)(NO_2)(Cl)(Br)(I)]$. The optical activity in such complexes is due to the presence of six different ligands around the central atoms.

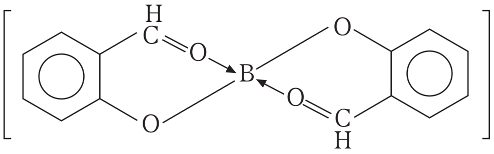


In such a compounds fifteen geometrical isomers are possible which can be resolved into optical isomers. Resolution of all the isomers is not achieved.

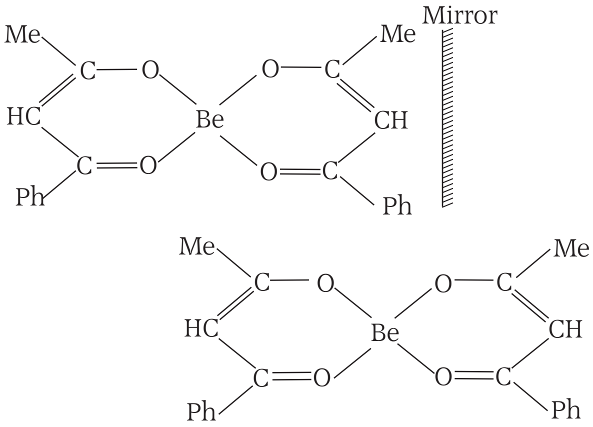
The optical activity has been observed for chelated tetrahedral and square planar complexes but only rarely. *In tetrahedral complexes only the type, which occurs in bis-chelates with unsymmetrical ligand has been detected*. These have been found in Be(II), B(III), Zn(II) and Cu(II) complexes. They are of the general type as represented below :



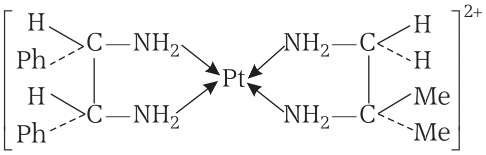
Thus, bis(salicylaldehyde) boron (III) cation has been found to be racemic and resolution has been accomplished.



The two enantiomers of bis (benzoylacetonato) beryllium (II) are shown below :



Square planar complexes are seldom optically active. One such compound which has been resolved into two forms is shown below. As can be seen, it has no plane or axis of symmetry.



Hot Spot 2

FINDING NUMBER of Stereoisomerism

Questions based on stereoisomers are frequently asked in JEE Main examination. The level of question is generally average and by a small practice, the question can be solved easily.

In order to find number of stereoisomers or whether a compound exhibit stereoisomerism or not, first find the general formula of the complex, and then compare with the following facts.

1. Geometrical isomerism is possible in square planar complexes of the type MA_2BC, MA_2B_2, $MABCD$. It is also possible in bridged binuclear planar complexes of the type $M_2A_4X_2$. Octahedral complexes of the type MA_3B_3, MA_4B_2, $M(AA)_2B_2$, $[M(ABCDEF)]$ exhibit geometrical isomerism.
2. Geometrical isomerism is not possible in square planar complexes of type MA_4 and MA_3B, tetrahedral complexes of type MA_4, MA_2B_2 and $MABCD$ and octahedral complexes of type MA_6 and MA_5B. In case of octahedral complexes of the types MA_3B_3, the *cis-trans* isomers are also called *fac-mer* isomers.
3. Octahedral complexes of the type $[M(AA)_2X_2]$, $[M(AA)_3]$, $[M(AA)B_2X_2]$ [where, AA = bidentate ligand] generally exhibits optical isomerism. $[M(\text{EDTA})]$ and $MABCDEF$ also exhibit optical isomerism. (A, B, C, D, E, F are different monodentate ligands)

Sample **Problem 9** *The number of geometrical isomers possible the following coordination entities are respectively.*

(i) $[Cr(C_2O_4)_3]^{2-}$ *(ii)* $[Co(NH_3)_3]Cl_3$ **[NCERT]**

(*a*) 2, 2 (*b*) 0, 2 (*c*) 2, 0 (*d*) 1, 2

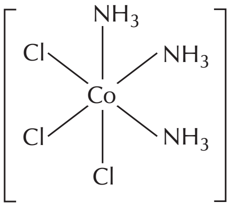
Interpret (*b*) In order to solve such problem recall the following facts

- I. Geometrical isomerism is exhibited by octahedral complexes of the type $[MA_3B_3]$, $[MA_2B_4]$ etc., where A and B are monodentate ligands.
- II. $[M(AA)_3]$ type complex does not exhibit geometrical isomerism, they exhibit optical isomerism.
- III. When the similar groups occupy adjacent positions, the isomer is called *fac* or *cis*-form, if not, it is called *mer* or *trans*-form.

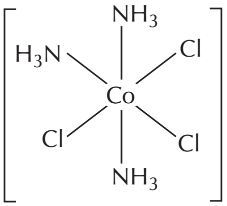
Thus,

(i) No geometrical isomer is possible.

(ii) Two geometrical isomers are possible for $[Co(NH_3)_3Cl_3]$



Facial (*fac*)



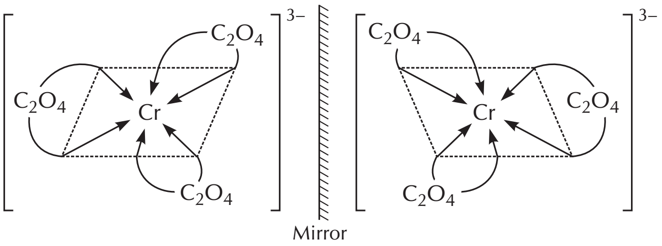
Meridional (*mer*)

Sample **Problem 10** *Trans form of which of the following is optically inactive?*

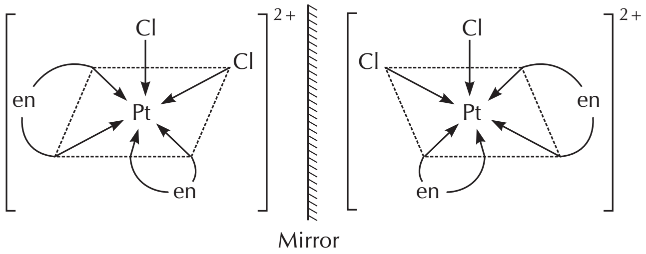
(*a*) $[Cr(C_2O_4)_3]^{3-}$ (*b*) $[PtCl_2(en)_2]^{2+}$

(*c*) $[Cr(NH_3)_2Cl_2(en)]^{+}$ (*d*) *All of these*

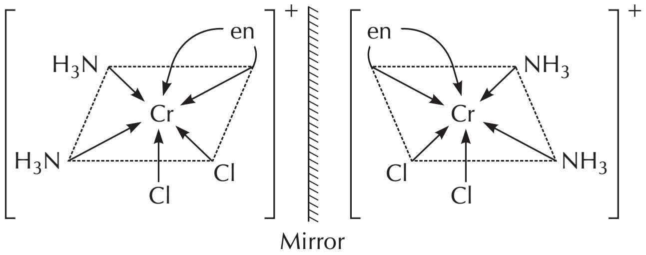
Interpret (*b*) (a) $[Cr(C_2O_4)_3]^{3-}$



(b) *Cis*-$[PtCl_2(en)_2]^{2+}$



(c) *Cis*-$[Cr(NH_3)_2Cl_2(en)]^{+}$



Thus, *trans*-$[PtCl_2(en_2)]^{2+}$ is optically inactive.

Sample **Problem 11** *Which of the following has largest number of isomers? (R = alkyl group, en = ethylenediamine)*

(*a*) $[Ru(NH_3)_4Cl_2]^{+}$ (*b*) $[Co(NH_3)_5Cl]^{2+}$

(*c*) $[Ir(PR_3)_2H(CO)]^{2+}$ (*d*) $[Co(en)_2Cl_2]^{+}$

Interpret (*d*) Among the given $[Co(en)_2Cl_2]^{+}$ is a $[M(AA)_2A_2]$ type complex, thus, it is possible for it to exhibit optical as well geometrical isomerism, which is not possible in case of other given complexes. Thus, it exhibits largest number of isomers.

Check Point 2

1. Why do ambidentate ligands show linkage isomerism?
2. Name a ligand, presence of which causes difficulty in finding the oxidation state and charge on the ligands.
3. Why do the complexes in which ligands undergo rapid displacement by other ligands, not show isomerism?
4. Why do the complexes with 2 or 3 coordination number not exhibit geometrical isomerism?
5. *Trans*-dichlorobis (en) cobalt (III) ion is optically inactive while its *cis*-form is optically active. Explain, why?

9.6 Bonding in Coordination Compounds

The formation of coordination compounds can be explained electronically by a number of theories like
(i) valence bond approach (ii) crystal field theory

Valence Bond Approach

This was evolved largely through the efforts of **Linus Pauling** based on attempted Lewis-Sidgwick ideas of the coordinate covalent bond. In this approach, the basic assumption made is that the metal ligand bonds arise by the donation of pairs of electron from ligands to the metal *i.e.,* through forming the coordinate covalent bond. In order to accommodate these electrons, the metal ion must possess requisite number of vacant orbitals of similar energy. These metal orbitals undergo hybridisation to give a set of hybrid orbitals of equal energy with the approach of the ligands.

The main assumptions of valence bond approach are

1. The ions of the transition elements have some incompletely filled *d*-orbitals.
2. Some or all the electrons in the incompletely filled *d*-orbitals are unpaired.
3. It was suggested that sometimes, the unpaired $(n-1)$ *d*-electrons couple as fully as possible prior to bond formation. In this process some $(n-1)$ *d*-orbitals become vacant.

   The central metal atom thus, makes available a number of empty orbitals equal to its coordination number for the formation of coordinate bonds with suitable ligand orbitals.
4. Since, the energy of the $(n-1)$ *d*-orbitals is only slightly less than that of *s*-and *p*-orbitals of the *n*th orbitals, these vacant orbitals mix together to form new equivalent orbitals, called **hybrid orbitals.**
5. Each ligand has at least one sigma orbital containing a lone pair of electrons.
6. The hybrid orbitals formed, take part in the formation of hybrid bonds with the ligands by overlapping. The bond formation takes place by accepting the lone pair of electrons by the hybrid orbitals of the metal from the ligands. Especially the orbitals that would be used for a metal ion of the first series, are the two 3*d*, one 4*s* and the three 4*p*-orbitals. The rest 3*d* or **inner orbitals on the metal ion do not** participate in the bonding. When $(n-1)$ *d*-orbitals are used in bond formation, the complex formed is called **inner orbital complex.**
7. Sometimes, in place of $(n-1)$ *d*-orbitals, outer *nd*-orbitals are used for hybridisation. The complex, thus, formed is called **outer orbital complex.**
8. The bond hybridisation involved and the resulting geometrical shapes of the complexes are given in the following table

Table 9.6 **Relation Between Hybridisation and Geometry of Complexes**

Bond hybridisation	Geometrical shape	*d*-orbital used	Typical example
d^2sp^3	octahedral (inner orbital complex)	d_{z^2} and $d_{x^2-y^2}$	$[Fe(CN)_6]^{3-}$
sp^3d^2	octahedral (outer orbital complex)	$d_{x^2-y^2}$ and d_{z^2}	$[FeF_6]^{3-}$
sp^3	tetrahedral		$[Zn(NH_3)_4]^{2+}$
dsp^2 or sp^2d	square planar	$d_{x^2-y^2}$	$Ni(CN)_4]^{2-}$

9. *A given complex is paramagnetic, if one or more unpaired electrons are present in the d-subshell. However, if there is no unpaired electrons, then complex is termed as diamagnetic.* Pauling made extensive use of magnetic measurements to discover the number of unpaired electrons in a complex and he also differentiated between complexes in which the bonding could be considered as ionic or those in which it was probably covalent.

   In deciding whether the hybridisation at the central metal ion of octahedral complexes is sp^3d^2 (outer orbital) or d^2sp^3 (inner orbital) we must know the results of magnetic measurements. These indicate the number of unpaired electrons (N). Magnetic moment is given by

$$\mu = \sqrt{N(N+2)}\ \text{BM}$$

(BM is Bohr Magneton)

Hot Spot 3

FINDING GEOMETRY and Magnetic Character of Complexes

Questions based on geometry, hybridisation, magnetic character and number of unpaired electrons were frequently asked in the AIEEE and JEE Main examination, thus it is a very important topic for the examination. The level of question is generally average.

In order to find the geometry, hybridisation and magnetic character, follow the following steps

Step I Find the oxidation number of central metal atom and write the electronic configuration of **central metal ion.**

Step II Find the nature of ligand,

(i) If it is CN^-, NH_3^-, CO, pair up the unpaired electrons of the metal ion (if they are more than 4 and less than 8 in case of octahedral complex.)

(ii) If it is Cl^-, Br^-, I^-, H_2O, etc., leave the unpaired electrons of the metal ion as such.

Step III Now fill the ligand's electrons in empty available orbitals. The orbitals occupied by ligands give an idea about the hybridisation.

Step IV From the hybridisation, find geometry (see table 9.7).

Step V Also see whether unpaired electrons are present, or not. If they are present, species is paramagnetic, otherwise diamagnetic.

Step VI If inner $[(n-1)d]$ orbital takes part in hybridisation, the complex is inner orbital, otherwise outer orbital.

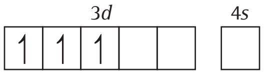
The above procedure can be best understood by following examples.

1. $[Cr(NH_3)_6]^{3+}$ ion

In this ion, oxidation state of Cr is +3.

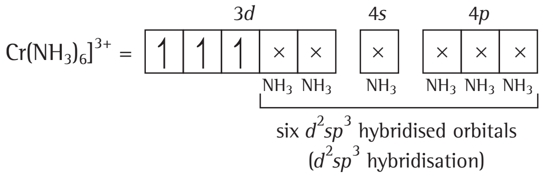
$$[x + 6 \times 0 = +3 \quad \text{or } x = +3]$$

$$Cr^{3+} = [Ar]\, 3d^3 4s^0$$



NH_3 is a strong field ligand but unpaired electrons are < 4. So, pairing does not occur.

Since, there are six NH_3 ligands, fill their electrons as



(Here x = a pair of electrons from ligand)

Since, hybridisation is d^2sp^3, geometry is octahedral. Because of the presence of three unpaired electrons, it is a paramagnetic complex.

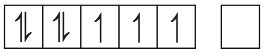
Since $(n-1)\,d$ (3d orbital) takes part in hybridisation, it is an inner orbital complex.

Other complexes of Cr with similar inner structure are $[Cr(CN)_6]^{3-}$ and $[Cr(H_2O)_6]^{3+}$. In a similar way, structure of $[V(H_2O)_6]^{3+}$ with d^2-configuration of V^{3+} ion can be explained.

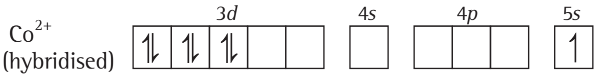
2. $[Co(NH_3)_6]^{2+}$

Co is present in +2 oxidation state, so

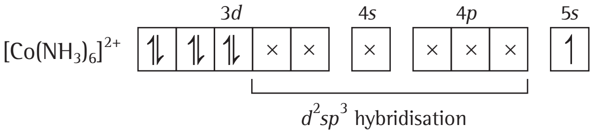
$$Co^{2+} = [Ar] \quad 3d^7 \quad 4s^0$$



NH_3 being strong field ligand pair up the unpaired electrons of Co and also transfers one remained unpaired electron into higher energy state, as



The inner two d-orbitals are made available for the required d^2sp^3 hybridisation after maximum pairing of electrons within the 3d level followed by promotion of one d-electrons to the higher energy level (5s). This is shown below



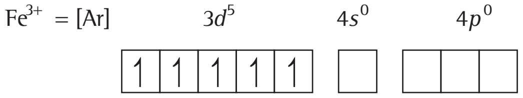
Thus, its geometry is octahedral. It is a paramagnetic complex. Moreover, it is an inner orbital complex.

As the promoted electron (shown above) has low ionisation energy, the complexed central metal ion Co^{2+} has a tendency to undergo oxidation easily to Co^{3+}. Thus, the paramagnetic complex changes to diamagnetic after oxidation. It should be noted however, that the **formation of such inner orbital**

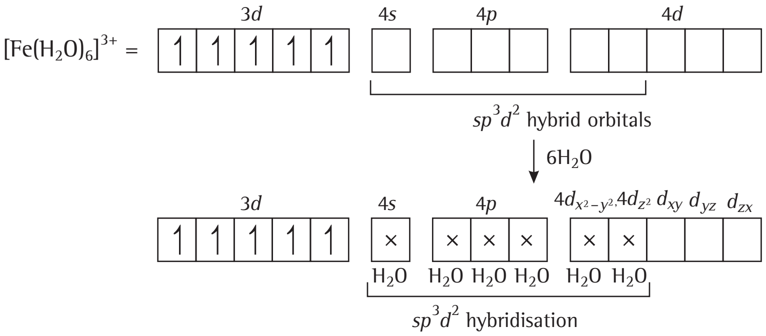
complex and promotion of electron can be brought about only by very strong ligands.

3. $[Fe(H_2O)_6]^{3+}$

Here, Fe is present as Fe^{3+}.



H_2O being weak field ligand is unable to pair up its unpaired electrons, thus, occupy the 4*s*, 4*p* and 4*d* empty orbitals as



Thus, its geometry is octahedral.

Because of the presence of five unpaired electrons, it is paramagnetic.

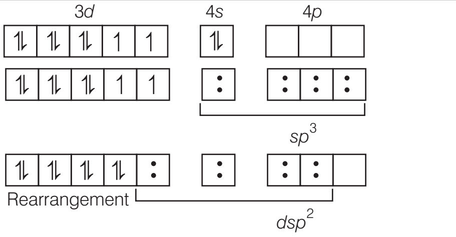
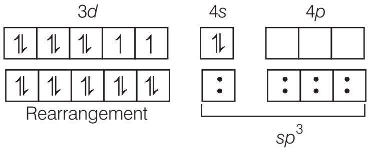
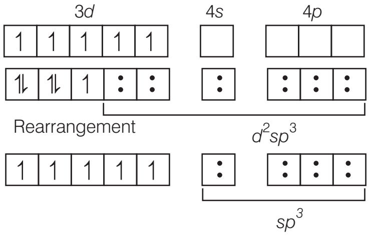
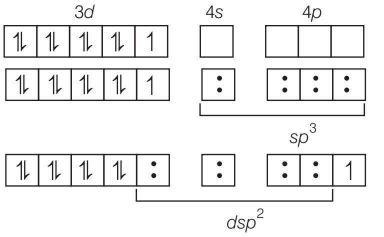
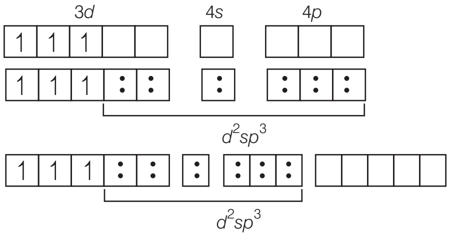
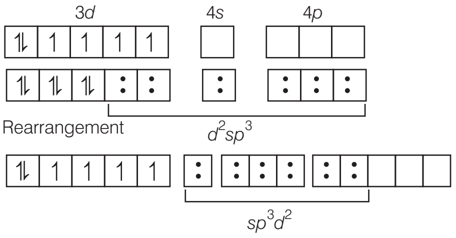
Since *nd* orbitals (4*d* orbitals) take part in hybridisation (bonding), it is an **outer orbital or high spin complex.**

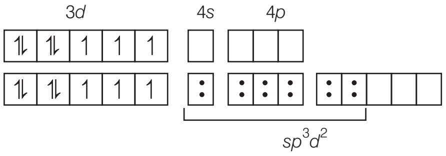
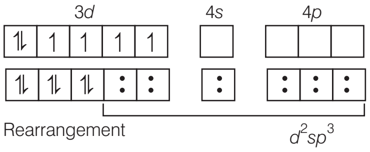
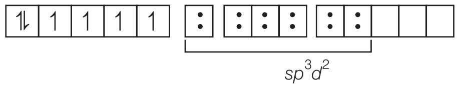
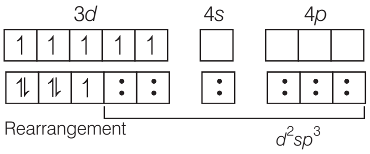
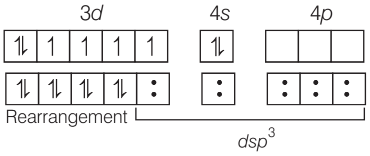
Caution Points

(i) *Electrons of ligands are only the bonding electrons. None of the* 3*d-electron of* Fe *take part in bonding.*

(ii) *In* d^5 *electronic configuration, an octahedral complex can exist in both high spin and low spin forms.*

Table 9.7 **Geometry and Hybridisation of Some Other Complexes on the Basis of VBT**

S.N.	Atom/Ion Complex	Configuration	Oxidation state of metal	Type of hybridisation	Geometry (Shape)	No. of unpaired electrons	Magnetic nature
1.	$Ni^{2+}(d^8)$ $[NiCl_4]^{2-}$ $[Ni(CN)_4]^{2-}$		+2 +2 +2	sp^3 dsp^2	Tetrahedral Square planar	2 2 0	Paramagnetic Paramagnetic Diamagnetic
2.	$Ni\ (d^8s^2)$ $[Ni(CO)_4]$		0 0	sp^3	Tetrahedral	2 0	Paramagnetic Diamagnetic
3.	$[Mn^{2+}(d^5)]$ $[Mn(CN)_6]^{4-}$ $[MnCl_4]^{2-}$		+2 +2 +2	d^2sp^3 (inner) sp^3	Octahedral Tetrahedral	5 1 5	Paramagnetic Paramagnetic Paramagnetic
4.	$Cu^{2+}(d^9)$ $[CuCl_4]^{2-}$ $[Cu(NH_3)_4]^{2+}$	 One electron is shifted from 3*d* to 4*p*-orbital	+2 +2 +2	sp^3 dsp^2	Tetrahedral Square planar	1 1 1	Paramagnetic Paramagnetic Paramagnetic
5.	$Cr^{3+}(d^3)$ $[Cr(NH_3)_6]^{3+}$ $[Cr(H_2O)_6]^{3+}$		+3 +3 +3	d^2sp^3(Inner) d^2sp^3(Inner)	Octahedral Octahedral	3 3 3	Paramagnetic Paramagnetic Paramagnetic
6.	$Co^{3+}(d^6)$ $[Co(NH_3)_6]^{3+}$ $[CoF_6]^{3-}$		+3 +3 +3	d^2sp^3(Inner) sp^3d^2(Outer)	Octahedral Octahedral	4 0 4	Paramagnetic Diamagnetic Paramagnetic

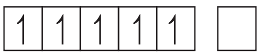
S.N.	Atom/Ion Complex	Configuration	Oxidation state of metal	Type of hybridisation	Geometry (Shape)	No. of unpaired electrons	Magnetic nature
7.	$Co^{2+}(d^7)$ $[Co(H_2O)_6]^{2+}$		+2 +2	 sp^3d^2(Outer)	 Octahedral	3 3	Paramagnetic Paramagnetic
8.	$Fe^{2+}(d^6)$ $[Fe(CN)_6]^{4-}$ $[Fe(H_2O)_6]^{2+}$ $[Fe(NH_3)_6]^{2+}$	  Same	+2 +2 +2 +2	 d^2sp^3(Inner) sp^3d^2(Outer) sp^3d^2(Outer)	 Octahedral Octahedral Octahedral	4 0 4 4	Paramagnetic Diamagnteic Paramagnetic Paramagnetic
9.	$Fe^{3+}(d^5)$ $[Fe(CN)_6]^{3-}$		+3 +3	 d^2sp^3 (Inner)	 Octahedral	5 1	Paramagnetic Paramagnetic
10.	$Fe(d^6, s^2)$ $[Fe(CO)_5]$		0 0	 dsp^3 (Inner)	 Trigonal bipyramidal	4 0	Paramagnetic Diamagnetic

Sample Problem 12 *Which of the following options are correct for* $[Fe(CN)_6]^{3-}$ *complex?* **[NCERT Exemplar]**

(i) d^2sp^3 *hybridisation* *(ii)* sp^3d^2 *hybridisation*
(iii) Paramagnetic *(iv) Diamagnetic*
(a) *(i) and (iii)* (b) *(i) and (iv)*
(c) *(ii) and (iii)* (d) *(ii) and (iv)*

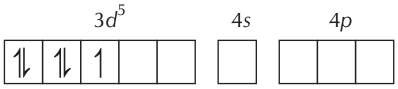
Interpret (a) In $[Fe(CN)_6]^{3+}$, Fe is present as Fe^{3+}.

Fe^{3+} = [Ar] $3d^5$ $4s^0$



CN^- being strong field ligand pair up these unpaired electrons, so that now the complex have only one unpaired electron as

$[Fe(CN)_6]^{3-}$



Now, the two $3d$, one $4s$ and three $4p$ orbitals hybridise to give six d^2sp^3 hybridised orbitals which are occupied by electrons of CN^-

Since, the complex contain one unpaired electron, it is paramagnetic in nature.

Sample Problem 13 *Atomic number of* Mn, Fe *and* Co *are 25, 26 and 27 respectively. Which of the following inner orbital octahedral complex ions are diamagentic?* **[NCERT Exemplar]**

(i) $[Co(NH_3)_6]^{3+}$ *(ii)* $[Mn(CN)_6]^{3-}$
(iii) $[Fe(CN)_6]^{4-}$ *(iv)* $[Fe(CN)_6]^{3-}$
(a) *(i) and (ii) only* (b) *(ii) and (iii) only*
(c) *(i) and (iii) only* (d) *All of these*

Interpret (c) Co^{3+} and Fe^{2+} contains d^6 configuration and the unpaired electrons are paired by strong field ligands, *i.e.*, NH_3 and CN^-, so $[Co(NH_3)_6]^{3+}$ and $[Fe(CN)_6]^{4-}$ are diamagnetic complexes.

In Fe^{3+} and Mn^{3+} unpaired electrons remain even after pairing, so these are paramagnetic.

Sample Problem 14 *Amongst the following ions which one has the highest magnetic moment value?* **[NCERT]**

(a) $[Cr(H_2O)_6]^{3+}$
(b) $[Fe(H_2O)_6]^{2+}$
(c) $[Zn(H_2O)_6]^{2+}$
(d) *All have same magnetic moment*

Interpret (*b*) More the number of unpaired electrons, higher is the magnetic moment. So, first find the number of unpaired electrons to find magnetic moment.

The oxidation states of metals in the complexes along with the electronic configuration are given

(a) Cr^{3+} : $3d^3$ configuration; no. of unpaired electrons (n) = 3

(b) Fe^{2+} : $3d^6$ configuration; $n = 4$

(c) Zn^{2+} : $3d^{10}$ configuration; $n = 0$

Thus, the complex $[Fe(H_2O)_6]^{2+}$ with maximum number of unpaired electrons has the highest magnetic moment.

Sample Problem 15 *The spin only magnetic moment of* $[MnBr_4]^{2-}$ *is 5.9 BM. Predict the geometry of the complex ion?*

(a) *Tetrahedral* (b) *Square planar*

(c) *Octahedral* (d) *Trigonal pyramidal*

Interpret (*a*) Since, the coordination number of Mn^{2+} ion in the complex ion is 4, it will be either tetrahedral (sp^3 hybridisation) or square planar (dsp^2 hybridisation). But the fact that the magnetic moment of the complex ion is 5.9 BM suggests that it should be tetrahedral in shape rather than square planar because of the presence of five unpaired electrons in the *d*-orbitals.

Limitations of Valence Bond Theory

Although this theory described the formation, structure and magnetic behaviour of complexes sucessfully but it suffers from the following short comings :

1. It involves a number of assumptions.
2. It describes bonding in coordination compounds only qualitatively.
3. It does not offer any explanation for the optical absorption spectra of complexes.
4. It does not describe the detailed magnetic properties of coordination compounds.
5. It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
6. It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes.
7. It does not distinguish between weak and strong ligands.

Crystal Field Theory

Most of the shortcomings of VBT of coordination compounds were removed in **Crystal Field Theory** (CFT). It attributes partial covalent character and partial ionic character to bonds. This **theory** was developed by **H. Bethe** and **V. Vleck** (1935) and proved to be more successful in explaining the bonding and properties of coordination complexes. **The theory is based upon the fact that the degenerate** (meaning energetically alike) ***d*-orbitals of** *metal ions are splitted energy wise due to the concentration of point charges in certain specific positions. This is seen because the energy of the orbitals lying in the direction of point charges increases more in comparison to orbitals lying in between the point charges as the electrons in former case experience greater repulsion than in latter case.* Thus, energy wise, two groups of orbitals are seen now, one with higher energy and other with lower energy. This splitting of 5 degenerate orbitals of metal ion into two sets of orbitals having different energies is called **crystal field splitting.** In case of octahedral complexes, e_g set ($d_{x^2-y^2}$, d_{z^2}) is of higher energy while in case of tetrahedral complexes t_{2g} set (d_{xy}, d_{yz}, d_{zx}) has higher energy.

The splitting of *d*-orbitals in octahedral and tetrahedral complexes is shown below

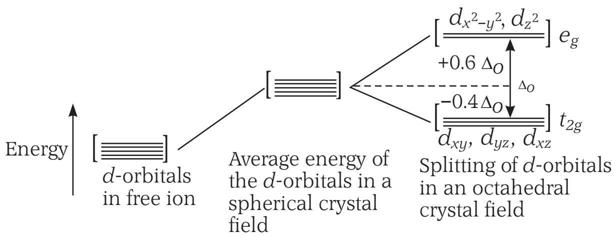


Fig. 9.4 *d*-orbital splitting in an octahedral crystal field.

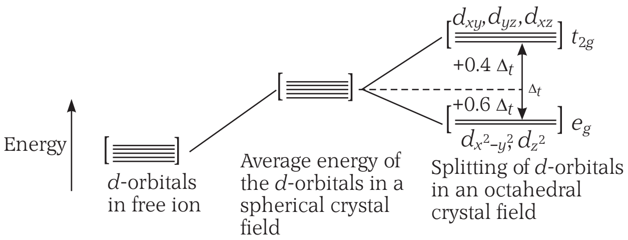


Fig. 9.5 *d*-orbital splitting in a tetrahedral crystal field

The difference in energy levels is arbitrarily taken to be Δ. The set of lower energy stabilises the complex ion by 0.4 units and that with higher energy destabilises the ion by 0.6 units. The gain in energy achieved by preferential filling of electrons in orbitals is called *crystal field stabilisation energy* (CFSE). *Higher the amount of* CFSE, *greater is the stability of the complex.*

The tetrahedral crystal field splitting is only 4/9 of the octahedral splitting and there is no known low spin tetrahedral complex.

Here, one point must always be kept in mind that **crystal field theory** considers purely electrostatic attractions between central metal ion and ligands. Factors which affect the magnitude of crystal field splitting are

1. Nature of ligands (the ligands with smaller size, large negative charge, with good σ donor and π acceptor properties will give large crystal field splitting). The

ligands are arranged in **spectro chemical series** on the basis of their crystal field splitting power as

$$I^- < Br^- < Cl^- < F^- < ox^- \approx H_2O < Py \approx NH_3 < en < NO_2^- < CN^- < CO$$

It is an experimentally determined series based on the absorption of light by complexes with different ligands. Let us assign electrons in the d-orbitals of metal ion in octahedral coordination entities. Obviously, the single d electron occupies one of the lower energy t_{2g} orbitals. In d^2 and d^3 coordination entities, the d-electrons occupy the t_{2g} orbitals singly in accordance with the Hund's rule. For d^4 ions, two possible patterns of electron distribution arise (i) the fourth electron could either enter the t_{2g} level and pair with an existing electron, or (ii) it could avoid paying the price of the pairing energy by occupying the e_g level. Which of these posibilities occurs, depends on the relative magnitude of the crystal field splitting, Δ_o and the pairing energy, P (P represents the energy required for electron pairing in a single orbital). *The two options are :*

(i) If $\Delta_o < P$, the fourth electron enters in one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$. Ligands for which $\Delta_o < P$ are known as **weak field ligands** and form high spin complexes.

(ii) If $\Delta_o > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4 e_g^0$. Ligands which produce this effect are known as **strong field ligands** and form low spin complexes.

2. Oxidation state of metal ion (More crystal field splitting is seen in metal ions with higher oxidation states).
3. Size of d-orbital (larger the size, more crystal field splitting is seen).
4. Geometry of the complex (as splitting is different for tetrahedral and octahedral complexes).

The number of unpaired electrons in octahedral and tetrahedral complex having different configuration can be summarised in table 9.9

Table 9.8 **Number of Unpaired Electrons in Octahedral and Tetrahedral Complexes**

Electronic configuration	Octahedral complex		Number of unpaired electrons	Tetrahedral complex		Number of unpaired electrons
	(t_{2g} set)	(e_g set)		(e_g set)	(t_{2g} set)	
d^1	t_{2g}^1	e_g^0	1	e^1	t_2^0	1
d^2	t_{2g}^2	e_g^0	2	e^2	t_2^0	2
d^3	t_{2g}^3	e_g^0	3	e^2	t_2^1	3
d^4 (a)*	t_g^3	e_g^1	4	e^2	t_2^2	4
(b)*	t_g^4	e_g^0	2	e^4	t_2^0	0
d^5 (a)*	t_{2g}^3	e_g^2	5	e^2	t_2^3	5
(b)*	t_{2g}^5	e_g^0	1	e^4	t_2^1	1
d^6 (a)*	t_{2g}^4	e_g^2	4	e^3	t_2^3	4
(b)*	t_{2g}^6	e_g^0	0	e^4	t_2^2	2
d^7 (a)*	t_{2g}^5	e_g^2	3	e^4	t_2^3	3
(b)*	t_{2g}^6	e_g^1	1	e^4	t_2^3	3
d^8	t_{2g}^6	e_g^2	2	e^4	t_2^4	2
d^9	t_{2g}^6	e_g^3	1	e^4	t_2^5	1
d^{10}	t_{2g}^6	e_g^4	0	e^4	t_2^6	0

*[(a) is the configuration for high spin and (b) is the configuration for low spin complexes]

Sample **Problem 16** *The CFSE for octahedral* $[CoCl_6]^{4-}$ *is* 18,000 *cm*$^{-1}$. *The CFSE for tetrahedral* $[CoCl_4]^{2-}$ *will be*

[NCERT Exemplar]

(*a*) 18000 cm^{-1} (*b*) 16000 cm^{-1}
(*c*) 8000 cm^{-1} (*d*) 20000 cm^{-1}

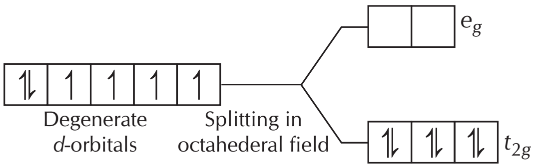
Interpret (*c*)

$$\Delta_t = -\frac{4}{9}\Delta_o$$
$$= -\frac{4}{9} \times 18000 = 8000 \text{ cm}^{-1}$$

Sample **Problem 17** *The electronic configuration of central matal atom/ion in* $[Co(CN)_6]^{3-}$ *is*

(*a*) $t_{2g}^5 e_g^0$ (*b*) $t_{2g}^4 e_g^2$ (*c*) $t_{2g}^6 e_g^0$ (*d*) $t_{2g}^4 e_g^3$

Interpret (*c*) $[Co(CN)_6]^{3-}$ *i.e.*, Co^{3+}



$$Co^{3+} = 3d^6 \text{ (or } t_{2g}^6 e_g)$$

There is no unpaired electron, so it is diamagnetic.

Sample **Problem 18** *Arrange the following complex ion in increasing order of crystal field splitting energy.* (Δ_o).
I. $[Cr(Cl)_6]^{3-}$, *II.* $[Cr(CN)_6]^{3-}$, *III.* $[Cr(NH_3)_6]^{3+}$

[NCERT Exemplar]

(*a*) *I* < *II* < *III* (*b*) *II* < *I* < *III*
(*c*) *III* < *II* < *I* (*d*) *I* < *III* < *II*

Interpret (*d*) CFSE is higher when the complex contains strong field ligand. Thus, crystal field splitting energy increases in the order $[Cr(Cl)_6]^{3-} < [Cr(NH_3)_6]^{3+} < [Cr(CN)_6]^{3-}$.

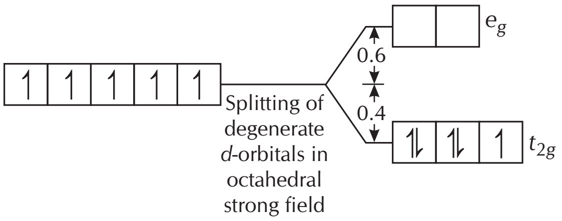
Because the order of field strength is

$$Cl^- < NH_3 < CN^-$$

Sample **Problem 19** *The CFSE for* $[Fe(CN)_6]^{3-}$ *is*

(*a*) −1.2 (*b*) −2.0 (*c*) −1.8 (*d*) +1.2

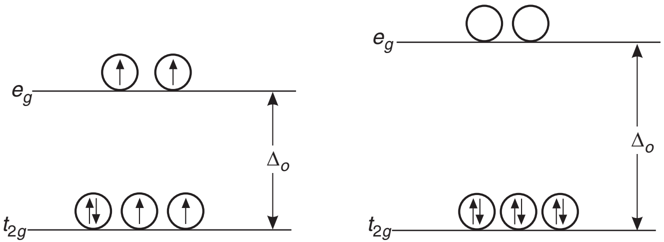
Interpret (*c*) $Fe^{3+} = [Ar]\,3d^5$



$$CFSE = -(0.4 \times t_{2g}e^-) + 0.6 \times e_g\, e^-$$
$$= -(0.4 \times 5) + 0.6 \times 0 = -2.0$$

Magnetic Properties

The diamagnetic (repulsion from applied magnetic field due to paired electrons) and **paramagnetic** (attraction from applied magnetic field due to unpaired electron) behaviour of coordination compounds can be explained on the basis of crystal field theory, *e.g.*, Co (III) shows diamagnetic properties in $[Co(NH_3)_6]^{3+}$ complex and paramagnetic properties in $[CoF_6]^{3-}$ complex. Such a difference in behaviour show that there must be some unpaired electrons in latter while former have all paired electrons (magnetic measurement shows the presence of four unpaired electrons in latter). This can be explained on the basis of crystal field theory if you observe the diagrams given below carefully.



(a) $[CoF_6]^{3-}$ complex (b) $[Co(NH_3)_6]^{3+}$ complex

Fig. 9.6 In fig. (a) as Δ_o is small, the energy required to pair up the 4th and 5th electron with the electrons in lower *d*-orbitals (t_{2g}) is higher as compared to that required to place the electron in higher *d*-orbital (e_g).
In fig. (b) as Δ_o is higher, the energy required to pair up the 4th and 5th electron with the electrons in lower *d*-orbitals (t_{2g}) is lower as compared to that required to place the electron in higher *d*-orbitals (e_g).

Magnetic moment (μ) is related to number of unpaired electrons '*n*' as, μ $\mu = \sqrt{n(n+2)}$ BM

Caution Point *The values of n calculated by applying the above formula for different magnetic moments are given in the following table :*

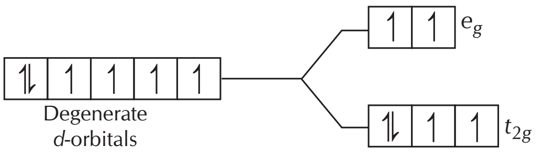
Magnetic moment (BM)	Number of unpaired electrons
1.73	1
2.83	2
3.87	3
4.90	4
5.92	5

Sample **Problem 20** *The magnetic moment of* $[CoF_6^{3-}]$ *by using CFT is*

[NCERT Exemplar]

(*a*) 0 (*b*) 4.9 (*c*) 5.9 (*d*) 1.73

Interpret (*b*) $[CoF_6]^{3-}$ *i.e.*, Co^{3+}



$$\text{Configuration of } Co^{3+} = 3d^6 \text{ (or } t_{2g}^4 e_g^2)$$

Number of unpaired electrons $(n) = 4$

$$\text{Magnetic moment } (\mu) = \sqrt{n(n+2)} = \sqrt{4\,(4+2)}$$
$$= \sqrt{24} = 4.9 \text{ BM}$$

Colour of the Complexes

A substance appears coloured because it absorbs light at specific wavelengths in the visible part of the electromagnetic spectrum (400 to 700 nm) and transmits or reflects the rest of the wavelength. Each wavelength of visible light represents a different colour. White light, such as sunlight, is a combination of all colours; an object that absorbs all visible light appears black.

When the energy of the photon ($h\nu$) is equal to the difference between the lower and higher *d*-orbital energy levels, an electtron is promoted from a lower to higher level. If the wavelength of the photon absorbed by an ion lies outside the visible region, then the transmitted light looks the same as the incident light white and the ion appears colourless.

The coloured nature of solutions of coordination compounds can also be explained on the basis of crystal field theory, because in coordination compounds the energy difference between two sets of *d*-orbitals is usually small (as explained by crystal field splitting) thus, excitation of an electron from lower energy to higher energy is very easy and can be achieved even by the absorption of low energy radiations of visible region. As a result of the absorption of such selected wavelengths of visible light, the complexes appeared coloured. Relationship between the λ of light absorbed and the colour observed can be examplified as

Table 9.9 **Wavelength Associated with Different Colours**

Coordination entity	Wavelength of light absorbed (nm)	Colour of light absorbed	Colour of coordination entity
$[CoCl(NH_3)_5]^{2+}$	535	Yellow	Violet
$[Co(NH_3)_5(H_2O)]^{3+}$	500	Blue green	Red
$[Co(NH_3)_6]^{3+}$	475	Blue	Yellow orange
$[Co(CN)_6]^{3-}$	310	Ultraviolet	Pale yellow
$[Cu(H_2O)_4]^{2+}$	600	Red	Blue
$[Ti(H_2O)_6]^{3+}$	498	Blue green	Purple

It is important to note that in the absence of ligand, crystal field splitting does not occur and hence, the substance is colourless. For example, removal of water from $[Ti(H_2O)_6]Cl_3$ on heating renders it colourless. Similarly, anhydrous $CuSO_4$ is white, but $CuSO_4 \cdot 5H_2O$ is blue in colour.

Sample **Problem 21** *The colour of the coordination compounds depends on the crystal field splitting. What will be the correct order of absorption of wavelength of light in the visible region, for the complexes,* $[Co(NH_3)_6]^{3+}$, $[Co(CN)_6]^{3-}$, $[Co(H_2O)_6]^{3+}$? **[NCERT Exemplar]**

(a) $[Co(CN)_6]^{3-} > [Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+}$

(b) $[Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+} > [Co(CN)_6]^{3-}$

(c) $[Co(H_2O)_6]^{3+} > [Co(NH_3)_6]^{3+} > [Co(CN)_6]^{3-}$

(d) $[Co(CN)_6]^{3-} > [Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+}$

Interpret (c) CFSE (Crystal field stabilisation energy) depends upon the strength of ligands.

Since, the order of splitting tendency of different ligands is as

$$H_2O < NH_3 < CN^-$$

Hence, the order of CFSE of different complexes is

$$[Co(H_2O)_6]^{3+} < [Co(NH_3)_6]^{3+} < [Co(CN)_6]^{3-}$$

Since, $$\text{Energy} \propto \frac{1}{\text{wavelength } (\lambda)}$$

$\therefore$ The order of absorption of wavelength is

$$[Co(H_2O)_6]^{3+} > [Co(NH_3)_6]^{3+} > [Co(CN)_6]^{3-}$$

Limitations of CFT

The crystal field theory can explain the spectra of the metal ions and complexes on the assumption that these arise from the transition of electrons from lower energy *d*-orbitals to higher energy *d*-orbitals. However, the position and intensities of spectral bands calculated on the basis of crystal field theory do not always coincide with those determined experimentally.

Apart from this, a pure electrostatic interaction between central metal ion and ligand fails to explain the relative positions of ligands in spectrochemical series. Along with this there is clear evidence that covalent bonding too makes a significant contribution towards the metal ligand bonding.

In the light of above written facts the crystal field theory was modified so as to include the contribution of covalent bonding in the metal ligand bond and is called **ligand field theory,** which assumes that the extent of covalent character in metal ligand bond is generally low as compared to the extent of the ionic character of the bond that means the conclusions arrived by the crystal field theory are still valid to a larger extent.

9.7 Stability of Complexes

The stability of a complex in solution is infact the degree of association between the two species involved in the state of equilibrium. The magnitude of the (stability or formation) equilibrium constant for the association, quantitatively expresses the stability. Thus, if we have a reaction of the type :

$$M + 4L \rightleftharpoons ML_4$$

then the *larger the stability constant K, the higher the proportion of* ML_4 *that exists in solution.* Alternatively $1/K$ values, called the **instability constant,** explain the dissociation of the complex into metal ion and ligands in the solution.

A coordination compound is formed in solution by the stepwise addition of ligands to a metal ion. Thus, the formation of the complex, ML_n (M = central metal cation, L = monodentate ligand and n = coordination number of metal ion) may be supposed to take place by the following n consecutive steps.

$$M + L \rightleftharpoons ML$$

$$K_1 = \frac{[ML]}{[M][L]}$$

$$ML + L \rightleftharpoons ML_2$$

$$K_2 = \frac{[ML_2]}{[M][L]}$$

$$ML_2 + L \rightleftharpoons ML_3$$

$$K_3 = \frac{[ML_3]}{[ML_2][L]}$$

$$\dots\ \dots\ \dots\ \dots\ \dots\ \dots\ \dots$$

$$\dots\ \dots\ \dots\ \dots\ \dots\ \dots\ \dots$$

$$ML_{n-1} + L \rightleftharpoons ML_n$$

$$K_n = \frac{[ML_n]}{[ML_{n-1}][L]}$$

$K_1, K_2, K_3, \dots, K_n$ are called stepwise stability constants. With a few exceptions, the values of successive stability constants decrease regularly from K_1 to K_n.

Alternatively, we can write the **overall stability constant** thus

$$M + 4L \rightleftharpoons ML_4$$

$$\beta_4 = \frac{[ML_4]}{[M][L]^4}$$

The stepwise and overall stability constant are therefore related as follows

$\beta_4 = K_1 \times K_2 \times K_3 \times K_4$ or more generally,

$\beta_i = K_1 \times K_2 \dots \times K_i$

Factors Affecting Stability of Complexes

The strength of a complex ion depends upon the following factors

(i) **Higher charge** of the central metal ion *i.e.,* greater ionic potential $\left(\frac{\text{ionic charge}}{\text{ionic radius}}\right)$ and greater is the stability.

(ii) **Greater base strength** of the ligand, greater will be the stability.

(iii) **Ring formation** (chelation) in structure of the complexes is the chief factor, which **increases** the stability of the complexes in solution.

(iv) If a multidentate ligand happens to be cyclic without any steric effects, a further increase in stability occurs. This is called **macrocyclic effect.**

Sample **Problem 22** *Which of the following complexes formed by* Cu^{2+} *ions is most stable?* **[NCERT Exemplar]**

(*a*) $Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$, $\log K = 11.6$

(*b*) $Cu^{2+} + 4CN \rightleftharpoons [Cu(CN)_4]^{2-}$, $\log K = 27.3$

(*c*) $Cu^{2+} + 2en \rightleftharpoons [Cu(en)_2]^{2+}$, $\log K = 15.4$

(*d*) $Cu^{2+} + 4H_2O \rightleftharpoons [Cu(H_2O)_4]^{2+}$, $\log K = 8.9$

Interpret (*b*) Stability of complexes depends upon stability constant. Higher the value of *K*, more stable is the complex. Since, *K* is highest when log *K* is 27.3.

Thus, $[Cu(CN)_4]^{2-}$ is the most stable complex among the given.

9.8 Importance of Coordination Compounds

Some important applications of coordination compounds are as follows

1. In Qualitative and Quantitative Analysis

(i) Nickel is detected and estimated as its red dimethyl glyoxime complex which is a chelate complex.

(ii) Mg and Al are estimated as complexes of 8-hydro-oxyquinoline (oxime).

(iii) The separation of Ag^+ from Hg_2^{2+} in the first group of analysis is based on the fact that while, silver chloride is soluble in aqueous ammonia, Hg_2Cl_2 forms a black insoluble material.

$$AgCl + 2NH_4OH \longrightarrow \underset{\text{soluble}}{[Ag(NH_3)_2]Cl} + 2H_2O$$

$$Hg_2Cl_2 + NH_4OH \longrightarrow \underset{\text{(black insoluble)}}{Hg(NH_2)Cl} + Hg + HCl + H_2O$$

(iv) The separation of IIB group sulphides from IIA group sulphides is based on the fact that sulphides of IIB group form, complex sulphides with yellow ammonium sulphide which are soluble while, sulphides of IIA group do not react.

$$As_2S_5 + 3(NH_4)_2S \longrightarrow 2(NH_4)_3[AsS_4]$$
$$Sb_2S_5 + 3(NH_4)_2S \longrightarrow 2(NH_4)_3[SbS_4]$$
$$SnS_2 + (NH_4)_2S \longrightarrow (NH_4)_2[SnS_3]$$

(v) The detection of Cu^{2+} is based on the formation of a blue tetra-ammine copper sulphate complex, which gives a deep blue coloured solution upon addition of NH_3 to Cu^{2+} ions.

$$CuSO_4 + 4NH_3 \longrightarrow [Cu(NH_3)_4]SO_4$$

It also forms a chocolate coloured precipitate with potassium ferrocyanide.

$$2CuSO_4 + K_4Fe(CN)_6 \longrightarrow \underset{\text{chocolate ppt.}}{Cu[Fe(CN)_6]} + 2K_2SO_4$$

(vi) Fe^{3+} is detected by formation of a blood red coloured complex with KSCN.

$$Fe^{3+} + KSCN \longrightarrow \underset{\substack{\text{blood red}\\\text{colour}}}{[Fe(SCN)]^{2+}} + K^+$$

(vii) S^{2-} is detected by the formation of a violet-coloured complex with sodium nitroprusside.

$$Na_2S + \underset{\substack{\text{sodium}\\\text{nitroprusside}}}{Na_2[Fe(CN)_5NO]} \longrightarrow \underset{\text{violet colour}}{Na_4[Fe(CN)_5NOS]}$$

(viii) EDTA is used in the complexometric determination of several metal ions such as Ca^{2+}, Zn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, etc.

2. In the Extraction of Metals

The formation of complex compounds is used in the extraction of some metals *e.g.,* Ag and Au are extracted as follows

$$2K[Ag(CN)_2] + Zn \longrightarrow K_2[Zn(CN)_4] + \underset{\text{silver}}{2Ag}$$

It is due to more electropositive nature of Zn as compared to Ag and Au.

Nickel tetracarbonyl complex is used for the extraction and purification of nickel.

$$\underset{\substack{\text{(associated with}\\\text{other elements)}}}{Ni} + 4\,CO \longrightarrow [Ni(CO)_4] \xrightarrow{\text{Heating}} Ni + 4CO$$

3. In Biological World

Cyclic ligands impart extra stability to coordinate compounds. Thus, Mg in chlorophyll and iron in haemoglobin are stable towards dissociation due to the formation of coordination compounds. Haemoglobin of the blood gets oxygenated through the binding of dioxygen, O_2 to the ferrous ions in haemoglobin.

4. Role of Coordination Compounds in Medicinal Chemistry

(i) The platinum complex *cis*-$[Pt(NH_3)_2Cl_2]$ (*cis*-platin) is used in the treatment of cancer.

(ii) EDTA complex of calcium is used in the treatment of lead poisoning. Ca-EDTA is a weak complex, when it is administered, calcium in the complex is replaced by the lead present in the body and is eliminated in the urine.

(iii) The excess of copper and iron present in animal system are removed by the chelating ligands *D*-penicillamine and desferroxime *B via* the formation of complexes.

5. In Estimation of Hardness of Water

EDTA is a hexadentate ligand and forms complex with various metal ions. This is used in the estimation of hardness of water by a volumetric method. Hardness of water is due to Ca^{2+} and Mg^{2+} ions. Since, stability constant values of EDTA complex with Ca^{2+} and Mg^{2+} are 10^7 and 10^8 respectively, it helps in selective estimation of different ions.

6. In Electroplating of Metals

Coordination compounds are used in **electroplating industry** *e.g.,* gold and silver are electroplated from their coordination compounds, such as $K[Ag(CN)_2]$ or $K[Au(CN)_4]$.

7. As Catalysts

A coordination complex of Ti and Al is used as a catalyst to convert ethylene and propylene into polyethene. *Ziegler-Natta* catalyst is $TiCl_4 + (C_2H_5)_3Al$ or $(CH_3)_3Al$.

8. In Pigments

Many pigments such as phthalocyanines used in paints are the coordination compounds.

Check Point 3

1. The hexaaqua complex $[Ni(H_2O)_6]^{2+}$ is green whereas, the corresponding ammonia complex $[Ni(NH_3)_6]^{2+}$ is violet. Explain.
2. Explain $[CoF_6]^{3-}$ is paramagnetic but $[Co(CN)_6]^{3-}$ is diamagentic.
3. Why is ligand field theory also called crystal field theory?
4. All the octahedral complexes of Ni^{2+} must be outer orbital complexes. Explain, why?

WORKED **OUT**
Examples

Example 1 *Which of the following complexes do not follow EAN rule?*

(a) $[Fe(CN)_6]^{4-}$ (b) $[Fe(CN)_6]^{3-}$

(c) $Ni(CO)_4$ (d) $[PdCl_4]^{2-}$

Solution (b) According to Sidgwick,

EAN = atomic number of nearest noble gas

In case of $[Fe(CN)_6]^{3-}$,

$$\begin{aligned}\text{EAN} &= 26 - 3 + 2 \times 6\\ &= 35\end{aligned}$$

While, the atomic number of nearest noble gas is 36. Thus, it does not follow EAN rule.

Example 2 *An aqueous solution of titanium chloride, when subjected to magnetic measurement, measured zero magnetic moment. The formula of the complex assuming it to be octahedral in aqueous solution is*

(a) $[Ti(H_2O)_6]Cl_4$ (b) $[Ti(H_2O)_6]Cl_3$

(c) $[Ti(H_2O)_5Cl]Cl_2$ (d) $[Ti(H_2O)_6]Cl$

Solution (a) $Ti_{22} = [Ar]\,3d^2 4s^2$

Since, its magnetic moment is zero, it is present in the form of Ti^{4+}. Thus, the formula of the complex is $[Ti(H_2O)_6]Cl_4$ as only in it the oxidation state of Ti is +4.

Example 3 *A metal complex having composition* $Cr(NH_3)_4Cl_2Br$ *has been isolated in two forms A and B. A reacts with* $AgNO_3$ *producing a white precipitate which was soluble in dilute ammonia solution. B reacts with* $AgNO_3$ *producing a pale yellow precipitate soluble in concentrated ammonia solution. The formulae of A and B are respectively*

(a) $[Cr(NH_3)_4Br]Cl_2$; $[Cr(NH_3)Cl_2]Br$

(b) $[Cr(NH_3)_4BrCl]Cl$; $[Cr(NH_3)_3Cl_2Br]NH_3$

(c) $[Cr(NH_3)_4Cl_2]Br$; $[Cr(NH_3)_4BrCl]Cl$

(d) $[Cr(NH_3)_4BrCl]Cl$; $[Cr(NH_3)_4Cl_2]Br$

Solution (d) Since, the compound *A* gives white precipitate with $AgNO_3$, which is soluble in dilute ammonia solution, it contains at least one Cl atom outside the coordination sphere. Thus, its formula is $[Cr(NH_3)_4BrCl]Cl$.

$$[Cr(NH_3)_4BrCl]Cl \longrightarrow [Cr(NH_3)_4BrCl]^+ + Cl^-$$

$$AgNO_3 + Cl^- \longrightarrow \underset{\text{white ppt}}{AgCl} + NO_3^-$$

Similarly, compound *B* gives a yellow precipitate which is soluble in concentrated ammonia solution, it contains a Br atom outside the sphere. Thus, its formula must be $[Cr(NH_3)_4Cl_2]Br$.

$$[Cr(NH_3)_4Cl_2]Br \longrightarrow [Cr(NH_3)_4Cl_2]^+ + Br^-$$

$$Br^- + AgNO_3 \longrightarrow \underset{\substack{\text{pale yellow}\\ \text{ppt}}}{AgBr} + NO_3^-$$

Example 4 *The complex ion which has no d-electrons in the central metal atom is*

(a) $[MnO_4]^-$ (b) $[Co(NH_3)_6]^{3+}$

(c) $[Fe(CN)_6]^{3-}$ (d) $[Cr(H_2O)_6]^{3+}$

Solution (a) In $[MnO_4]^-$, the oxidation state of Mn is +7.

$$Mn\,(25) = [Ar]\,3d^5 4s^2$$

$$Mn^{7+} = [Ar]$$

Thus, in $[MnO_4]^-$ no *d*-electron is present.

Example 5 *Amongst the following, the lowest degree of paramagnetism per mole of the compound at 298 K will be shown by*

(a) $MnSO_4 \cdot 4H_2O$ (b) $NiSO_4 \cdot 6H_2O$

(c) $FeSO_4 \cdot 6H_2O$ (d) $CuSO_4 \cdot 5H_2O$

Solution (d) In $MnSO_4 \cdot 4H_2O$, Mn is present as Mn^{2+}.

$$Mn^{2+} = \overset{3d^5}{\begin{array}{|c|c|c|c|c|}\hline \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\ \hline\end{array}}\quad \overset{4s^0}{\begin{array}{|c|}\hline \\ \hline\end{array}}\quad \text{(unpaired electrons = 5)}$$

In $CuSO_4 \cdot 5H_2O$, Cu is present as Cu^{2+}.

$$Cu^{2+} = \overset{3d^9}{\begin{array}{|c|c|c|c|c|}\hline \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow \\ \hline\end{array}}\quad \overset{4s^0}{\begin{array}{|c|}\hline \\ \hline\end{array}}\quad \text{(unpaired electron = 1)}$$

In $FeSO_4 \cdot 6H_2O$, Fe is present as Fe^{2+}

$$Fe^{2+} = \overset{3d^6}{\begin{array}{|c|c|c|c|c|}\hline \uparrow\downarrow & \uparrow & \uparrow & \uparrow & \uparrow \\ \hline\end{array}}\quad \overset{4s^0}{\begin{array}{|c|}\hline \\ \hline\end{array}}\quad \text{(unpaired electrons = 4)}$$

In $NiSO_4 \cdot 6H_2O$, Ni is present as Ni^{2+}

$$Ni^{2+} = \overset{3d^8}{\begin{array}{|c|c|c|c|c|}\hline \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow & \uparrow \\ \hline\end{array}}\quad \overset{4s^0}{\begin{array}{|c|}\hline \\ \hline\end{array}}\quad \text{(unpaired electrons = 2)}$$

Since, paramagnetic character $\propto$ unpaired electrons.

Thus, $CuSO_4 \cdot 5H_2O$ has the lowest degree of paramagnetism among the given at 298 K.

Example 6 *Which of the following compounds has same oxidation state of the central metal atom in the cationic and anionic part?*

(*a*) $[Pt(NH_3)_4][PtCl_6]$ (*b*) $[Pt(py)_4][PtCl_4]$

(*c*) $[Pt(NH_3)_4Cl_2][PtCl_4]$ (*d*) $K_4[Ni(CN)_6]$

Solution (*b*) $[Pt(py)_4][PtCl_4]$

Let the oxidation state of Pt is *x*.

$$x + 0 \times 4 + x + (-1) \times 4 = 0$$
$$2x = 4$$
$$x = +2$$

Thus, it is the complex in which the central metals atom in cationic and anionic parts have same oxidation state.

Example 7 *The most stable ion is*

(*a*) $[Fe(OH)_5]^{3-}$ (*b*) $[FeCl_6]^{3-}$

(*c*) $[Fe(CN)_6]^{3-}$ (*d*) $[Fe(H_2O)_6]^{3+}$

Solution (*c*) Stability of complex increases with increase in charge on the central metal ion and with increase in basic strength of ligand.

In $[Fe(CN)_6]^{3-}$, oxidation state of Fe is $+3$ and basicity of CN^- is higher than that of OH^-, Cl^- and H_2O. Thus, $[Fe(CN)_6]^{3-}$ is the most stable ion among the given.

Example 8 *The pair in which both species have same magnetic moment (spin only value) is*

(*a*) $[Cr(H_2O)_6]^{2+}, [CoCl_4]^{2-}$

(*b*) $[Cr(H_2O)_6]^{2+}, [Fe(H_2O)_6]^{2+}$

(*c*) $[Mn(H_2O)_6]^{2+}, [Cr(H_2O)_6]^{2+}$

(*d*) $[CoCl_4]^{2-}, [Fe(H_2O)_6]^{2+}$

Solution (*b*) Species having the same number of unpaired electrons, have same magnetic moment because magnetic moment is related with number of unpaired electrons (*n*) as, $\mu = \sqrt{n(n+2)}$

$Cr^{2+} = [Ar]\,3d^4$ (4 unpaired electrons)

$Co^{2+} = [Ar]\,3d^7$ (3 unpaired electrons)

$Mn^{2+} = [Ar]\,3d^5$ (5 unpaired electrons)

$Fe^{2+} = [Ar]\,3d^6$ (4 unpaired electrons)

Thus, $[Cr(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{2+}$ have same magnetic moment.

Example 9 *Identify the complexes which is expected to be coloured.*

(*a*) $[Ti(NO_3)_4]$ (*b*) $[Cu(NCCH_3)]^+BF_4$

(*c*) $[Fe(CN)_6]^{4-}$ (*d*) $K_3[VF_6]$

Solution (*d*) (a) In $[Ti(NO_3)_4]$, ON of Ti is $+4$.

Hence, in Ti(IV) $(1s^2, 2s^2, 2p^6, 3s^2, 3p^6)$ incomplete *d*-orbital is not present, so it is colourless.

(b) In $[Cu(NCCH_3)]^+ BF_4^-$, ON of Cu is $+1$.

Hence, in Cu(I) $[1s^2, 2s^2 2p^6, 3s^2, 3p^6, 3d^{10}]$ incomplete *d*-orbital is not present, so it is also colourless.

(c) In $[Fe(CN)_6]^{4-}$, ON of Fe is $+2$.

Hence, Fe(II) $[1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6]$ But CN^-, being a strong field ligand, causes pairing, thus no unpaired electron is present in *d*-orbital. Hence, it is also colourless.

(d) In $K_3[VF_6]$, ON of V is $+3$.

Hence, V(III) $(1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^2)$ incomplete *d*-orbitals are present, so it is coloured.

Example 10 *A solution made by dissolving* 0.875 g *of compound* $Co(NH_3)_4Cl_3$ *in* 25 g *of water freezes at* $-0.56°C$. *The structural formula of the complex, if cryoscopic constant of water is* 1.86 *K kg mol*$^{-1}$, *is*

(*a*) $[Co(NH_3)_4]Cl_3$ (*b*) $[Co(NH_3)_4Cl]Cl_2$

(*c*) $[Co(NH_3)_4Cl_2]Cl$ (*d*) $[Co(NH_3)_3Cl_3]NH_3$

Solution (*c*) $-\Delta T_f = 0.56 = i \times 1.86 \times \dfrac{0.875}{233.5} \times \dfrac{1000}{25}$

$[\because \ \Delta T_f = i\,k_f \cdot m]$

$\therefore \quad i = 2$

Hence, the formula of the complex ion is $[Co(NH_3)_4Cl_2]Cl$.

[For details see chapter 2 'solutions']

Start **Practice** *for* JEE Main

Round I (Topically Divided Problems)

General Terms Related to Coordination Compounds

1. Potassium ferrocyanide is a

(a) complex salt (b) double salt
(c) normal salt (d) mixed salt

2. In the compound lithium tetrahydroaluminate, the ligand is

(a) H (b) H^+
(c) H^- (d) None of these

3. A chelating agent has two or more than two donor atoms to bind to a single metal ion. Which of the following is not a chelating agent? **[NCERT Exemplar]**

(a) Thiosulphato
(b) Oxalato
(c) Glycinato
(d) Ethane-1,2-diamine

4. Which of the following species is not excepted to be a ligand? **[NCERT Exemplar]**

(a) NO (b) NH_4^+
(c) $NH_2CH_2CH_2NH_2$ (d) CO

5. The oxidation number of cobalt in $K[Co(CO)_4]$ is **[NCERT]**

(a) +1 (b) +3
(c) −1 (d) −3

6. The coordination number of Pt in $[Pt(NH_3)_4Cl_2]^{2+}$ ion is

(a) 2 (b) 4
(c) 6 (d) 8

7. EDTA has coordination number

(a) 3 (b) 4 (c) 5 (d) 6

8. The effective atomic number of cobalt in the complex $[Co(NH_3)_6]^{3+}$ is

(a) 36 (b) 24
(c) 33 (d) 30

9. The pair of the compounds in which both the metals are in the higher possible oxidation state is

(a) CrO_2Cl_2, MnO_4^- (b) $[Co(CN)_6]^{3-}, MnO_3$
(c) TiO_3, MnO_2 (d) $[Fe(CN)_6]^{3-}, [Co(CN)_6]^{3-}$

10. Given the molecular formula of the hexa coordinated complexes (*A*) $CoCl_3 \cdot 6NH_3$ (*B*) $CoCl_3 \cdot 5NH_3$ (*C*) $CoCl_3 \cdot 4NH_3$. If the number of coordinated NH_3 molecules in *A*, *B*, and *C* respectively are 6, 5 and 4, primary valency in (*A*), (*B*) and (*C*) are

(a) 0, 1, 2 (b) 3, 2, 1
(c) 6, 5, 4 (d) 3, 3, 3

11. In the complex $K_2Fe[Fe(CN)_6]$

(a) the complex is high spin complex
(b) both Fe atoms are in the same oxidation state
(c) the coordination number of iron is 4
(d) both Fe atoms are in different oxidation state

12. Complex salt can be made by the combination of $[Co^{III}(NH_3)_5Cl]^x$ with

(a) Cl^- (b) $2Cl^-$
(c) PO_4^{3-} (d) $2K^+$

13. How many ions are produced, from the complex, $Co(NH_3)_6Cl_2$ in solution? **[NCERT]**

(a) 6 (b) 4 (c) 3 (d) 2

14. What is the coordination entity formed when excess of aqueous KCN is added to an aqueous solution of copper sulphate? **[NCERT]**

(a) CuCN (b) $K_3[Cu(CN)_6]$
(c) $K[Cu(CN)_4]$ (d) $K_2[Cu(CN)_4]$

15. When 1 mole of $CrCl_3 \cdot 6H_2O$ is treated with excess of $AgNO_3$, 3 moles of AgCl are obtained. The formula of the complex is **[NCERT Exemplar]**

(a) $[CrCl_3(H_2O)_3] \cdot 3H_2O$ (b) $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$
(c) $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$ (d) $[Cr(H_2O)_6]Cl_3$

16. Which of the following ions forms most stable complex compound?
(a) Fe^{3+} (b) Mn^{2+}
(c) Ni^{2+} (d) Cu^{2+}

17. Ammonia forms the complex ion $[Cu(NH_3)_4]^{2+}$ with copper ions in alkaline solution but not in acidic solution. What is the reason for it?
(a) In acidic solutions, hydration protects copper ions.
(b) In alkaline solution, insoluble $Cu(OH)_2$ is precipitated.
(c) Copper hydroxide is an amphoteric substance
(d) In acidic solutions, protons coordinate with ammonia molecules forming NH_4^+ ions and NH_3 molecules are not available

18. Amongst the following, the most stable complex is **[NCERT]**
(a) $[Fe(H_2O)_6]^{3+}$ (b) $Fe(NH_3)_6]^{3+}$
(c) $[Fe(C_2O_4)_3]^{3-}$ (d) $[FeCl_6]^{3-}$

Nomenclature of Coordination Compounds

19. The correct IUPAC name of $[Pt(NH_3)_2Cl_2]$ is **[NCERT Exemplar]**
(a) diamminedichloridoplatinum (II)
(b) diamminedichloridoplatinum (IV)
(c) diamminedichloridoplatinum (0)
(d) dichloridodiammineplatinum (IV)

20. IUPAC name of $[Pt(NH_3)_2Cl(NO_2)]$ is **[NCERT Exemplar]**
(a) platinum diaminechloronitrite
(b) chloronitrito-N-ammineplatinum (II)
(c) diamminechloridonitrito-N-platinum (II)
(d) diamminechloronitrito-N-platinate (II)

21. The IUPAC name of the coordination compound $K_2[Zn(OH)_4]$ is
(a) potassium tetrahydroxozinc (II)
(b) dipotassium tetrahydroxo zinc (II)
(c) potassium tetrahydroxozincate (II)
(d) potassium tetrahydroxozincate (III)

22. Pick the correct name of $[Co(NH_3)_5Cl]Cl_2$.
(a) chloropentamminecobalt (III) chloride
(b) chloropentamminecobalt (III)
(c) chloropentamminecobalt (II) chloride
(d) pentamminechloridocobalt (III) chloride

23. The IUPAC name of $K_2[Cr(CN)_2O_2(O)_2(NH_3)]$ is
(a) potassium amminedicyanodioxoperoxochromate (VI)
(b) potassium amminecyanoperoxodioxochromatic (IV)
(c) potassium amminecyanoperoxodioxochromium (IV)
(d) potassium amminecyanoperoxodioxochromium (IV)

24. The correct name of $[Pt(NH_3)_4Cl_2][PtCl_4]$ is
(a) tetrachloridoplatinum (II) dichloridotetrammine platinate
(b) dichloridotetrammineplatinum (IV) tetrachlorido platinate (II)
(c) tetramminedichloridoplatinum (IV) tetrachlorido platinate (II)
(d) tetrachloridoplatinum (II) tetrammineplatinate (IV)

25. The IUPAC name of $[Ni(NH_3)_4][NiCl_4]$ is
(a) tetrachloridonickel (II) tetraamminenickel (II)
(b) tetraamminenickel (II) tetrachloridonickel (II)
(c) tetraamminenickel (II) tetrachloridonickelate (II)
(d) tetrachloridonickel (II) tetraamminenickel (0)

Isomerism in Coordination Compounds

26. The compounds $[Co(SO_4)(NH_3)_5]Br$ and $[Co(SO_4)(NH_3)_5]Cl$ represent **[NCERT Exemplar]**
(a) linkage isomerism
(b) ionisation isomerism
(c) coordination isomerism
(d) no isomerism

27. The complexes $[Co(NH_3)_6][Cr(C_2O_4)_3]$ and $[Cr(NH_3)_6][Co(C_2O_4)_3]$ exhibit
(a) geometrical isomerism
(b) ionisation energy
(c) coordination isomerism
(d) linkage isomerism

28. Which of the following cannot show linkage isomerism?
(a) NO_2^- (b) NH_3
(c) CN^- (d) SCN^-

29. Due to the presence of ambidentate ligands coordination compounds show isomerism. Palladium complexes of the type $[Pd(C_6H_5)_2(SCN)_2]$ and $[Pd(C_6H_5)_2(NCS)_2]$ are **[NCERT Exemplar]**
(a) linkage isomers (b) coordination isomers
(c) ionisation isomers (d) geometrical isomers

30. What kind of isomerism exists between $[Cr(H_2O)_6]Cl_3$ (violet) and $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ (greyish-green)? **[NCERT Exemplar]**
(a) Linkage isomerism (b) Solvate isomerism
(c) Ionisation isomerism (d) Coordination isomerism

31. Optical isomerism is shown by octahedral complexes
(a) having all monodentate ligands
(b) having all the three bidentate ligands
(c) having two *trans* bidentate ligands
(d) having two *trans* monodentate ligands

32. Which of the following will exhibit optical isomerism?
(a) $[Cr(en)(H_2O)_4]^{3+}$ (b) $[Cr(en)_3]^{3+}$
(c) *trans*-$[Cr(en)_2Cl_2]^+$ (d) $[Cr(NH_3)_6]^{3+}$

33. Which one of the following is expected to exhibit optical isomerism [en = ethylenediamine]?
(a) *Trans*-$[Co(en)_2Cl_2]$
(b) *Cis*-$[Pt(NH_3)_2Cl_2]$
(c) *Cis*-$[Co(en)_2Cl_2]$
(d) *Trans*-$[Pt(NH_3)_2Cl_2]$

34. Indicate the complex ion which shows geometrical isomerism. **[NCERT Exemplar]**
(a) $[Cr(H_2O)_4Cl_2]^+$ (b) $[Pt(NH_3)_3Cl]$
(c) $[Co(NH_3)_6]^{3+}$ (d) $[Co(CN)_5(NCl)]^{3-}$

35. The total number of possible isomers for the complex compound $[Cu(NH_3)_4][PtCl_4]$
(a) 6 (b) 5
(c) 4 (d) 3

36. For square planar complex of platinum (II), $[Pt(NH_3)(Br)(Cl)Py)]^{2+}$, how many isomeric forms are possible?
(a) Two (b) Three
(c) Four (d) Six

37. Among the geometrical isomers of $[Pt(NH_3)(Br)(Cl)(Py)]$ how many will exhibit optical isomers? **[NCERT]**
(a) 0 (b) 1
(c) 2 (d) All

38. A complex of the type $[M(AA)_2X_2]^{n+}$ is known to be optically active. What does this indicate about the structure of the complex? **[NCERT Exemplar]**
(a) It has an octahedral geometry
(b) It is a tetrahedral complex
(c) It is a *trans* complex
(d) None of the above

Bonding in Coordination Compounds

39. Among the following ions, which one has the highest unpaired electrons?
(a) $[Cr(H_2O)_6]^{3+}$ (b) $[Zn(H_2O)_6]^{2+}$
(c) $[Fe(H_2O)_6]^{2+}$ (d) $[Fe(H_2O)_6]^{3+}$

40. $[Pt(NH_3)_4]Cl_2$ is
(a) pyramidal (b) pentagonal
(c) tetrahedral (d) square planar

41. Which one is an example of octahedral complex?
(a) $Cu(NH_3)_4^{2+}$ (b) FeF_6^{3-}
(c) $Zn(NH_3)_4^{2+}$ (d) $Ni(CN)_4^{2-}$

42. The species having tetrahedral shape is
(a) $[NiCl_4]^{2-}$ (b) $[Ni(CN)_4]^{2-}$
(c) $[PdCl_4]^{2-}$ (d) $[Pd(CN)_4]^{2-}$

43. The geometry of $Ni(CO)_4$ and $Ni(PPh_3)_2Cl_2$ are
(a) square planar and tetrahedral respectively
(b) Both tetrahedral
(c) tetrahedral and square planar respectively
(d) Both square planar

44. What is the magnetic moment of $K_3[FeF_6]$?
(a) 3.87 BM (b) 4.89 BM
(c) 5.91 BM (d) 6.92 BM

45. The value of 'spin only' magnetic moment for one of the following configuration is 2.84 BM. The correct one is
(a) d^4 (in weak ligand field)
(b) d^4 (in strong ligand field)
(c) d^3 (in weak as well as in strong field)
(d) d^5(in strong ligand field)

46. Why do compounds having similar geometry have different magnetic moment? **[NCERT Exemplar]**
(a) Due to different reactivity
(b) Due to their labile nature
(c) Due to the presence of weak and strong field ligands
(d) None of the above

47. $CuSO_4 \cdot 5H_2O$ is blue in colour while $CuSO_4$ is colourless why? **[NCERT Exemplar]**
(a) Because H_2O is a strong field ligand than SO_4^{2-}
(b) Because SO_4^{2-} is a strong field ligand
(c) Because $CuSO_4$ is not a complex
(d) Because no *d-d* transition is possible in $CuSO_4$

48. Among $[Fe(H_2O)_6]^{3+}$, $[Fe(CN)_6]^{3-}$, $[Fe(Cl)_6]^{3-}$ species, the hybridisation state of the Fe atom are, respectively.
(a) d^2sp^3, d^2sp^3, sp^3d^2
(b) sp^3d^2, d^2sp^3, d^2sp^3
(c) sp^3d^2, d^2sp^3, sp^3d^2
(d) None of the above

49. Amongst $Ni(CO)_4$, $[Ni(CN)_4]^{2-}$ and $[NiCl_4]^{2-}$
(a) $Ni(CO)_4$ is diamagnetic, $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ are paramagnetic
(b) $Ni(CO)_4$ and $[NiCl_4]^{2-}$ are diamagnetic and $[Ni(CN)_4]^{2-}$ is paramagnetic
(c) $Ni(CO)_4$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $[NiCl_4]^{2-}$ is paramagnetic
(d) $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $Ni(CO)_4$ is paramagnetic

50. $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ are of different colours in dilute solutions. This is because of **[NCERT]**

(a) difference in the nature of ligands
(b) the presence of unpaired electrons
(c) the *d-d* transition
(d) All of the above

51. On the basis of VBT, find which is an inner orbital complex with 0 magnetic moment? **[NCERT Exemplar]**

(a) $[Mn(CN)_6]^{3-}$
(b) $[Co(NH_3)_6]^{3+}$
(c) $[Cr(H_2O)_6]^{3+}$
(d) $[FeCl_6]^{4-}$

52. The low spin tetrahedral complexes are not formed because

(a) $\Delta_t > P$
(b) $\Delta_t < P$
(c) $\Delta_t \geq P$
(d) $\Delta_t > \Delta_0$

53. The correct order for the wavelengths of absorption in the visible region for the following is
I. $[Ni(NO_2)_6]^{4-}$ II. $[Ni(NH_3)_6]^{2+}$ III. $[Ni(H_2O)_6]^{2+}$ **[NCERT]**

(a) I > II > III
(b) II > I > III
(c) III > II > I
(d) III > I > II

54. Calculate the overall complex dissociation equilibrium constant for the $Cu(NH_3)_4^{2+}$ ions, given that β_4 for this complex is 2.1×10^{13}.

(a) 8.27×10^{-13}
(b) 4.7×10^{-14}
(c) 2.39×10^{-7}
(d) 1.83×10^{14}

55. Which of the following pair is not correctly matched?

(a) Absorption peak for $[Cr^{III}(NH_3)_6]^{3+} = 21680\ cm^{-1}$
(b) Effective atomic no. of Pt in $[PtCl_6]^{2-} = 84$
(c) Crystal field stabilisation energy of d^2 in weak ligand field $= (-)0.8\ \Delta_o$
(d) Example of weak ligand field for d^5 configuration $= [Mn^{II}F_6]^{4-}$

Applications of Coordination Compounds

56. Coordination compounds have great importance in biological systems. In this context which of the following statements is incorrect?

(a) Haemoglobin is the red pigment of blood and contains iron
(b) Cyanocobalamin is B_{12} and contains cobalt
(c) Chlorophylls are green pigments in plants and contains calcium
(d) Carboxypeptidase-A, an enzyme, contains zinc

57. The complex used as an anticancer agent is

(a) *cis*-$[PtCl_2(NH_3)_2]$
(b) Na_2CO_3
(c) *trans*-$[Co(NH_3)_3Cl_3]$
(d) *cis*-$K_2[PtCl_2Br_2]$

58. Dimethyl glyoxime gives a red precipitate with Ni^{2+} which is used for its detection. To get this precipitate readily, the best pH range is

(a) < 1
(b) 3–4
(c) 9–11
(d) 2–3

59. When EDTA solution is added to Mg^{2+} ion solution, then which of the following statements is not true?

(a) Four coordinate sites of Mg^{2+} are occupied by EDTA and remaining two sites are occupied by water molecules
(b) All six coordinate sites of Mg^{2+} are occupied
(c) pH of the solution is decreased
(d) Colourless $[Mg\text{-}EDTA]^{2-}$ chelate is formed

Round II (Mixed Bag)

Only One Correct Option

1. The coordination number and oxidation state of Cr in $K_3[Cr(C_2O_4)_3]$ are respectively

(a) +6 and +3
(b) 3 and 0
(c) 4 and +2
(d) 3 and +3

2. The oxidation state of Fe in the brown ring complex $[Fe(H_2O)_5NO]SO_4$ is

(a) +3
(b) 0
(c) +2
(d) +1

3. Which of the following statements is correct?

(a) In $K_3[Fe(CN)_6]$, the ligand has satisfied both primary and secondary valencies of ferric ion.
(b) In $[Cu(NH_3)_4]SO_4$, the ligand has satisfied only the secondary valency of copper.
(c) In $K_3[Fe(CN)_6]$, the ligand has satisfied only the secondary valency of ferric ion.
(d) Both (b) and (c)

4. According to IUPAC nomenclature sodium nitroprusside is named as

(a) sodium pentacyanonitrosylferrate (II)
(b) sodium pentacyanonitrosylferrate (III)
(c) sodium nitroferricyanide
(d) sodium nitroferrocyanide

5. I. $K_4[Fe(CN)_6]$ II. $K_3[Cr(CN)_6]$
III. $K_3[Co(CN)_6]$ IV. $K_2[Ni(CN)_4]$

Select the complexes which are diamagnetic.

(a) I, II and III (b) II, III and IV
(c) I, III and IV (d) I, II and IV

6. In spectrochemical series chlorine is above than water, *i.e.*, Cl > H_2O, this is due to

(a) good π-acceptor properties of Cl
(b) strong σ-donor and good π-acceptor properties of Cl
(c) good π-donor properties of Cl
(d) larger size of Cl than H_2O

7. Mixture $X = 0.02$ mole of $[Co(NH_3)_5SO_4]Br$ and 0.02 mole of $[Co(NH_3)_5Br]SO_4$ was prepared in 2 L of solution

1 L of mixture X + excess $AgNO_3 \longrightarrow Y$
1 L of mixture X + excess $BaCl_2 \longrightarrow Z$

Number of moles of Y and Z are

(a) 0.01, 0.01 (b) 0.01, 0.02
(c) 0.02, 0.01 (d) 0.02, 0.02

8. The hybridisation of central metal ion and shape of Wilkinson's catalyst is

(a) sp^3d, trigonal bipyramidal
(b) sp^3, tetrahedral
(c) dsp^2, square planar
(d) d^2sp^2, octahedral

9. An aqueous solution of $CoCl_2$ on addition of excess of concentrated HCl turns blue due to formation of

(a) $[CoCl_4]^{2-}$ (b) $[Co(H_2O)_2Cl_4]^{2-}$
(c) $[Co(H_2O)_2 2Cl_4]^{2-}$ (d) $[Co(H_2O)_4Cl_2]$

10. Which one of the following complexes is an outer orbital complex?

(a) $[Fe(CN)_6]^{4-}$ (b) $[Co(NH_3)_6]^{3+}$
(c) $[Ni(NH_3)_6]^{2+}$ (d) None of these

11. Which one of the following has highest number of isomers?

(a) $[Co(NH_3)_5Cl]^{2+}$
(b) $[Co(en)_2Cl_2]^+$
(c) $[Ru(NH_3)_4Cl^-]$
(d) $[In(Ph_3)_2H(CO)]^{2+}$

12. In which of the following pairs both the complex show optical isomerism?

(a) *Cis*-$[Cr(C_2O_4)_2Cl_2]^{3-}$; *cis*-$[Co(NH_3)_4Cl_2]$
(b) $[PtCl(dien)]Cl$, $[NiCl_2Br_2]^{2-}$
(c) $[Co(NO_3)_3(NH_3)_3]$, *cis*-$[Pt(en)_2Cl_2]$
(d) $[Co(en)_3]Cl_3$, *cis*-$[Co(en)_2Cl_2]Cl$

13. Match the complex ions given in Column I with the colours given in Column II and assign the correct code : **[NCERT Exemplar]**

	Column I (Complex ion)		Column II (Colour)
A.	$[Co(NH_3)_6]^{3+}$	1.	Violet
B.	$[Ti(H_2O)_6]^{3+}$	2.	Green
C.	$[Ni(H_2O)_6]^{2+}$	3.	Pale blue
D.	$[Ni(H_2O)_4(en)]^{2+}(aq)$	4.	Yellowish orange
		5.	Blue

Codes

	A	B	C	D		A	B	C	D
(a)	1	2	4	5	(b)	4	3	2	1
(c)	3	2	4	1	(d)	4	1	2	3

14. Match the complex species given in Column I with the possible isomerism given in Column II and assign the correct code : **[NCERT Exemplar]**

	Column I (Complex species)		Column II (Isomerism)
A.	$[Co(NH_3)_4Cl_2]^+$	1.	Optical
B.	*cis* - $[Co(en)_2Cl_2]^+$	2.	Ionisation
C.	$[Co(NH_3)_5(NO_2)]Cl_2$	3.	Coordination
D.	$[Co(NH_3)_6][Cr(CN)_6]$	4.	Geometrical
		5.	Linkage

Codes

	A	B	C	D		A	B	C	D
(a)	1	2	4	5	(b)	4	3	2	1
(c)	4	1	5	3	(d)	4	1	3	2

15. Match the complex ions given in Column I with the hybridisation number of unpaired electrons given in Column II and assign the correct code : **[NCERT Exemplar]**

	Column I (Complex ion)		Column II (Hybridisation and number of unpaired electrons)
A.	$[Cr(H_2O)_6]^{3+}$	1.	dsp^2, 1
B.	$[Co(CN)_4]^{2-}$	2.	sp^3d^2, 5
C.	$[Ni(NH_3)_6]^{2+}$	3.	d^2sp^3, 3
D.	$[MnF_6]^{4-}$	4.	sp^3, 4
		5.	sp^3d^2, 2

Codes

	A	B	C	D		A	B	C	D
(a)	3	1	5	2	(b)	4	3	2	1
(c)	3	2	4	1	(d)	4	1	3	2

16. Match the coordination compounds given in Column I with the central metal atoms given in Column II and assign the correct code : **[NCERT Exemplar]**

	Column I (Coordination compound)		Column II (Central metal atom)
A.	Chlorophyll	1.	Rhodium
B.	Blood pigment	2.	Cobalt
C.	Wilkinson catalyst	3.	Calcium
D.	Vitamin B_{12}	4.	Iron
		5.	Magnesium

Codes

	A	B	C	D
(a)	5	4	1	2
(b)	3	4	5	1
(c)	4	3	2	1
(d)	3	4	1	2

More than One Correct Option

17. Which of the following complexes are heteroleptic? **[NCERT Exemplar]**

(a) $[Cr(NH_3)_6]^{3+}$ (b) $[Fe(NH_3)_4Cl_2]^+$

(c) $[Mn(CN)_6]^{4-}$ (d) $[Co(NH_3)_4Cl_2]$

18. In which of the following, the chemical formula and the name correctly matched?

(a) $K_3[Cr(C_2O_4)_3]$ — Potassium trioxalatochromate (III)

(b) $K[Pt(NH_3)Cl_5]$ — Potassium amminepentachlorido platinate (IV)

(c) $Na_2[Ni(EDTA)]$ — Sodium ethylenediaminetetra acetatonickel (I)

(d) $[Ag(CN)_2]^-$ — Dicyanoargentate (I) ion

19. Which of the following statements is/are false?

(a) $[Ni(CO)_4]$ is high spin complex

(b) Weak ligands like F^-, Cl^- and OH^- usually form low spin complexes

(c) $[FeF_6]^{3-}$ is a high spin complex

(d) Strong ligand like CN^- and NO_2^-, generally form high spin complexes

20. An aqueous pink solution of cobalt (II) chloride changes to deep blue on addition of excess of HCl. This is because …… **[NCERT Exemplar]**

(a) $[Co(H_2O)_6]^{2+}$ is transformed into $[CoCl_6]^{4-}$

(b) $[Co(H_2O)_6]^{2+}$ is transformed into $[CoCl_4]^{2-}$

(c) tetrahedral complexes have smaller crystal field splitting than octahedral complexes

(d) tetrahedral complexes have larger crystal field splitting than octahedral complex

21. Identify the optically active compounds from the following **[NCERT Exemplar]**

(a) $[Co(en)_3]^{3+}$

(b) *trans*-$[Co(en)_2Cl_2]^+$

(c) *cis*-$[Co(en)_2Cl_2]^+$

(d) $[Cr(NH_3)_5Cl]$

Assertion and Reason

Directions (Q. Nos. 22 to 26) *Each of these questions contains two statements : Statement* I (*Assertion*) *and Statement* II (*Reason*). *Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes* (*a*), (*b*), (*c*), (*d*) *given below :*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I.

(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.

(c) Statement I is true; Statement II is false.

(d) Statement I is false; Statement II is true.

22. **Statement I** Ions with more than five $3d$ electrons have usually slightly larger magnetic moment than calculated on the basis of $\mu = \sqrt{n(n+2)}$.

Statement II The maximum number of unpaired d-electrons is five as in Mn^{2+} and Fe^{3+} and so, $\mu = 5.92$ for 5 unpaired electrons.

23. **Statement I** Toxic metal ions are removed by the chelating ligands. **[NCERT Exemplar]**

Statement II Chelate complexes tend to be more stable.

24. **Statement I** $[Cr(H_2O)_6]Cl_2$ and $[Fe(H_2O)_6]Cl_2$ are reducing in nature. **[NCERT Exemplar]**

Statement II Unpaired electrons are present in their d-orbitals.

25. **Statement I** Complexes of MX_6 and MX_5L type (X and L are unidentate) do not show geometrical isomerism. **[NCERT Exemplar]**

Statement II Geometrical isomerism is not shown by complexes of coordination number 6.

26. **Statement I** d-d transition is not possible in $[Sc(H_2O)_6]^{3+}$.

Statement II $[Ti(H_2O)_6]^{4+}$ is coloured while $[Sc(H_2O)_6]^{3+}$ is colourless.

Comprehension Based Questions

Directions (Q. Nos. 27 to 29) $CoSO_4Cl \cdot 5NH_3$ exists in two isomeric forms 'A' and 'B'. Isomer 'A' reacts with $AgNO_3$ to give white precipitate, but does not react with $BaCl_2$. Isomer 'B' gives white precipitate with $BaCl_2$ but does not react with $AgNO_3$. Answer the following questions. **[NCERT Exemplar]**

27. Write the structural formulae of A and B respectively

(a) $[Co(NH_3)_5SO_4]Cl$, $[Co(NH_3)_5SO_4]Cl_2$

(b) $[Co(NH_3)_5Cl]SO_4$, $[Co(NH_3)_5SO_4]Cl$

(c) $[Co(NH_3)_5SO_4]Cl$, $[Co(NH_3)_5Cl]SO_4$

(d) $[CoClSO_4(NH_3)_3](NH_3)_2$, $[CoSO_4(NH_4)_4]NH_3 \cdot Cl$

28. Name the type of isomerism involved.

(a) Solvated (b) Coordination

(c) Ionisation (d) Geometrical

29. Give the IUPAC name of 'B'.

(a) Pentaamminesulphatocobalt (III) chloride

(b) Pentaamminechloridocobalt (III) sulphate

(c) Pentaamminesulphatocobalt (II) chloride

(d) tetraamminesulphatecobalt (III) ammonium chloride

Directions (Q. Nos. 30 to 32) Splitting energy (Δ_o) can usually be measured from the absorption spectra of the complex ions. In simple cases when light is absorbed by a complex ion, an electron in one of the lower energy orbitals is excited to one of the higher energy orbital. The energy corresponding to the frequency of absorbed light is equal to Δ_o. If value of Δ_o for the complex is in visible region, the complex is coloured and the value of Δ_o lies in ultraviolet or infrared region, the complex is colourless. For octahedral complexes, the crystal field stabilisation energy is given by $CFSE = [-0.4\, t_{2g}N + 0.6 e_g\, N']\Delta_o$, where N and N' are number of electrons in t_{2g} and e_g orbitals respectively.

30. Among the following pairs of complexes, in which case the Δ_o value is higher for the first one?

(a) $[CoF_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$

(b) $[Co(H_2O)_6]^{2+}$ and $[Co(H_2O)_6]^{3+}$

(c) $[Rh(H_2O)_6]^{3+}$ and $[Co(H_2O)_6]^{3+}$

(d) $[Co(NH_3)_6]^{3+}$ and $[Co(CN)_6]^{3-}$

31. Which of the following statements is correct?

(a) Zinc (II) ion has a zero CFSE for any geometry

(b) A solution of $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ appear colourless in dil solutions

(c) A solution of $[Ni(H_2O)_6]^{2+}$ is green as the value of Δ for the H_2O complex is in the visible region

(d) All of the above

32. In which of the following complex ion, the metal ion will have t_{2g}^6, e_g^0 configuration according to CFT?

(a) $[Fe(CN)_6]^{3-}$ (b) $[FeF_6]^{3-}$

(c) $[Fe(CN)_6]^{4-}$ (d) None of these

Previous Years' Questions

33. Which among the following will be named as dibromidobis (ethylenediamine) chromium (III) bromide? **[AIEEE 2012]**

(a) $[Cr(en)_3]Br_3$

(b) $[Cr(en)_2Br_2]Br$

(c) $[Cr(en)Br_4]^-$

(d) $[Cr(en)Br_2]Br$

34. Which of the following facts about the complex $[Cr(NH_3)_6]Cl_3$ is wrong? **[AIEEE 2011]**

(a) The complex involves d^2sp^3 hybridisation and is octahedral in shape

(b) The complex is paramagnetic

(c) The complex is an outer orbital complex

(d) The complex gives white precipitate with silver nitrate solution

35. The magnetic moment (spin only) of $[NiCl_4]^{2-}$ is **[AIEEE 2011]**

(a) 1.82 BM (b) 5.46 BM

(c) 2.82 BM (d) 1.41 BM

36. Among the ligands NH_3, en, CN^- and CO, the correct order of their increasing field strength, is **[AIEEE 2011]**

(a) $CO < NH_3 < en < CN^-$ (b) $NH_3 < en < CN^- < CO$

(c) $CN^- < NH_3 < CO < en$ (d) $en < CN^- < NH_3 < CO$

37. Which one of the following complex ions has geometrical isomers? **[AIEEE 2011]**

(a) $[Co(en)_3]^{3+}$ (b) $[Ni(NH_3)_5Br]^+$

(c) $[Co(NH_3)_2(en)_2]^{3+}$ (d) $[Cr(NH_3)_4(en)]^{3+}$

38. Which of the following has an optical isomer? **[AIEEE 2009]**

(a) $[Co(NH_3)_3Cl]^+$ (b) $[Co(en)(NH_3)_2]^{2+}$

(c) $[Co(H_2O)_4(en)]^{3+}$ (d) $[Co(en)_2(NH_3)_2]^{3+}$

39. Which of the following pairs represents linkage isomers? **[AIEEE 2009]**

(a) $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$

(b) $[Pd(PPh_3)_2(NCS)_2]$ and $[Pd(PPh_3)_2(SCN)_2]$

(c) $[Co(NH_3)_5NO_3]SO_4$ and $[Co(NH_3)_5SO_4]NO_3$

(d) $[PtCl_2(NH_3)_4]Br_2$ and $[PtBr_2(NH_3)_4]Cl_2$

40. The coordination number and the oxidation state of the element 'E' in the complex $[E(\text{en})_2(C_2O_4)]\,NO_2$ (where (en) is ethylene diamine) are, respectively. **[AIEEE 2008]**

(a) 6 and 2 (b) 4 and 2
(c) 4 and 3 (d) 6 and 3

41. In which of the following octahedral complexes of Co (at. no. 27), will the magnitude of Δ_o be the highest? **[AIEEE 2008]**

(a) $[Co(CN)_6]^{3-}$ (b) $[Co(C_2O_4)_3]^{3-}$
(c) $[Co(H_2O)_6]^{3+}$ (d) $[Co(NH_3)_6]^{3+}$

42. Which one of the following has a square planar geometry? **[AIEEE 2007]**

(At. no. Co = 27, Ni = 28, Fe = 26, Pt = 78)

(a) $[CoCl_4]^{2-}$ (b) $[FeCl_4]^{2-}$
(c) $[NiCl_4]^{2-}$ (d) $[PtCl_4]^{2-}$

43. The IUPAC name for the complex $[Co(NO_2)(NH_3)_5]\,Cl_2$ is **[AIEEE 2006]**

(a) nitrito-N-pentamminecobalt (III) chloride
(b) nitrito-N-pentamminecobalt (II) chloride
(c) pentaamminenitrito-N-cobalt (II) chloride
(d) pentaamminenitrito-N-cobalt (III) chloride

44. Nickel ($Z = 28$) combines with a uninegative monodentate ligand X^- to form a paramagnetic complex $[NiX_4]^{2-}$. The number of unpaired electron (s) in the nickel and geometry of this complex ion are, respectively **[AIEEE 2006]**

(a) one, tetrahedral (b) two, tetrahedral
(c) one, square planar (d) two, square planar

45. Which of the following compounds shows optical isomerism? **[AIEEE 2005]**

(a) $[Co(CN)_6]^{3-}$ (b) $[Cr(C_2O_4)_3]^{3-}$
(c) $[ZnCl_4]^{2-}$ (d) $[Cu(NH_3)_4]^{2+}$

46. The coordination number of a central metal atom in a complex is determined by **[AIEEE 2004]**

(a) the number of ligands around a metal ion bonded by sigma bonds
(b) the number of ligands around a metal ion bonded by pi bonds
(c) the number of ligands around a metal ion bonded by sigma and pi bonds both
(d) the number of only anionic ligands bonded to the metal ion

47. The correct order of magnetic moments (spin only values in BM) among the following is
(At. no. Mn = 25, Fe = 26, Co = 27) **[AIEEE 2004]**

(a) $[MnCl_4]^{2-} > [CoCl_4]^{2-} > [Fe(CN)_6]^{4-}$
(b) $[MnCl_4]^{2-} > [Fe(CN)_6]^{4-} > [CoCl_4]^{2-}$
(c) $[Fe(CN)_6]^{4-} > [MnCl_4]^{2-} > [CoCl_4]^{2-}$
(d) $[Fe(CN)_6]^{4-} > [CoCl_4]^{2-} > [MnCl_4]^{2-}$

48. One mole of the complex compound $Co(NH_3)_5Cl_3$, gives 3 moles of ions on dissolution in water. One mole of the same complex reacts with two moles of $AgNO_3$ solution to yield two moles of AgCl(s). The structure of the complex is **[AIEEE 2003]**

(a) $[Co(NH_3)_5Cl]Cl_2$ (b) $[Co(NH_3)_3Cl_3]\cdot 2NH_3$
(c) $[Co(NH_3)_4Cl_2]Cl\cdot NH_3$ (d) $[Co(NH_3)_4Cl]Cl_2\cdot NH_3$

49. A square planar complex is formed by hybridisation of the following atomic orbitals **[AIEEE 2002]**

(a) s, p_x, p_y, p_z (b) s, p_x, p_y, p_z, d
(c) d, s, p_x, p_y (d) s, p_x, p_y, p_z, d, d

Answers

Round I

1. (a) **2.** (c) **3.** (a) **4.** (b) **5.** (c) **6.** (c) **7.** (d) **8.** (a) **9.** (a) **10.** (b)
11. (b) **12.** (a) **13.** (c) **14.** (d) **15.** (d) **16.** (b) **17.** (d) **18.** (c) **19.** (a) **20.** (c)
21. (c) **22.** (d) **23.** (a) **24.** (c) **25.** (c) **26.** (d) **27.** (c) **28.** (b) **29.** (a) **30.** (b)
31. (b) **32.** (b) **33.** (c) **34.** (a) **35.** (a) **36.** (b) **37.** (a) **38.** (d) **39.** (d) **40.** (d)
41. (b) **42.** (a) **43.** (c) **44.** (c) **45.** (b) **46.** (c) **47.** (d) **48.** (c) **49.** (c) **50.** (d)
51. (b) **52.** (b) **53.** (c) **54.** (b) **55.** (b) **56.** (c) **57.** (a) **58.** (c) **59.** (a)

Round II

1. (a) **2.** (d) **3.** (c) **4.** (b) **5.** (c) **6.** (b) **7.** (a) **8.** (c) **9.** (a) **10.** (c)
11. (b) **12.** (d) **13.** (b) **14.** (c) **15.** (a) **16.** (a) **17.** (b,d) **18.** (a,b,d) **19.** (a,b,d) **20.** (b,c)
21. (a,c) **22.** (b) **23.** (a) **24.** (b) **25.** (c) **26.** (c) **27.** (c) **28.** (c) **29.** (b) **30.** (c)
31. (d) **32.** (c) **33.** (b) **34.** (c) **35.** (c) **36.** (b) **37.** (c) **38.** (d) **39.** (b) **40.** (d)
41. (a) **42.** (d) **43.** (d) **44.** (b) **45.** (b) **46.** (a) **47.** (a) **48.** (a) **49.** (c)

the Guidance

Round I

1. In $K_4Fe(CN)_6$, the species retains its identity in solid as well as solution state so, it is a complex salt.

2. Lithium tetrahydroaluminate is $Li[Al(H)_4]$.

3. Chelating agent coordinates through more than one coordinating sites. Thiosulphate ($S_2O_3^{2-}$) although coordinate through only one coordinating site, so it is not referred as chelating agent.

4. Ligands have tendency to donate its lone pair. NH_4^+ ion have no lone pair so it is unable to behave like a ligand.

5. Oxidation number of Co : $K[Co(CO)_4]$

$$x + (4 \times 0) = -1; x = -1$$

8. CO ligand has zero oxidation state, that is why $[Ni(CO)_4]$ is a zero valent metal complex.

10. The complexes can be written as follows

$$[Co(NH_3)_6]Cl_3, [Co(NH_3)_5Cl]Cl_2, [Co(NH_3)_4Cl_4]Cl$$

Hence, number of primary valencies are 3, 2 and 1 respectively.

11. In the complex $K_2Fe[Fe(CN)_6]$ both the iron atoms are present in the same oxidation state *i.e.,* +2.

12. $[Co(NH_3)_5Cl]^{2+} + 2Cl^- \longrightarrow [Co(NH_3)_5Cl]Cl_2$

13. The complex will dissociate in aqueous solution to produce 3 ions.

$$Co(NH_3)_6Cl_2 \xrightarrow{aq} [Co(NH_3)_6]^{2+} + 2Cl^-$$

14. When excess of KCN(*aq*) is mixed with $CuSO_4(aq)$, a complex named potassium tetracyanocuprate (II) is formed. Since, CN^- ions are strong ligands, the complex is quite stable. It is evident from the stability constant value ($K = 2.0 \times 10^{27}$).

$$\underset{\text{(excess)}}{4KCN(aq)} + CuSO_4(aq) \longrightarrow \underset{\text{(soluble)}}{K_2[Cu(CN)_4](aq)} + K_2SO_4(aq)$$

$$\downarrow + H_2S$$

No cleavage and no production of Cu^{2+} ions

15. Formation of 3 mol AgCl from 1 mole complex suggests the presence of all the three Cl^- outside the coordination sphere. Thus, the formula of the complex should be $[Cr(H_2O)_6]Cl_3$.

16. Mn^{2+} will have half filled more stable d^5 configuration and without distributing it an outer orbital complex can be formed.

17. In acidic solution, proton coordinates with ammonia to form NH_4^+. NH_4^+ does not act as ligand because nitrogen atom has no lone pair of electrons which it can donate to metal atom.

18. In all these complexes, Fe is in +3 oxidation state. However, the complex (c) is a chelate because three $C_2O_4^{2-}$ ions act as the chelating ligands. Thus, the most stable complex is $[Fe(C_2O_4)_3]^{3-}$.

19. IUPAC name of $[Pt(NH_3)_2Cl_2]$ is diamminedichloridoplatinum (II).

20. IUPAC name of $[Pt(NH_3)_2Cl(NO_2)]$ is diamminechlorido nitrito-N-platinum (II).

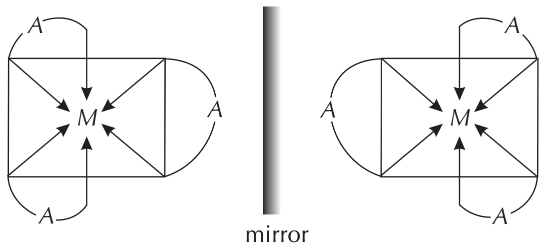
26. The given complexes are not isomers as their composition is not same. (Isomers have same composition but different arrangement and properties.)

27. Coordination isomerism is possible when both positive and negative ions of a salt are complex ions and the two isomers differ in distribution of ligands in the cation and the anion.

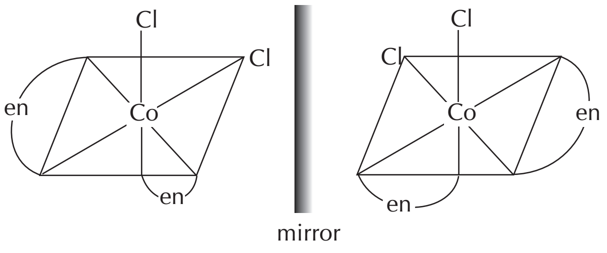
29. Complexes having ambidentate ligands like SCN exhibit linkage isomerism.

30. Since the two complexes differ in number of water (solvent) molecules inside and outside the coordination sphere, so they exhibit solvate isomerism.

31. Octahedral complexes containing three bidentate ligands shows optical isomerism. If *A* is a bidentate ligand then complex of type MA_3 show optical isomerism.



33.

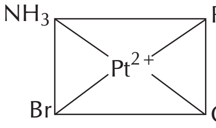


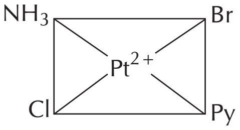
34. Octahedral complexes of the type $[MA_4B_2]^+$ [where A and B are two different monodentate ligands] exhibit geometrical isomerism.

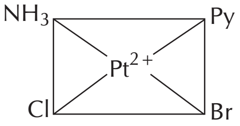
Hence, among the given only $[Cr(H_2O)_4Cl_2]^+$ exhibit geometrical isomerism.

35. 1. $[Cu(NH_3)_4][PtCl_4]$
2. $[Cu(NH_3)_3Cl]\cdot[PtCl_3(NH_3)]$
3. $[Cu(NH_3)_2Cl_2]\cdot[PtCl_2(NH_3)_2]$ *cis*
4. $[Cu(NH_3)_2Cl_2][PtCl_2(NH_3)_2]$ *trans*
5. $[Cu(NH_3)Cl_3]\cdot[Pt(Cl)(NH_3)_3]$
6. $[Pt(NH_3)_4]\cdot[CuCl_4]$

36. [*Mabcd*] type complexes exist in three isomeric forms.

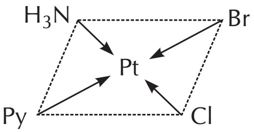




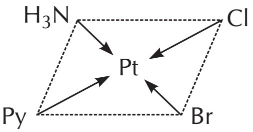


37. Three geometrical isomers are possible for

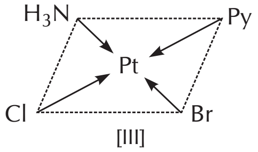
$[Pt(NH_3)(Br)(Cl)(Py)]$



[I]



[II]



[III]

Optical isomerism is not exhibited by this compound with CN = 4 and square planar geometry, because of the presence of horizontal plane of symmetry.

38. An optically active complex of the type $[M(AA)_2X_2]^{n+}$ indicates *cis*-octahedral structure, *e.g., cis*-$[Pt(en)_2Cl_2]^{2+}$ or *cis*-$[Cr(en)_2Cl_2]^+$

39. $[Fe(H_2O)_6]^{3+}$ has five unpaired electrons.

40. Since, hybridisation is dsp^2 so, it is square planar.

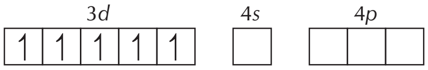
41. The coordination number in $[FeF_6]^{3-}$ is 6, hence it is a octahedral complex.

42. $[NiCl_4]^{2-}$ has tetrahedral shape. In this complex, Ni is in the +2 oxidation state and Ni^{2+} ion always forms tetrahedral complexes.

43. Both $Ni(CO)_4$ and $Ni(PPh_3)_2Cl_2$ have sp^3-hybridisation but later is square planar.

44. $K_3[FeF_6]$

$$Fe^{3+} = [Ar]\,3d^5\,4s^0$$



Number of unpaired electrons = 5

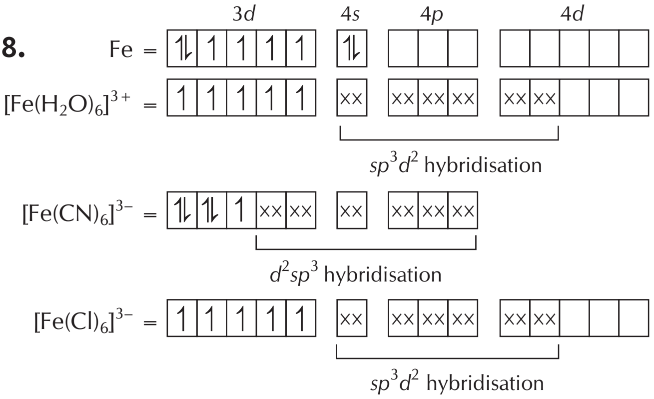
Magnetic moment $= \sqrt{5(5+2)} = \sqrt{s(s+2)}$

$= \sqrt{35} = 5.91$ BM

46. It is due to the presence of weak and strong field ligands in complexes. If CFSE is high, the complex will show low value of magnetic moment and *vice-versa, e.g.* $[CoF_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$, the former is paramagnetic, and the latter is diamagnetic because F^- is a weak field ligand and NH_3 is a strong field ligand.

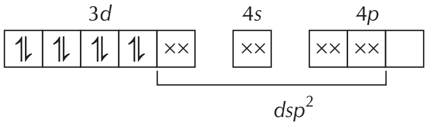
47. In $CuSO_4\cdot5H_2O$ water acts as ligand as a result it causes crystal field splitting. Hence, *d-d* transition is possible thus $CuSO_4\cdot5H_2O$ is coloured. In the anhydrous $CuSO_4$ due to the absence of water (ligand), crystal field splitting is not possible and hence, it is colourless.

48.

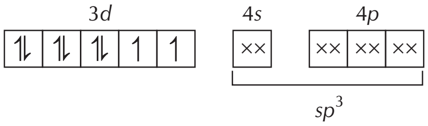


49. The electronic configuration of Ni in $[Ni(CN)_4]^{2-}$, $[NiCl_4]^{2-}$ and $Ni(CO)_4$ are as follows

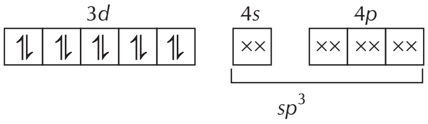
Ni^{2+} in $[Ni(CN)_4]^{2-}$



Ni^{2+} in $[NiCl_4]^{2-}$



Ni in $[Ni(CO)_4]$

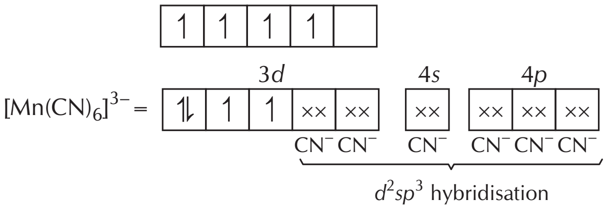


CO and CN^- are strong ligands so, they induces pairing of electrons so, their complexes are diamagnetic while, Cl^- is a weak field ligand so, it does not induce the pairing of electrons so, its complex is paramagnetic.

50. In both the complex compounds, Fe is in +2 oxidation state with configuration $3d^6$, *i.e.,* it has four unpaired electrons. In the presence of weak H_2O ligands, the unpaired electrons do not pair up. But in the presence of strong ligand CN^-, they get paired up. Then, no unpaired electron is left. Due to this difference in the number of unpaired electrons, both complex ions have different colours.

51. (a) $[Mn(CN)_6]^{3-}$

$$Mn^{3+} = 3d^4$$



(i) d^2sp^3 hybridisation

(ii) Inner orbital complex because $(n-1)\,d$-orbitals are used.

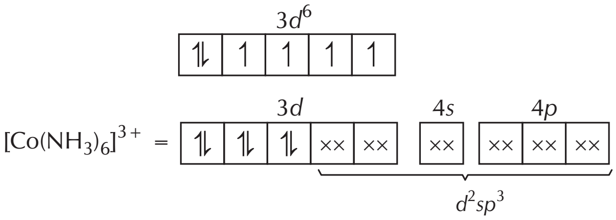
(iii) Paramagnetic, as two unpaired electrons are present.

(iv) Spin only magnetic moment

$$(\mu) = \sqrt{2\,(2+2)} = \sqrt{8} = 2.82 \text{ BM}$$

(b) $\mathbf{[Co(NH_3)_6]^{3+}}$

$$Co^{3+} = 3d^6\ 4s^0$$



(NH$_3$ pair up the unpaired $3d$ electrons.)

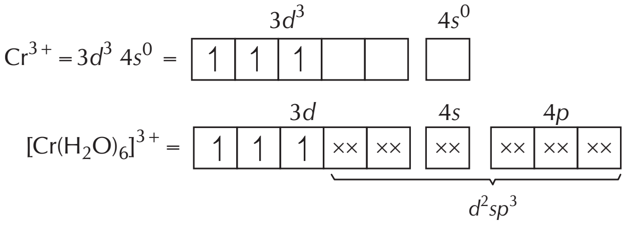
(i) d^2sp^3 hybridisation

(ii) Inner orbital complex because of the involvement of $(n-1)$ d-orbital in bonding.

(iii) Diamagnetic, as no unpaired electron is present.

(iv) $\mu = \sqrt{n\,(n+2)} = \sqrt{0\,(0+2)} = 0$ (Zero)

(c) $\mathbf{[Cr(H_2O)_6]^{3+}}$



(i) d^2sp^3 hybridisation

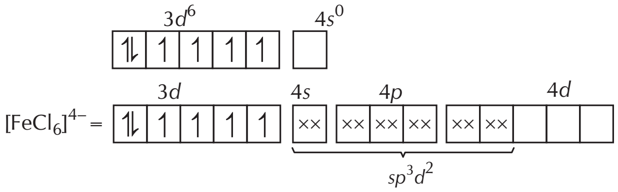
(ii) Inner orbital complex (as $(n-1)$ d-orbitals take part.)

(iii) Paramagnetic (as three unpaired electrons are present.)

(iv) $\mu = \sqrt{n\,(n+2)} = \sqrt{3\,(3+2)} = \sqrt{15} = 3.87$ BM

(d) $\mathbf{[Fe(Cl)_6]^{4-}}$

$$Fe^{2+} = 3d^6$$



(i) sp^3d^2 hybridisation

(ii) Outer orbital complex because nd-orbitals are involved in hybridisation.

(iii) Paramagnetic (because of the presence of four unpaired electrons).

(iv) $\mu = \sqrt{n\,(n+2)} = \sqrt{4\,(4+2)} = \sqrt{24} = 4.9$ BM

52. For tetrahedral complexes, the crystal field stabilisation energy is lower than pairing energy, so they are not formed in low spin state.

53. We know that, CFSE is higher for the complex having strong field ligand and varies inversely with wavelength.

In all the given complexes, the metal ion is Ni^{2+}. The increasing field strengths of the ligands present as per electrochemical series are in the order :

$$H_2O < NH_3 < NO_2^-$$

The energies absorbed for excitation will be in the order :

$$[Ni(H_2O)_6]^{2+} < [Ni(NH_3)_6]^{2+} < [Ni(NO_2)_6]^{4-}$$

As $E = \dfrac{hc}{\lambda}$, *i.e.,* $E \propto \dfrac{1}{\lambda}$; the wavelengths will be in the opposite order, that is as follows

$$[Ni(H_2O)_6]^{2+} > [Ni(NH_3)_6]^{2+} > [Ni(NO_2)_6]^{4-}$$

54. Dissociation constant is the reciprocal of β_4, the stability constant.

Overall complex dissociation equilibrium constant $= \dfrac{1}{\beta_4}$

$$= \frac{1}{2.1 \times 10^{13}} = 4.7 \times 10^{-14}$$

55. EAN of Pt in $[PtCl_6]^{2-} = 86$

56. Chlorophyll are green pigment in plant and contain magnesium instead of calcium.

57. *Cis*-isomer of $[Pt(NH_3)_2Cl_2]$ is used as an anticancer drug for treating several type of malignant tumours. When it is injected into the blood stream, the more reactive Cl groups are lost so, the Pt atom bonds to a N-atom in guanosine (a part of DNA). This molecule can bond to two different guanosine units and by bridging between them it upsets the normal reproduction of DNA.

58. The reaction carried out in alkaline pH, *i.e.,* 9 – 11.

59. $[H_2EDTA]^{2-} + Mg^{2+} \longrightarrow [MgEDTA]^{2-} + 2H^+$

(a) In this complex, four donor sites are occupied by oxygen and two donor sites are occupied by nitrogen.

(b) This complex is six coordinated.

(c) Complex $[MgEDTA]^{2-}$ is colourless.

(d) Increase in $[H^+]$ decreases pH of the solution.

Round II

1. Its coordination number will be 6 because it is bonded with three bidentate ligands.

Let x be the oxidation state of Cr.

$\therefore \quad x + 3(-2) + 3(+1) = 0 \Rightarrow x = +3$

2. Let the oxidation state of Fe in $[Fe(H_2O)_5NO]SO_4$ is x.

$$[Fe(H_2O)_5NO]^{2+}$$

$$\Rightarrow \quad x + 0 + 1 = 2$$

$$\therefore \quad x = +1$$

Hence NO exists as nitrosyl ion (NO^+).

3. In $K_3[Fe(CN)_6]$, the ligands are negative which is present in coordination spheres shows a dual behaviour. It may satisfied both primary and secondary valencies while neutral ligand satisfied only secondary valencies.

4. IUPAC name of sodium nitroprusside $Na_2[Fe(CN)_5NO]$ is sodium pentacyanonitrosoyl ferrate (III) because in it NO is neutral ligand and the oxidation number of Fe is III, which is calculated as

$$2 \times \text{O.N. of Na} + \text{O.N. of Fe} + 5 \times \text{O.N. of CN} + 1 \times \text{O.N. of NO} = 0$$

$$2 \times (+1) + \text{O.N. of Fe} + 5 \times (-1) + 1 \times 0 = 0$$

$$\therefore \quad \text{O.N. of Fe} = 5 - 2 = +3$$

5. Structure $K_4[Fe(CN)_6]$, $K_3[Co(CN)_6]$, $K_2[Ni(CN)_4]$ are diamagnetic.

6. When ligands are arranged in ascending order of crystal field splitting energy, Δ, they produced a spectrochemical series.

In comparison to H_2O, Cl is a strong σ donor and good π-acceptor, therefore, it is a strong ligand than H_2O. Hence, in the spectrochemical series is Cl is above than water.

7. $$[Co(NH_3)_5SO_4]Br + AgNO_3 \longrightarrow [Co(NH_3)_5SO_4] + \underset{(Y)}{\underset{0.02\text{ mol}}{AgBr}}$$

$$\underset{\frac{0.02}{2}\text{ mol L}^{-1}}{[Co(NH_3)_5Br]SO_4} + BaCl_2 \longrightarrow [Co(NH)_5Br]Cl_2 + \underset{0.01\text{ mol L}^{-1}}{\underset{(Z)}{BaSO_4}}$$

8. Wilkinson's catalyst, $(Ph_3P)_3RhCl$

$$Rh^+ = [Kr]\,4d^8\,s^0$$

i.e., dsp^2 hybridisation.

Rh atom in Wilkinson's catalyst is dsp^2 hybridised giving a square planar shape to the molecule.

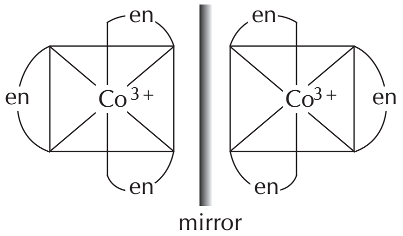
9. $CoCl_2$ is a weak Lewis acid, It reacts with chloride ions to produce salt containing the tetrahedral $[CoCl_4]^{2-}$ ion. $CoCl_2$ is blue when anhydrous, and a deep magenta colour when hydrated, for this reason it is widely used as an indicator for water.

10.

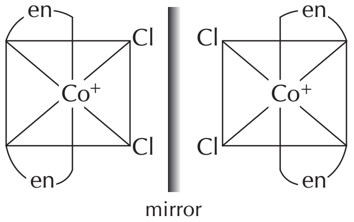
Complex ion	Hybridisation of central atom
$[Fe(CN)_6]^{4-}$	d^2sp^3 (inner)
$[Co(NH_3)_6]^{3+}$	d^2sp^3 (inner)
$[Ni(NH_3)_6]^{2+}$	sp^3d^2 (outer)

11. $[Co(en)_2Cl_2]^+$ shows geometrical as well as optical isomerism.

12. $[Co(en)_3]Cl_3$ *i.e.,* $[Co(en)_3]^{3+}$



cis-$[Co(en)_2Cl_2]Cl$ *i.e.,* *cis* $[Co(en)_2Cl_2]^+$



13. In $[Co(NH_3)_6]^{3+}$, Co is present as $Co^{3+}(d^6)$ and NH_3 is a strong field ligand, so unpaired electrons = 0.

So, it is yellowish orange.

In $[Ti(H_2O)_6]^{3+}$, Ti is present as $Ti^{3+}(d^1)$ so it contains one unpaired electron. It is pale blue in colour.

In $[Ni(H_2O)_6]^{2+}$, Ni is present as Ni^{2+} (d^8) so it have two unpaired electrons. It is of green colour.

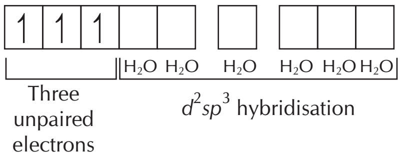
$[Ni(H_2O)_4(en)]^{2+}$ is violet as en is a strong field ligand.

14. $[Co(NH_3)_4Cl_2]^+$ exhibits geometrical isomerism. *Cis* $[Co(en)_2Cl_2]^+$ because of the absence of symmetry elements exhibits optical isomerism.

$[Co(NH_3)_5(NO_2)]Cl_2$ because of the presence of ambidentate (NO_2) ligand exhibit linkage isomerism. $[Co(NH_3)_6][Cr(CN)_6]$ exhibits coordination isomerism because here cation and anion both are complex.

15. In $[Cr(H_2O)_6]^{3+}$, Cr is present as Cr^{3+}.

$$Cr^{3+} = 3d^3, \quad 4s^0, \quad 4p^0$$

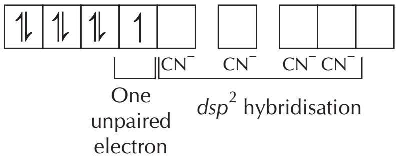


In $[Co(CN)_4]^{2-}$, Co is present as Co^{2+}

$$Co^{2+} = 3d^7, 4s^0, 4p^0$$

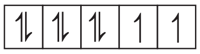
[CN^- being strong field ligand pair up the unpaired *d* electrons.]

$[Co(CN)_4]^{2-} =$

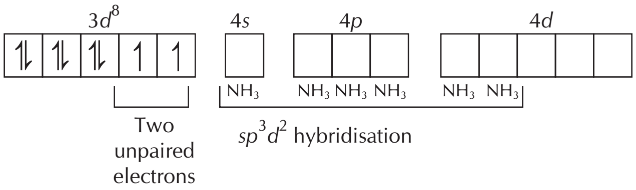


(c) In $[Ni(NH_3)_6]^{2+}$, Ni is present as Ni^{2+}.

$$Ni^{2+} = [Ar]\,3d^8, 4s^0$$



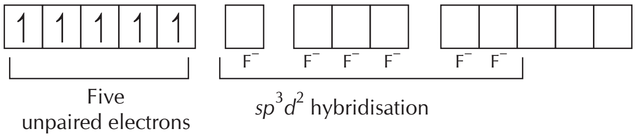
$[Ni(NH_3)_6]^{2+} =$



(d) In $[MnF_6]^{4-}$, Mn is present as Mn^{2+}.

$$Mn^{2+} = 3d^5\ 4s^0$$

$[MnF_6]^{4-} =$



16. Chlorophyll contains Mg, blood pigment, *i.e.,* haemoglobin contains iron (Fe), Wilkinson catalyst contains Rh (rhodium) and vitamin B_{12} have cobalt metal.

17. Heteroleptic complexes are those in which more than one kind of ligands are present. *e.g.,* $[Fe(NH_3)_4Cl_2]^{4+}$, $[Co(NH_3)_4Cl_2]$ etc.

18. Three names and formulas are correctly matched.

$K_3[Cr(C_2O_4)_3]$ — Potassium trioxalatochridomate (III)

$K[Pt(NH_3)Cl_5]$ — Potassium amminepentachloroplatinate (IV)

$[Ag(CN)_2]^-$ — Dicyanoargentate (I) ion

19. F^-, Cl^- and OH^- are weak field ligands usually form high spin complexes. CN^- and NO_2^- are strong field ligands usually form low spin complexes. $[Ni(CO)_4]$ is a low spin complex.

20. $$\underset{\text{(octahedral)}}{\underset{\text{pink}}{[Co(H_2O)_6]^{2+}}} \xrightarrow{HCl} \underset{\text{(tetrahedral)}}{\underset{\text{deep blue}}{[CoCl_4]^{2-}}}$$

The colour changes because crystal field splitting is more in case of octahedral complexes as compared to tetrahedral complexes.

21. $[Co(en)_3]^{3+}$ and *cis*-$[Co(en)_2Cl_2]^+$ are optically active compounds because of the absence of symmetry elements.

22. The slightly larger value of μ than expected from the formula $\mu = \sqrt{n(n+2)}$ is due to a small contribution from the orbital angular momentum of the electrons to the magnetic moment.

23. Chelating agents form more stable complexes thus, these are used to remove toxic metal ions.

24. $[Cr(H_2O)_6]Cl_2$ contains Cr as Cr^{2+}, which is less stable than Cr^{3+}, so it have higher tendency to get oxidised or it is a better reducing agent.

Similar is true for $[Fe(H_2O)_6]Cl_2$. Both the complex have unpaired electrons in their *d*-orbitals.

25. MX_6 and MX_5L type complexes do not exhibit geometrical isomerism although many 6 coordinated complexes like complex of the type MA_3B_3 exhibits geometrical isomerism.

26. Both $[Ti(H_2O)_6]^{4+}$ and $[Sc(H_2O)_6]^{3+}$ are colourless due to the absence of free electrons in 3*d* subshell.

27. '*A*' gives precipitate with $AgNO_3$, so in it Cl is present outside the coordination sphere.

'*B*' gives precipitate with $BaCl_2$, so in it SO_4^{2-} is present outside the coordination sphere.

So, *A*-$[Co(NH_3)_5SO_4]$ Cl

B-$[Co(NH_3)_5Cl]$ SO_4

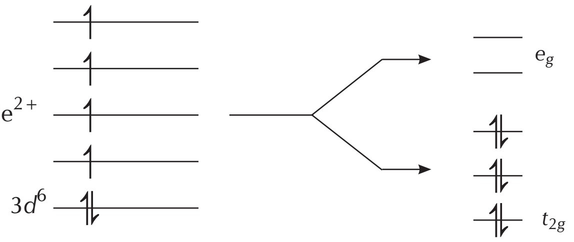
28. Ionisation isomerism (as give different ions when subjected to ionisation.)

29. [*B*], Pentaamminechloridocobalt (III) sulphate.

30. In complexes $[Rh(H_2O)_6]^{3+}$ and $[Co(H_2O)_6]^{3+}$, central metal cations have same oxidation state as well as same ligands and they fall in same group, but Δ_o of $[Rh(H_2O)_6]^{3+} > \Delta_o$ of $[Co(H_2O)_6]^{3+}$ because Rh^{3+} has high Z_{eff} value than Co^{3+}.

31. Δ_o is so large for $[Fe(CN)_6]^{4-}$ that its absorption peak is in ultraviolet region. Δ_o for $[Fe(H_2O)_6]^{2+}$ is so small that its absorption peak is in infrared region.

32. Fe^{2+}



CN^- is a strong field ligand, therefore $\Delta_o > \Delta P$ and hence, pairing of electrons takes place.

33. Two Br, two (en) and one Cr are parts of complex. Charge on the complex is

$$\left.\begin{array}{r} 2\,(\text{Br}) = -2 \\ 2\,(\text{en}) = 0 \\ 1\,(\text{Cr}) = +3 \end{array}\right\} = +1$$

Thus, complex ion is $[Cr(en)_2Br_2]^+$.

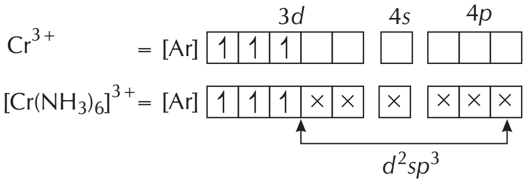
Since, anion is bromide thus, complex is $[Cr(en)_2Br_2]Br$.

34. $\underbrace{[Cr(NH_3)_6]}_{\text{coordinate sphere}} \quad \underbrace{Cl_3}_{\text{ionisable}} \rightleftharpoons$

$$[Cr(NH_3)_6]^{3+} + 3Cl^- \xrightarrow{AgNO_3} \underset{\text{white precipitate}}{AgCl\downarrow}$$

$$Cr(24) = [Ar]3d^5\,4s^1$$

$$Cr^{3+} = [Ar]\,3d^3\,4s^0$$



☒ Indicates lone-pair of NH_3 donated to Cr

(a) d^2sp^3-hybridisation, octahedral. Thus, correct.

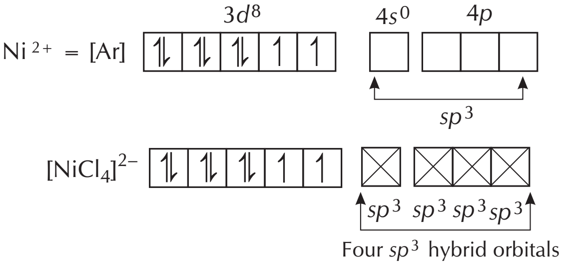
(b) There are three unpaired electrons, hence paramagnetic. Thus, correct.

(c) d^2sp^3-inner orbital complex, thus incorrect.

(d) Due to ionisable Cl^- ions, white precipitate with $AgNO_3$, thus, correct.

35. $[NiCl_4]^{2-}$; oxidation number of Ni, $x - 4 = -2$

$\therefore \quad x = +2, Ni_{(28)}\ [Ar]\ 3d^8, 4s^2$



sp^3-hybrid orbitals, tetrahedral

Cl^- is a weak field ligand and thus, unpaired electrons are not paired. Lone pairs from 4 Cl^- are accomodated in four sp^3 hybrid orbitats.

N = unpaired electrons = 2 , paramagnetic

Magnetic moment (spin only)

$$= \sqrt{N\,(N+2)}\ \text{BM}$$

$$= \sqrt{8} = 2.828\ \text{BM}$$

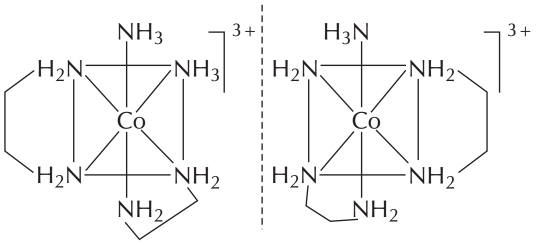
36. Based on spectrochemical series, ligands arranged in increasing order of crystal field strength are as

$$NH_3 < en < CN^- < CO$$

37.

	Complex	Isomerism shown
(a)	$[Co(en)_3]^{3+}$	Optical only
(b)	$[Ni(NH_3)_5Br]^+$	No geometrical isomer
(c)	$[Co(NH_3)_2(en)_2]^{3+}$	*Cis* and *trans*
(d)	$[Cr(NH_3)_4(en)]^{3+}$	No geometrical isomer

38. *Cis*-form of $[Co(en)_2(NH_3)_2]^{3+}$ is optically active.



39. Linkage isomerism are caused due to presence of ambidentate ligands. $[Pd(PPh_3)_2(NCS)_2]$ and $[Pd(PPh_3)_2(SCN)_2]$ are linkage isomers due to SCN, ambidentate ligands.

40. en, $\begin{array}{l} CH_2\text{—}NH_2 \\ | \\ CH_2\text{—}NH_2 \end{array}$ is a bidentate ligand.

$C_2O_4^{2-}$ is also a bidentate ligand.

Hence, coordinating head are six

(en : 2 × 2 = 4 + (ox) 2)

Coordination number 6

Complex can be ionised as

$$[E\,(en)_2(C_2O_4)]\,NO_2 \longrightarrow [E\,(en)_2\,(C_2O_4)]^+ NO_2^-$$

Oxidation number $x + 0 + (-2) = +1$

$\Rightarrow$ Oxidation number, $x = 3$

41. CFSE (crystal field splitting energy) for octahedral complex, Δ_o depends on the strength of negative ligand. Spectrochemically it has been found that the strength of splitting is as follows:

$$CO > \underline{CN^-} > NO_2^- > en > \underline{NH_3} > py >$$

$$NCS^- > H_2O > O^{2-} > OX^{2-} > OH^- > F^- >$$

$$Cl^- > SCN^- > S^{2-} > Br^- > I^-$$

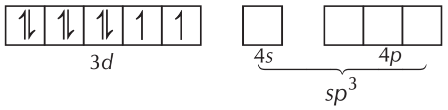
42. Cl^- is a weak ligand but Cl^- cause the pairing of electrons with large Pt^{2+} and consequently give dsp^2 hybridisation and square planar geometry.

43. $[Co(NO_2)\,(NH_3)_5]\,Cl_2$

Pentaamminenitrito-N-cobalt (III) chloride

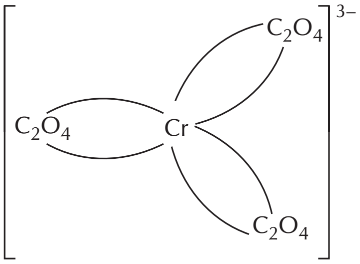
44. $_{28}Ni = [Ar]\ 4s^2, 3d^8$

$Ni^{2+} = [Ar]\ 3d^8$



Nickel has two unpaired electrons and geometry is tetrahedral due to sp^3 hybridisation.

45.



Mirror image is not superimposable, hence optical isomerism is possible.

46. Coordination number is the maximum covalency shown by a metal or metal ion. It is the maximum number of ligands attached to metal by sigma bonds or coordinate bonds.

47. Number of unpaired electrons in $[Fe(CN)_6]^{4-}$ is zero.

Thus, magnetic moment $= \sqrt{n(n+2)} = 0$ BM

(n = unpaired electrons)

n in $[MnCl_4]^{2-} = 5, \sqrt{35}$ BM

n in $[CoCl_4]^{2-} = 3, \sqrt{15}$ BM

48. $$[Co(NH_3)_5Cl]Cl_2 \rightleftharpoons \underbrace{[Co(NH_3)_5Cl]^{2+} + 2Cl^-}_{\text{three ions}}$$

$$\underset{\text{free}}{2Cl^-} + 2Ag^+ \longrightarrow 2AgCl$$

2 mol 2 mol 2 mol

49. A square planar geometry is the result of dsp^2 hybridisation where inner d sub-shell ($d_{x^2-y^2}$ orbital) participates.

10 Organic Compounds Containing Halogens

JEE Main MILESTONE

- Classification of Halogen Derivatives
- Nomenclature of Halogen Derivatives
- Monohaloalkanes
- Dihaloalkanes
- Trihaloalkanes
- Polyhaloalkanes
- Aryl halides

10.1 Classification of Halogen Derivatives

Halogen compounds are classified into several classes depending upon the mode of classification.

On the Basis of Nature of Carbon Atom

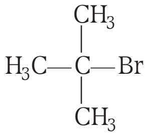
Halogen derivatives can be classified as primary, secondary and tertiary halides depending upon the fact that hydrogen is attached to primary, secondary or tertiary C-atom. *e. g.*,

$H_3C—Br$
methyl bromide
(1°)

$H_3C—CH_2Br$
primary
(1°)

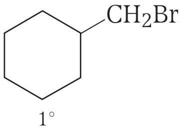
$H_3C—\overset{\overset{\large CH_3}{|}}{C}H—Br$

secondary
(2°)

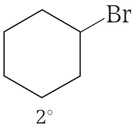


$H_3C—\underset{\underset{\large CH_3}{|}}{\overset{\overset{\large CH_3}{|}}{C}}—Br$

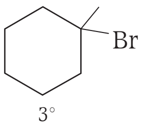
tertiary
(3°)



1°



2°



3°

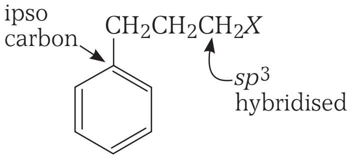
The halogen derivatives are called vinylic and allylic derivatives, if the halogen atom is attached to vinyl and allyl group respectively.

$CH_2{=}CHCl$
vinyl chloride

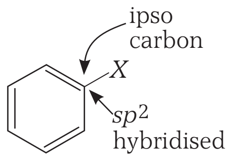
$CH_2Cl—CH{=}CH_2$
allyl chloride

If halogen atom is attached to aliphatic chain, it is called **aliphatic halogen compound** or **haloalkanes** and if it is attached to aromatic carbon, it is called **aromatic halogen compound** or **haloarenes.**

Organic compounds formed by the replacement of one or more hydrogen atoms of the aliphatic and aromatic hydrocarbons by an equal number of halogen atoms are called ***aliphatic*** *and* ***aromatic halogen*** *derivatives respectively. Term alkyl halide is used for aliphatic halogen derivatives and aryl halide is used for aromatic halogen derivatives. Here halogen atom serves as a functional group.*



aliphatic halogen compound (because X is attached with the aliphatic chain, not with the aromatic chain)

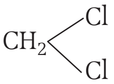


aromatic halogen compound (As X is attached directly to the benzene nucleus)

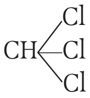
On the Basis of Number of Halogen Atoms

The halogen derivatives (both aliphatic and aromatic) can also be classified as mono, di, tri and tetra halogen derivatives depending upon the number of halogen atoms present in the molecule, *i.e.*,

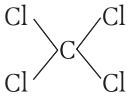
CH_3Cl
(one halogen atom)
monohalogen
derivative



(two halogen atoms)
(dihalogen derivative)



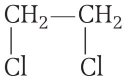
trihalogen derivative
(chloroform)



tetrahalogen derivative
(carbon tetrachloride)

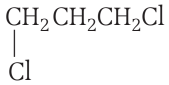
Remember in halogen derivatives, if both the halogen atoms are present at the same carbon atom, it is called geminal (*gem*-) dihalides and if present at adjacent carbon atoms, it is called vicinal (*vic*) dihalides. An another kind of dihalide, in which the two halogen atoms neither occupy the same nor the successive carbon atoms are also known. These are named as α or ω dihalogen derivatives (usually in these the halogen atoms occupy the terminal positions). *e. g.*,

CH_3CHCl_2
gem dihalide



$\underset{Cl}{CH_2}—\underset{Cl}{CH_2}$

vic dihalide



$\underset{Cl}{CH_2}CH_2CH_2Cl$

ω–dihalogen derivatives

10.2 Nomenclature of Halogen Derivatives

In trivial system of nomenclature, halogen derivatives are named as alkyl halide. *e. g.*,

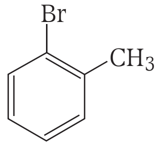
CH_3Cl methyl chloride
$CH_2{=}CHCl$ vinyl chloride
$CH_2Br—CH_2Br$ ethylene dibromide

In IUPAC system, alkyl halides are named as 'haloalkanes' and aryl halides as 'haloarenes'. The longest chain is numbered so that the smallest number is used to indicate the positions of the substituent and different substituents are named alphabetically. *e. g.*,

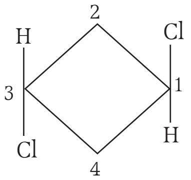
$\overset{5}{CH_3}\overset{4}{CH_2}\overset{3}{CH_2}\overset{2}{CH_2}\overset{1}{CH_2}Br$
1-bromopentane

$\overset{1}{CH_2}Br_2$
1, 1-dibromomethane

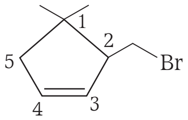
$CHCl_3$
1,1,1-trichloromethane



1-bromo-2-methyl benzene or 2-bromotoluene (*o*-bromotoluene; general name)



trans-1, 3-dichloro cyclobutane



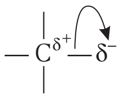
2-bromomethyl-1, 1-dimethyl cyclopentane

10.3 Monohaloalkanes

These are the compounds in which only one halogen atom is attached to the alkyl chain. Their general formula is $C_nH_{2n+1}X$.

Nature of C—*X* Bond

Since, there is a large difference in the electronegativity of halogen atom and carbon, the C atom of the halogen derivative acquires partial positive charge while the halogen atom gets partial negative charge. Hence, the C—X bond is polar in nature. This polar nature of halogen derivatives is responsible for their high reactivity and makes them useful organic compound.



Methods of Preparation

Important methods used to prepare monohaloalkanes are as follows

(a) Halogenation of Alkanes

This reaction takes place in the presence of heat or light and follows free radical mechanism. The reaction looks as

$$RH + X_2 \xrightarrow{h\nu} RX + HX \quad (\text{where, } X = \text{Cl, Br, I})$$

The free radical mechanism of the reaction is fully described in chapter "some basic principles of organic chemistry" under free radical substitution mechanism, (also see properties of alkanes) Remember that

(i) iodination occurs only in the presence of an oxidising agent such as HgO, HIO_3, HNO_3 because direct iodination is a reversible reaction.

(ii) reaction of F_2 with alkanes is explosive therefore, fluorides are generally prepared by halogen exchange method which we shall discuss later.

In the presence of light and trace of peroxide, allylic bromination takes place with NBS (It occurs by free radical mechanism.)

$$CH_3CH{=}CH_2 + NBS \longrightarrow BrCH_2CH{=}CH_2 + HCl$$

(b) Addition of Halogen Acids to Alkenes

It is an electrophilic addition reaction. In case of unsymmetrical alkene, addition takes place according to Markownikoff's rule *i.e.*, negative part goes to more hindered carbon.

$$RCH{=}CH_2 + HBr \longrightarrow RCHBrCH_3$$

The reaction is fully described in alkenes properties and mechanism is fully described in 'some basic prinicples of organic chemistry' under electrophilic addition, Markownikoff rule and Kharasch effect.

At high temperature the addition of halogens to alkenes becomes reversible and hence, does not occur.

(c) Substitution of —OH Group of Alcohol

These reactions are infact nucleophilic substitution reactions and follow S_N1 or S_N2 accordingly depending upon the alcohol used. The mechanisms are fully described in chapter some basic principles of organic chemistry under nucleophilic substitutions. The reactions are

(i) $3ROH + PX_3 \longrightarrow 3RX + H_3PO_3$

(ii) $ROH + PX_5 \longrightarrow RX + POX_3 + HX$

(PBr_5 and PI_5 are highly unstable compounds due to steric hindrance therefore, only chlorides are prepared by this method.)

(iii) $ROH + \text{dry HCl} \xrightarrow{\text{Anh. } ZnCl_2} RCl + H_2O$

Mixture of (1 : 1) dry HCl and anhydrous $ZnCl_2$ is called **Lucas reagent**.

(iv) $R{—}OH + HX \longrightarrow RX + H_2O$

The reactivity of alcohols towards HX is allyl, benzyl > 3° > 2° > 1° and the reactivity of halogen acids is HI > HBr > HCl > HF.

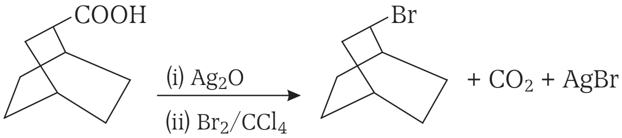
(v) $ROH + SOCl_2 \xrightarrow{\text{Pyridine}} RCl + HCl + SO_2$

The reaction of $SOCl_2$ is called Darzens procedure. Bromide and iodide are not prepared by this method, because thionyl bromide is unstable and thionyl iodide does not exist.

(d) Borodine-Hunsdicker Method

This is the decarboxylation of silver salt of fatty acids, when these are treated with Br_2 in refluxing CCl_4.

$$CH_3COOAg + Br_2 \xrightarrow{CCl_4} CH_3Br + AgBr + CO_2$$



The yield of halide is 1° > 2° > 3°

The reaction follows free radical mechanism; yield of alkyl chloride is less than alkyl bromide.

If iodine is used in the place of Br_2, the reaction is modified as

$$2RCOOAg + I_2 \longrightarrow RCOOR + CO_2 + 2AgI$$

This modified reaction is called **Birnbaurn Simonini reaction.**

(e) Halide Exchange Method

Alkyl chloride and bromides are converted into their iodides or fluorides as :

Alkyl chloride or bromide $\xrightarrow{\text{NaI/acetone}}$ Alkyl iodide + Na chloride or bromide

$\xrightarrow{\text{Inorganic fluorides like } Hg_2F_2}$ Alkyl fluoride + Hg chloride or bromide

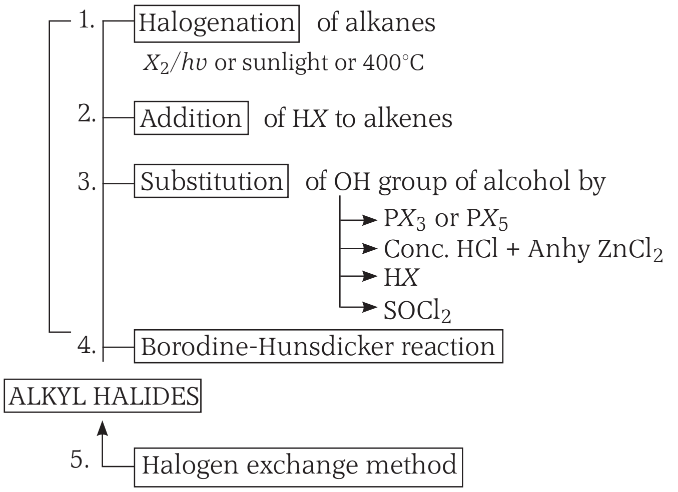
This reaction is called **Finkelstein reaction**.

Alkyl fluorides which can't be prepared by the **Finkelstein reaction** may be obtained from corresponding chlorides by the action of mercurous fluoride or antimony trifluoride or AgF **(Swarts reaction)**.

$$2CH_3Cl + Hg_2F_2 \longrightarrow 2CH_3F + Hg_2Cl_2$$

$$CH_3Br + AgF \longrightarrow CH_3F + AgBr$$

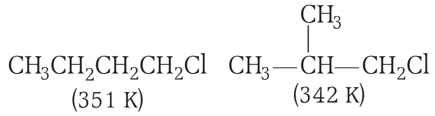
The outline of the methods of preparation of monohaloalkanes looks like (All methods give chloride and bromide in good yield but fluorides or iodides in poor yield.



FINKELSTEIN method for converting chlorides and bromides to iodides.

Physical Properties

1. Chloride, bromide and fluoride of methane and chloride of ethane are gases at room temperature, rest alkyl halides up to C_{18} are colourless liquids and beyond it, these are colourless solids. Bromides and particularly iodides develop colour when exposed to light.
2. Haloalkanes have polar nature but are insoluble in polar solvents like water as they have no ability of forming H-bonding with water. However, these are soluble in organic solvents like ether, benzene etc.
3. Fluoro and chloro compounds are lighter than water whereas bromo and iodo derivatives are heavier. The density of alkyl halides decreases, as the size of alkyl group increases.
4. These have higher boiling point than alkanes of comparable molecular weight. *For a given alkyl group their boiling points follow the order* $RI > RBr > RCl > RF$*; while for a given halogen atom the boiling points of alkyl halides increase with increase in the size of alkyl group. Boiling point decreases with branching e.g.,*



$$\underset{(351\ K)}{CH_3CH_2CH_2CH_2Cl} \qquad \underset{(342\ K)}{CH_3-\overset{\overset{\large CH_3}{|}}{C}H-CH_2Cl}$$

5. The dipole moment of halogen derivatives is due to the polar nature of C—X bond. Vinyl chloride and chlorobenzene showing resonance, have low dipole moment (as compared to alkyl halide) because unusual positive charge decreases the electronegativity of Cl atom and thus, the polarity of the bond. Dipole moment of alkyl halides decreases as the electronegativity of halogen atom decreases. However, the dipole moment of fluorides is lower than that of chlorides because of very small size of fluorine.

Sample Problem 1 *Arrange the given set of compounds in order of increasing boiling points.*

I. I-chloropropane, II. iso-propyl chloride, III 1-chlorobutane.

[**NCERT**]

(a) I < II < III   *(b)* II < III < I
(c) I < III < II   *(d)* II < I < III

Interpret (*d*) As the size of *R* group (alkyl group) or halogen atom increases, boiling point increases, because, now more surface area is available. Boiling point decreases with branching due to decrease in van der Waals' forces. Thus, the correct order of boiling point is

$$\underset{\substack{\text{isopropyl chloride}\\ \text{or}\\ \text{2-chloropropane}}}{(CH_3)_2CHCl} < \underset{\text{1–chloropropane}}{ClCH_2CH_2CH_3} < \underset{\text{1–chlorobutane}}{ClCH_2CH_2CH_2CH_3}$$

Chemical Properties

Because of the presence of polar C–X bond, alkyl halides readily undergo nucleophilic substitution, elimination, reduction etc. So, their reactions can be studied under the following headings.

1. Nucleophilic substitution reaction
2. Reduction
3. Reaction with metals
4. Elimination reactions
5. Friedel-Crafts alkylation

Hot Spot 1

NUCLEOPHILIC SUBSTITUTION Reactions

It is an important topic for JEE Main examination point of view. For solving problems based on the topic, deep understanding of the topic is required. The questions are mainly based only mechanism and sometimes on direct reactions.

When a methyl halide or primary alkyl halide reacts with a Lewis base such as sodium ethoxide, Lewis base replaces the halogen as halide. This is an example of a very general type of reaction, called a **nucleophilic substitution reaction,** or nucleophilic **displacement reaction** (S_N). The ethoxide ion is the nucleophile and it substitutes for the bromide which is called the leaving group.

$$\overset{\text{nucleophile}}{\overset{\downarrow}{Na^+CH_3CH_2O^-}} + \underset{\text{leaving group}}{\underset{\uparrow}{Br}}—CH_2CH_3 \longrightarrow CH_3CH_2O—CH_2CH_3 + Na^+Br^-$$

Alkyl halides react with a large number of nucleophilic reagents, both organic and inorganic, to form various other products. (Detailed mechanism of S_N1 and S_N2 was discussed in chapter "some basic principles of organic chemistry").

$$R—X \overset{\text{slow}}{\rightleftharpoons} \overset{\delta+}{R}\cdots\overset{\delta-}{X} \xrightarrow{\text{fast}} R^+ + X^- \xrightarrow[\text{fast}]{OH^-} R—OH$$

$$\left(\frac{dx}{dt}\right) = k[R—X], \text{ a case of } S_N1 \text{ reaction.}$$

The order of reactivity of alkyl halide for such reaction is 3° > 2° > 1° because 3° carbocation is most stable and involve as intermediate.

$$OH^- + R—X \overset{\text{slow}}{\rightleftharpoons} \overset{\delta-}{HO}\cdots R\cdots\overset{\delta-}{X} \xrightarrow{\text{fast}} R—OH + X^-$$

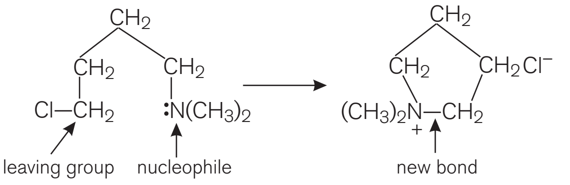
$$\left(\frac{dx}{dt}\right) = k[R—X]\,[OH^-], \text{ a case of } S_N2 \text{ reaction.}$$

The order of reactivity of alkyl halides for S_N2 reaction is 1° > 2° > 3° because transition state is involved which is more stable in case of unhindered carbons.

In all cases, X^- is a good leaving group which is in an increasing order (easiness, leaveability).

$$H^-, R^- <<< MeO^-, OH^- < CN^- < MeCOO^- < ROSO_2^-, ArSO_2O^-$$

Caution Point *The given reaction is an example of an intramolecular nucleophilic substituion reaction—a reaction in which the nucleophile and the leaving group are a part of the same molecule. In this case, S_N reaction causes ring formation.*



Some nucleophilic substitution reactions have been summarised below.

(i) **With aqueous alkali** It is also called "hydrolysis of alkyl halide".

$$RX + KOH(aq) \longrightarrow ROH + KX$$

(ii) **With moist silver oxide** Moist silver oxide is AgOH and the reactions look like

$$RX + AgOH \longrightarrow ROH + AgX$$

(iii) **With dry silver oxide** Ether are formed by heating alkyl halides with dry silver oxide.

$$2RX + Ag_2O \longrightarrow ROR + 2AgX$$

(iv) **With sodium alkoxide** This reaction is also called "Williamson's ether synthesis".

$$R'O^-Na^+ + R''X \longrightarrow R'OR'' + Na^+X^-$$

(v) **With NH_3** The reaction proceeds

$$RX + NH_3 \longrightarrow RNH_2 + HX;$$
$$RNH_2 + RX \longrightarrow R_2NH + HX$$
$$R_2NH + RX \longrightarrow R_3N + HX;$$
$$R_3N + RX \longrightarrow R_4N^+X^-$$

Thus, a mixture of primary amine (RNH_2), secondary amine (R_2NH), tertiary amine (R_3N) and quaternary ammonium salt ($R_4N^+X^-$) is obtained.

This reaction is called **Hofmann ammonolysis** of alkyl halides.

(vi) **With NaCN and AgCN** With NaCN, alkyl cyanide and with AgCN, alkyl isocyanide is produced. The reason is **electrovalent nature of NaCN and covalent linear structure of AgCN** as Ag—C≡N**:** Ag—C≡N etc., where Ag atom is linked to C and N both, thus both the isomers are possible. The reactions looks like

$$RX + Na^+CN^- \longrightarrow RCN + Na^+X^-$$

$$RX + AgCN \longrightarrow N \overset{\rightarrow}{\equiv} C + AgX$$

The cyanide obtained are of great importance and are used to prepare many other types of compounds.

1. Amides are obtained by partial hydrolysis of cyanides with alk. H_2O_2 or conc. HCl.

$$RC\equiv N + H_2O \xrightarrow[\text{or conc. HCl}]{\text{Alk. } H_2O_2} RCONH_2$$

2. Acids are obtained by hydrolysis of cyanides with mineral acids or alkalies.

$$RC\equiv N \xrightarrow[\text{conc. HCl}]{H_2O} RCONH_2 \xrightarrow{H_2O,\ \text{dil. HCl}} \underset{\text{acid}}{RCOOH} + NH_3$$

3. Primary amines are obtained by the reduction of cyanides with nascent hydrogen (Mendius reaction)

$$RC\equiv N + 4[H] \longrightarrow RCH_2NH_2$$

4. Aldehydes are obtained by partial reduction of cyanides with $SnCl_2$ and HCl and then steam distillation. (Stephen's reaction).

$$RC\equiv N + 2H \xrightarrow[\text{HCl}]{SnCl_2} R\text{—}CH{=}NH\cdot HCl \xrightarrow[H^+]{H_2O} RCHO + NH_4Cl$$

(vii) **With *R*COOAg** This reaction looks like

$$RCOO\,Ag + X\,R' \longrightarrow RCOOR' + AgX$$

(viii) **With sodium salt of alkynes** This method is used to prepare higher alkynes and has already been described in methods of preparation of alkynes.

(ix) **With KSH** The reaction looks like

$$R\,X + K\,SH \longrightarrow \underset{\substack{\text{thioalcohol or}\\ \text{mercaptan}}}{RSH} + KX$$

(x) **With K_2S** The reaction looks like

$$2RX + K_2S \longrightarrow \underset{\text{thioether}}{RSR} + 2KX$$

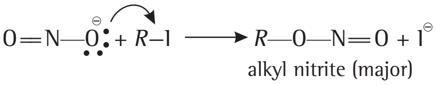
(xi) **With KNO_2 and $AgNO_2$** With KNO_2 (ionic), alkyl nitrites (R—O—N=O) and with $AgNO_2$ (covalent), nitro alkanes are produced.

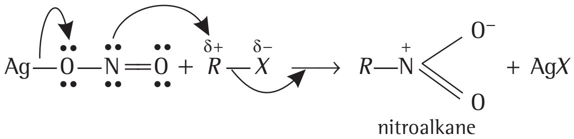
Alkali metal nitrites are predominantly ionic to give $NO_2^{\ominus}$ ion. The reaction can occur through either O or N, which can give both nitrites and nitro compounds. But since (C—O) bonds are stronger than (C—N) bonds, alkyl nitrites are the main products.

On the other hand, silver nitrite is a covalent compound and only electron pair of nitrogen is available for bond formation. As a result nitroalkanes are the chief products.

Silver nitrite exibits small amount of ionic character which also explains the formation of alkyl nitrite in small amount.

$$NaNO_2 \longrightarrow Na^+ + NO_2^{\ominus}$$





(xii) **With $(C_6H_5)_3P$** The reaction looks like

$$RX + (C_6H_5)_3P \longrightarrow [R(C_6H_5)_3P]^+X^-$$

(xiii) **With NaN_3** NaN_3 is the sodium salt of hydrazoic acid (HN_3) in which N have oxidation state of $-\frac{1}{3}$.

$$R\,\boxed{X + Na}\,N_3 \longrightarrow RN_3 + NaX$$

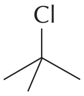
All the above written reactions proceed through S_N1 or S_N2 mechanisms depending upon the type of alkyl halide.

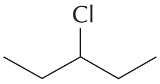
Sample Problem 2 *Which of the following alkyl halides will undergo S_N1 reaction most readily?* **[NCERT Exemplar]**

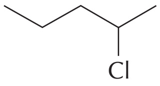
(*a*) $(CH_3)_3C$—F
(*b*) $(CH_3)_3C$—Cl
(*c*) $(CH_3)_3C$—Br
(*d*) $(CH_3)_3C$—I

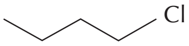
Interpret (*d*) Among the given $(CH_3)_3C-I$ is most reactive because C—I bond is weakest due to the large size of I atom among halogens.

Sample Problem 3 *In the following compounds which compound undergo faster S_N1 reaction?* **[NCERT]**

(*a*)


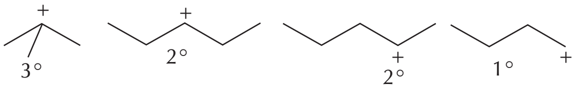
(*b*)


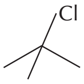
(*c*)


(*d*)


Interpret (*a*) In S_N1 mechanism, carbocation intermediate is involved, so the alkyl halide that gives more stable carbocation readily undergo faster S_N1 reaction.

The order of stability of carbocations is 3° > 2° > 1°



Thus,  readily undergoes S_N1 reaction.

Reduction

With Zn/acid or LiAlH$_4$ or catalytic hydrogenation Alkyl halides on reduction with these reagents give alkanes.

$$RX \xrightarrow[\text{or LiAlH}_4 \text{ or catalytic hydrogenation}]{\text{Zn/acid}} R\text{—H}$$

The reaction is completely described in alkanes (methods of preparation).

Reaction with Metals

(i) With Mg

The reactions proceed as

$$RX + \text{Mg} \xrightarrow{\text{Dry ether}} R\text{Mg}X \qquad \text{(Grignard's reagent)}$$

Reactivity order with Mg : $R\text{I} > R\text{Br} > R\text{Cl}$.

(ii) With Li

$$RX + 2\text{Li} \xrightarrow{\text{Dry ether}} \underset{\text{(alkyl lithium)}}{R\text{Li}} + \text{Li}X$$

The application of alkyl lithium is seen in **Corey House Synthesis** of late 1960s. The process can be summerised as

(i) $CH_3Br + 2Li \xrightarrow{\text{Ether}} CH_3Li + LiBr$

(ii) $2CH_3Li + CuI \xrightarrow{\text{Ether}} \underset{\text{lithium dimethyl cuperate}}{Li(CH_3)_2Cu} + LiI$

(iii) $Li(CH_3)_2Cu + CH_3CH_2Br \longrightarrow CH_3CH_2—CH_3 + CH_3Cu + LiBr$

(iii) With Na

$$2RX + 2\text{Na} \xrightarrow{\text{Dry ether}} \underset{\text{alkane}}{R\text{—}R} + 2\text{Na}X \qquad \text{(Wurtz reaction)}$$

Just like Wurtz reaction, **Wurtz-Fittig** and **Fittig reaction** are also given which looks like

(a) $C_6H_5X + 2Na + RX \xrightarrow{\text{Dry ether}} R — C_6H_5 + 2NaX$

It is **Wurtz-Fittig reaction.**

(b) $2C_6H_5X + 2Na \xrightarrow{\text{Dry ether}} C_6H_5 — C_6H_5 + 2NaX$

This is **Fittig reaction.**

TEL (tetra ethyl lead) the antiknock compound of petroleum industry is produced as

$$4C_2H_5Cl + 4Na / 4Pb \longrightarrow (C_2H_5)_4Pb + 4NaCl + 3Pb$$

(iv) With Zn

$$2\ RX + \text{Zn} \xrightarrow[\text{ether}]{\text{Dry}} \underset{\text{alkane}}{R\text{—}R} + \text{Zn}X_2 \qquad \text{(Frankland reaction)}$$

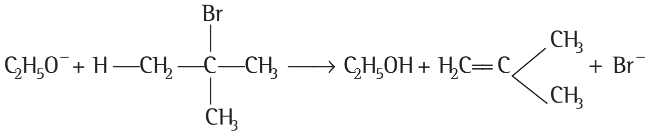
(Zn also form organometallic compounds like RMg but its reactivity is less than Mg).

Hot Spot 2

ELIMINATION Reactions

It is also an important topic of the chapter for JEE Main examination. Many a times question is from this topic. However the level of question is generally typical as it also involve stereo chemistry of the reaction.

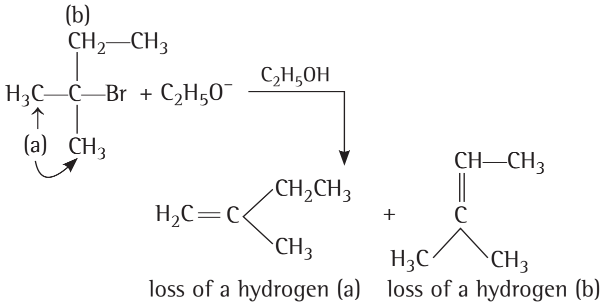
When an alkyl halide (better a tertiary one) reacts with a Bronsted base (such as ethoxide ion ($C_2H_5O^-$), elimination reaction takes place in which two or more groups are lost from the same molecule (in the following case H and Br).



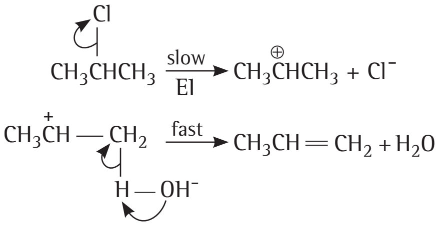
$$C_2H_5O^- + H—CH_2—\overset{\overset{\large Br}{|}}{\underset{\underset{\large CH_3}{|}}{C}}—CH_3 \longrightarrow C_2H_5OH + H_2C{=}C(CH_3)_2 + Br^-$$

Remember! OH^- is used in aqueous solution (H_2O). $C_2H_5O^-$ (ethoxide ion) is used in ethanol (C_2H_5OH). $(CH_3)_3CO^-$ (*tert*-butoxide ion) is used in *tert*-butyl alcohol [$(CH_3)_3COH$].

If there are more than one β hydrogen, it results in more than one elimination products as

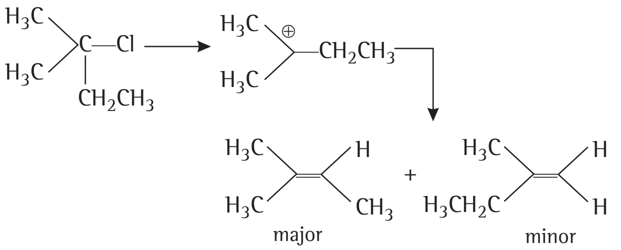


Elimination can be E1 (unimolecular elimination) in which alkyl halide dissociates first to form carbocation and halide ion.



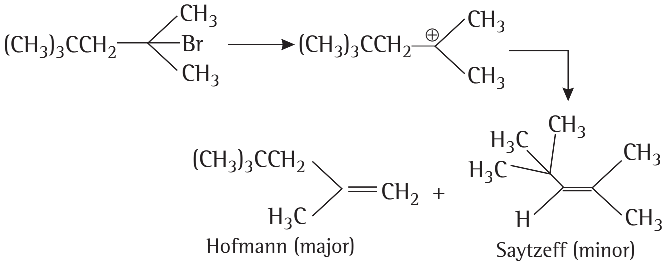
The order of reactivity of alkyl group is; tertiary > secondary > primary, since, the rate-determining step is the formation of a carbocation, which has stability in order; 3° > 2° > 1°.

Most substituted alkene is the Saytzeff product and less substituted alkene is the Hofmann product.



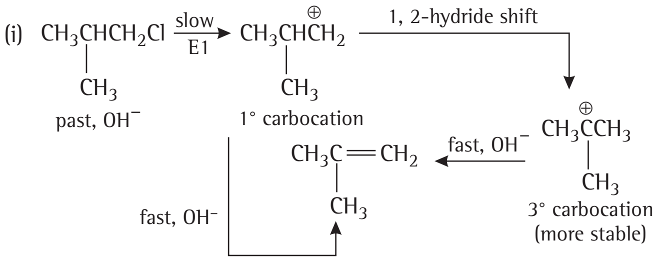
However, when the product of Saytzeff elimination is more sterically compressed, the less substituted alkene may be formed.

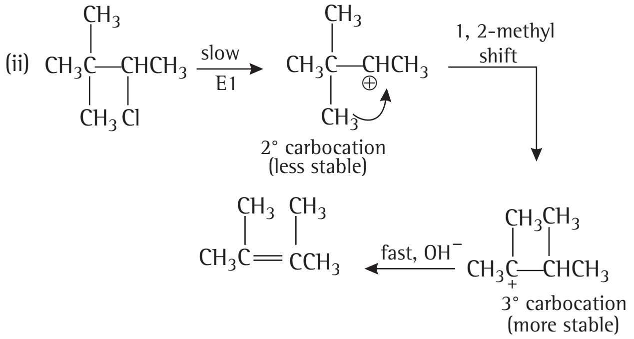
Saytzeff product has significant repulsive forces between the hydrogens on the *t*-butyl group and those on the methyl group *cis* to it.



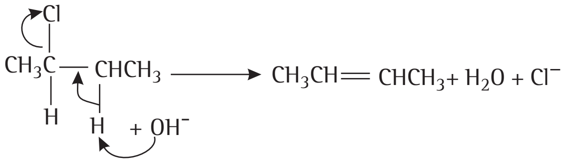
The carbocation may not only eliminate but may also add a nucleophilic species to give a substitution product by S_N1 reaction. The E1 and S_N1 reactions are therefore, competitive.

There can be 1, 2-hydride or 1, 2-methyl shift to attain greater stability of carbocation.

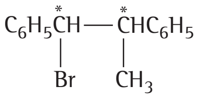




Elimination can be E$_2$ (bimolecular elimination)

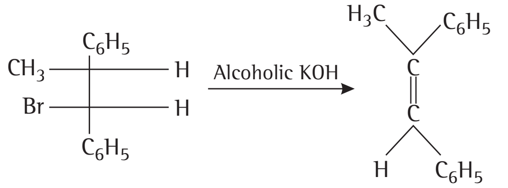


Reactivity towards E2 or E1 elimination is 3° > 2° > 1° alkyl halides. E2 elimination is stereospecific. 1-bromo-1,2-diphenyl propane contains two chiral carbon atoms (*)

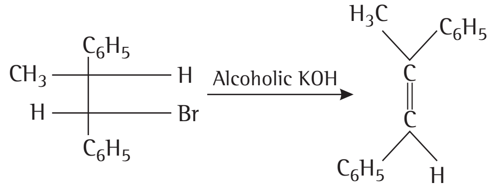


$$C_6H_5\overset{*}{C}H(Br)—\overset{*}{C}H(CH_3)C_6H_5$$

Dehydrohalogenation follows *trans*-**elimination.**

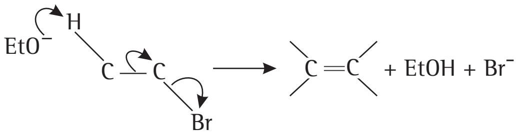


cis-1,2-diphenyl-1-propene



trans

E2 reaction is facilitated by attack by a base on the hydrogen atom which is to be removed.



Reaction rate increases with the increasing strength of the base

$$CH_3CO_2^- < OH^- < EtO^- < Me_3CO^- < NH_2^-$$

The ease of the E2 reaction on alkyl halides is —I > —Br > —Cl > —F (bond strengths being in order C — F > C — Cl > C — Br > C — I) and amongst the alkyl groups, the order of reactivity is

tertiary > secondary > primary.

$$(CH_3)_3C—Br \xrightarrow{EtO^-} (CH_3)_2C{=}CH_2 \text{ faster than}$$

$$(CH_3)_2CH—Br \xrightarrow{EtO^-} CH_3CH{=}CH_2 \text{ faster than}$$

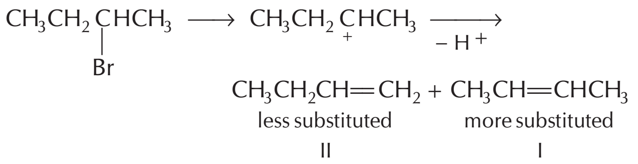
$$CH_3CH_2—Br \xrightarrow{EtO^-} CH_2{=}CH_2$$

A nucleophile is also a base, so that E2 reaction competes with substitution.

Sample **Problem 4** *Ellimination of bromine from 2-bromobutane results in the formation of*

- (a) *predominantly 2-butyne*
- (b) *predominantly -1-butene*
- (c) *predominantly 2-butene*
- (d) *equimolar mixture of 1- and 2 butene*

Interpret (c)



$$CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3 \longrightarrow CH_3CH_2\underset{+}{C}HCH_3 \xrightarrow[-H^+]{} \underset{\substack{\text{less substituted}\\ \text{II}}}{CH_3CH_2CH{=}CH_2} + \underset{\substack{\text{more substituted}\\ \text{I}}}{CH_3CH{=}CHCH_3}$$

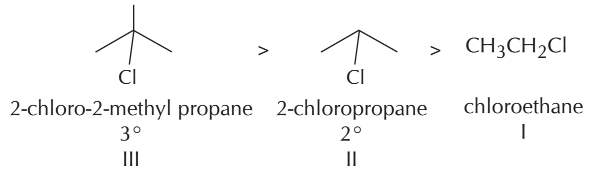
Stability of I > II, hence I is the predominant product.

Sample **Problem 5** *The ease of dehydrohalogenation with alcoholic KOH in case of chloroethane (I), 2-chloropropane (II) and 2-chloro-2-methylpropane (III) is of the order*

- (a) *III > II > I*
- (b) *I > II > III*
- (c) *II > I > III*
- (d) *I > III > II*

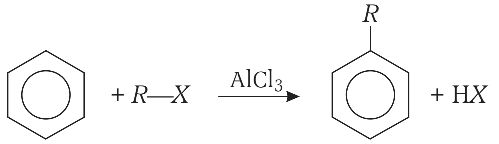
Interpret (a) Dehydrohalogenations are also called β-elimination reaction and for such reactions, the reactivity of haloalkanes towards elimination reaction is

3° > 2° > 1°



Friedel-Craft Alkylation

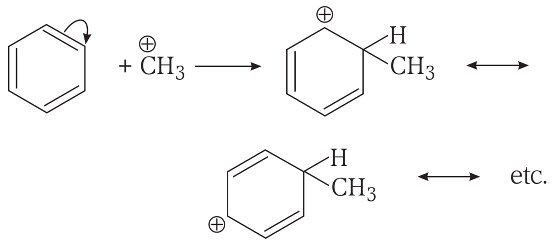
Alkyl benzene are the product of this reaction. The reaction takes place as



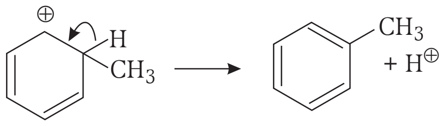
Intermediate is σ complex stabilised by resonance.

Function of anhydrous $AlCl_3$ (Lewis acid) is to generate electrophile, which is carbocation in this case. It is thus, S_E reaction.

$$CH_3Cl + AlCl_3 \longrightarrow AlCl_4^{\ominus} + \overset{\oplus}{C}H_3$$

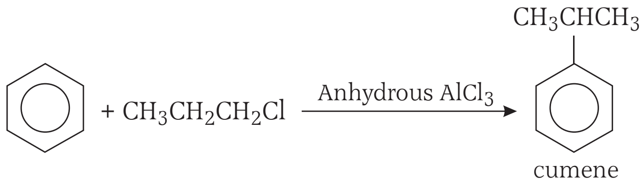


σ complex (stable due to resonance)



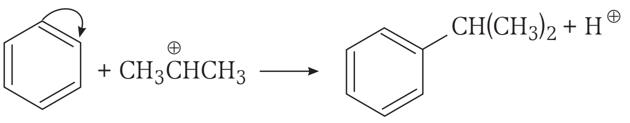
$$H^{\oplus} + AlCl_4^{\ominus} \longrightarrow AlCl_3 + HCl$$

In the carbocation, there may be 1, 2-hydride or 1, 2-methyl shift to attain its greater stability.



$$CH_3CH_2CH_2Cl + AlCl_3 \longrightarrow CH_3CH_2\underset{1^\circ}{\overset{\oplus}{C}}H_2 + AlCl_4^{\ominus}$$

$$CH_3CH_2\overset{\oplus}{C}H_2 \xrightarrow{\text{1,2-hydride shift}} \underset{\substack{2^\circ\\ \text{(more stable than 1°)}}}{CH_3\overset{\oplus}{C}HCH_3}$$



This reaction can also be extended to alkylation of alkenes.

$$(CH_3)_3\,C—Cl + CH_2{=}CH_2 \xrightarrow{AlCl_3,\ 263\ K} (CH_3)_3CCH_2CH_2Cl$$

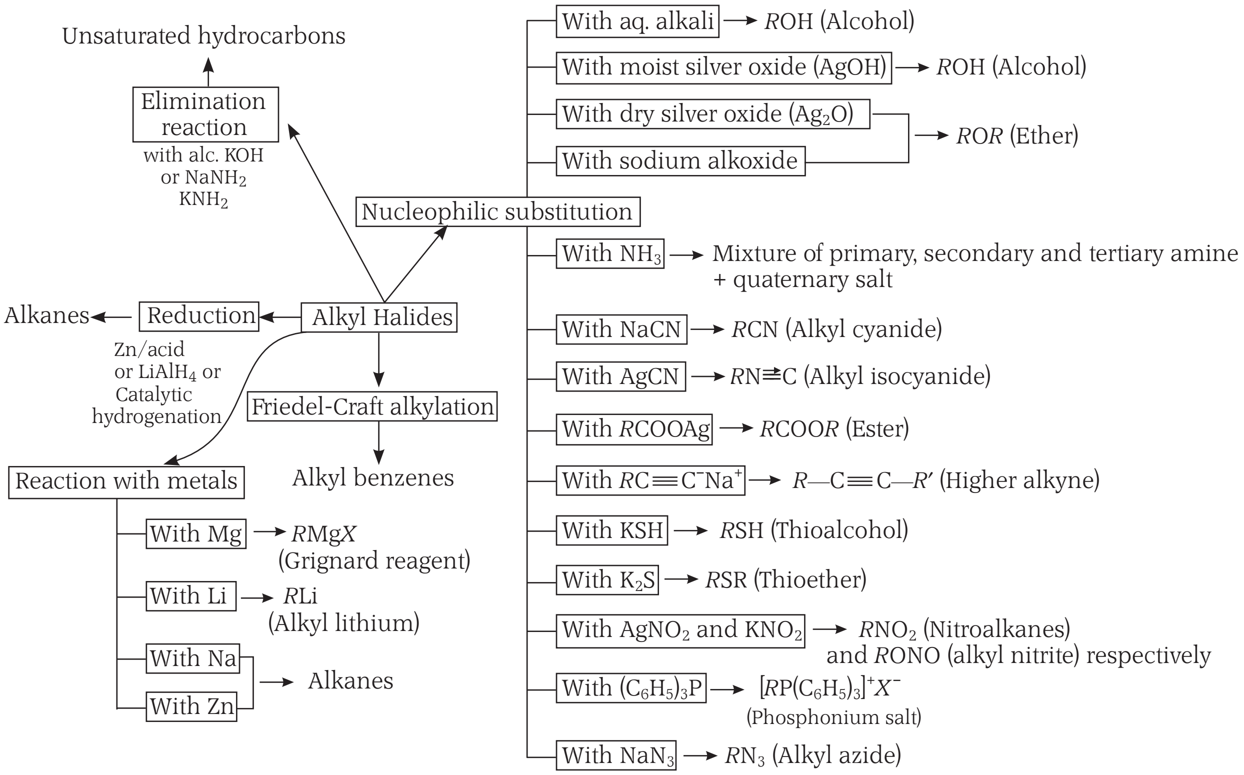
$$(CH_3)_3\,C—Cl + AlCl_3 \xrightarrow[-AlCl_4^{\ominus}]{} (CH_3)_3C^{\oplus}$$

$$(CH_3)_3C^{\oplus} + CH_2{=}CH_2 \longrightarrow (CH_3)_3CCH_2CH_2^{\oplus}$$

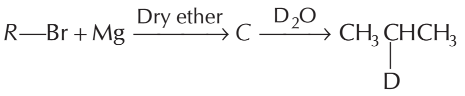
$$(CH_3)_3\,CCH_2CH_2^{\oplus} + AlCl_4^{\ominus} \longrightarrow (CH_3)_3CCH_2CH_2Cl + AlCl_3$$

This reaction is described fully in properties of benzene and for meachanism see some basic principles of organic chemistry also.

The outline of chemical properties of monohalogen derivatives looks like



Sample Problem 6 *Identify C in the following reaction sequence.* **[NCERT]**



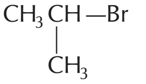
$$R\text{—Br} + \text{Mg} \xrightarrow{\text{Dry ether}} C \xrightarrow{D_2O} CH_3\underset{\underset{D}{|}}{C}HCH_3$$

(a) $(CH_3)_2\,CHMgBr$

(b) $CH_3\ CH_2CH_2MgBr$

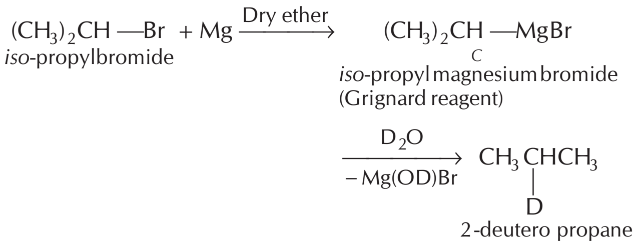
(c) $(CH_3)_3\ CMgBr$

(d)



$$CH_3\underset{\underset{CH_3}{|}}{C}H\text{—Br}$$

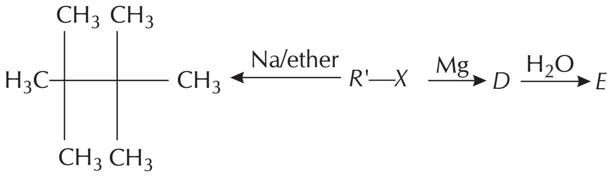
Interpret (a) Since the product contains three carbon atoms, so there must be three C atoms in '*C*'. Moreover, D gets attached to second carbon atom. So, —MgBr must be at second carbon atom. So, *R* is $(CH_3)_2CH$— and *C* is $(CH_3)_2CHMgBr$.



$$\underset{\textit{iso}\text{-propylbromide}}{(CH_3)_2CH\text{—Br}} + \text{Mg} \xrightarrow{\text{Dry ether}} \underset{\substack{C \\ \textit{iso}\text{-propyl magnesium bromide} \\ \text{(Grignard reagent)}}}{(CH_3)_2CH\text{—MgBr}}$$

$$\xrightarrow[-\,Mg(OD)Br]{D_2O} \underset{\text{2-deutero propane}}{CH_3\underset{\underset{D}{|}}{C}HCH_3}$$

Sample Problem 7 *E in the following reaction sequence is* **[NCERT]**



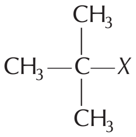
(a) *propane*

(b) *butane*

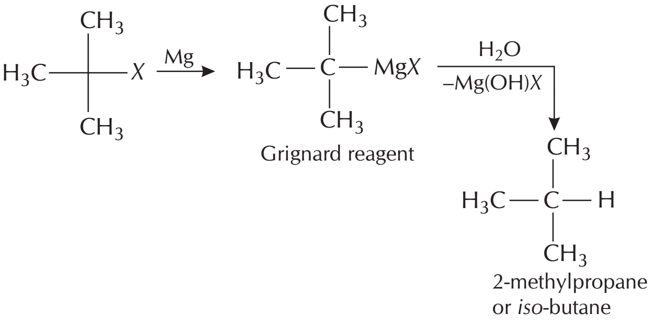
(c) *isobutane*

(d) *Neo-pentane*

Interpret (c) Since, *R′* — *X* gives $(CH_3)C\text{—}C(CH_3)_3$ when subjected to Wurtz reaction. So, *R′* must be $(CH_3)_3C$— group. Hence, *R′*—*X* must be



$$CH_3\text{—}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\text{—}X$$



$$H_3C-C(CH_3)_2-X \xrightarrow{Mg} \underset{\text{Grignard reagent}}{H_3C-C(CH_3)_2-MgX} \xrightarrow[-Mg(OH)X]{H_2O} \underset{\text{2-methylpropane or } iso\text{-butane}}{H_3C-C(CH_3)_2-H}$$

Check Point 1

1. Why is allyl alcohol more reactive than propane-2-ol towards HCl?
2. Protonation of alcohol is a Bronsted Lowry acid-base reaction as well as a Lewis acid-base reaction. Explain.
3. Alkyl halides, though polar, are insoluble in water, Explain.
4. CH_3CH_2OH does not react with NaBr but on adding H_2SO_4, CH_3CH_2Br is formed. Explain.
5. Although the C—I bond is longer than a C—Cl bond, the C—Cl bond has a larger dipole moment. Explain.
6. KCN reacts with *R*I to form alkyl cyanide while AgCN gives isocyanides as a major product in the same reaction. Explain.

10.4 Dihaloalkanes

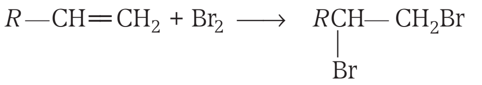
In these compounds two halogen atoms are present in a molecules. They may occupy the same place or different place. They have the general formula $C_nH_{2n}X_2$.

Methods of Preparation

Following methods can be employed to prepare dihalogen derivatives of alkanes.

(a) Addition Reactions

(i) **Addition of Br_2 to alkenes** This reaction gives *vic* dihalides.

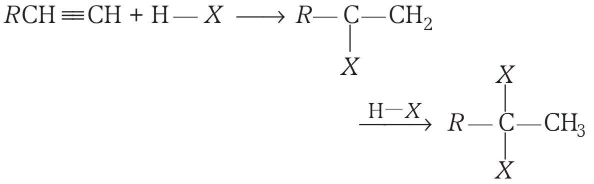


$$R-CH{=}CH_2 + Br_2 \longrightarrow RCH(Br)-CH_2Br$$

alkylene bromide
(*vic* dihalides)

(*gem*-dihalides are not prepared by this method.)

(ii) **Addition of halogen acids to alkynes** By this method only *gem* dihalides can be prepared.

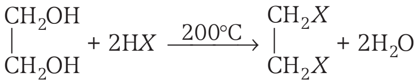


$$RCH{\equiv}CH + H-X \longrightarrow R-C(X){=}CH_2 \xrightarrow{H-X} R-CX_2-CH_3$$

gem-dihalide

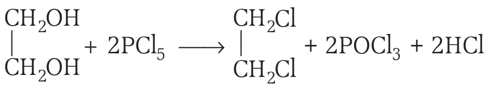
(b) Substitution Reactions

(i) **Reaction of glycol with H*X*** This method gives *vic* dihalides.



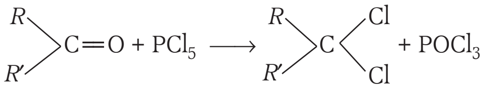
$$\begin{matrix}CH_2OH\\ |\\ CH_2OH\end{matrix} + 2HX \xrightarrow{200°C} \begin{matrix}CH_2X\\ |\\ CH_2X\end{matrix} + 2H_2O$$

(ii) **Reaction of glycol with PCl_5** This method also gives only *vic* dihalides.



$$\begin{matrix}CH_2OH\\ |\\ CH_2OH\end{matrix} + 2PCl_5 \longrightarrow \begin{matrix}CH_2Cl\\ |\\ CH_2Cl\end{matrix} + 2POCl_3 + 2HCl$$

(iii) **Reaction of aldehydes and ketones with PCl_5** By this method *gem*-dihalides are prepared.



$$RR'C{=}O + PCl_5 \longrightarrow RR'CCl_2 + POCl_3$$

(where, *R′* = H or alkyl group)

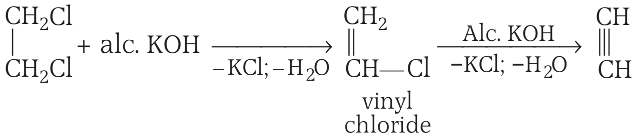
Physical and Chemical Properties

(a) Physical Properties

These are colourless, sweet smelling liquids. The boiling points of CH_2Cl_2 is 313K. Because of its low boiling point and low inflammability, it is an effective extraction solvent used in pharamaceutical and food industries.

(b) Reaction with Alcoholic KOH

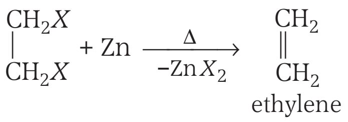
This is a dehydrohalogenation reaction. Both *gem*-dihalides and *vic* dihalides give alkynes as final product when treated with alc. KOH.



$$\begin{matrix}CH_2Cl\\ |\\ CH_2Cl\end{matrix} + \text{alc. KOH} \xrightarrow[-KCl;\,-H_2O]{} \underset{\text{vinyl chloride}}{\begin{matrix}CH_2\\ \|\\ CH-Cl\end{matrix}} \xrightarrow[-KCl;\,-H_2O]{\text{Alc. KOH}} \begin{matrix}CH\\ |||\\ CH\end{matrix}$$

(c) Reaction with Zn Dust

Gem and *vic*-dihalides when heated with Zn dust, give alkenes by losing both the halogen atoms. Thus, it is a dehalogenation reaction.

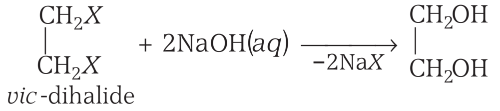


$$\begin{matrix}CH_2X\\ |\\ CH_2X\end{matrix} + Zn \xrightarrow[-ZnX_2]{\Delta} \underset{\text{ethylene}}{\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix}}$$

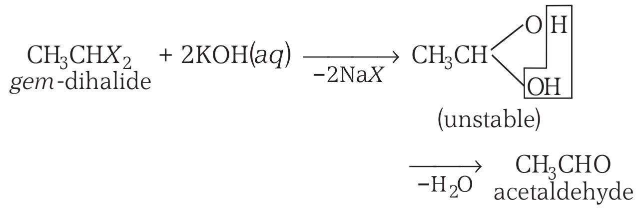
$$CH_3-CHX_2 + Zn \xrightarrow[-ZnX_2]{\Delta} \underset{\text{ethylene}}{CH_2{=}CH_2}$$

(d) Reaction with Aqueous Alkali

vic-dihalides give glycol while *gem*-dihalides give ketones when treated with aqueous alkali. *e.g.,*



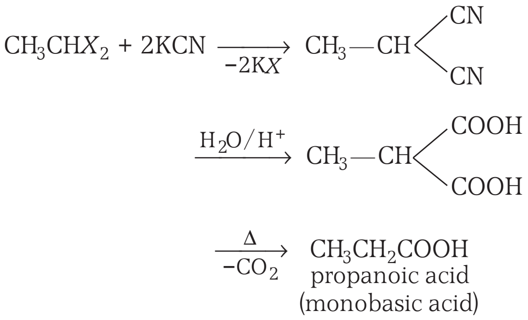
$$\underset{vic\text{-dihalide}}{\begin{matrix}CH_2X\\|\\CH_2X\end{matrix}} + 2NaOH(aq) \xrightarrow[-2NaX]{} \begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}$$



$$\underset{gem\text{-dihalide}}{CH_3CHX_2} + 2KOH(aq) \xrightarrow[-2NaX]{} \underset{\text{(unstable)}}{CH_3CH\begin{matrix}OH\\OH\end{matrix}} \xrightarrow[-H_2O]{} \underset{\text{acetaldehyde}}{CH_3CHO}$$

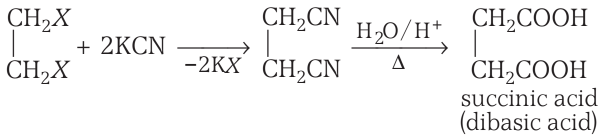
(e) Reaction with KCN Followed by Hydrolysis and Heating

Gem-dihalides when treated with KCN, form alkylidene cyanide which on hydrolysis and heating gives monobasic acid as



$$CH_3CHX_2 + 2KCN \xrightarrow[-2KX]{} CH_3{-}CH\begin{matrix}CN\\CN\end{matrix} \xrightarrow{H_2O/H^+} CH_3{-}CH\begin{matrix}COOH\\COOH\end{matrix} \xrightarrow[-CO_2]{\Delta} \underset{\substack{\text{propanoic acid}\\\text{(monobasic acid)}}}{CH_3CH_2COOH}$$

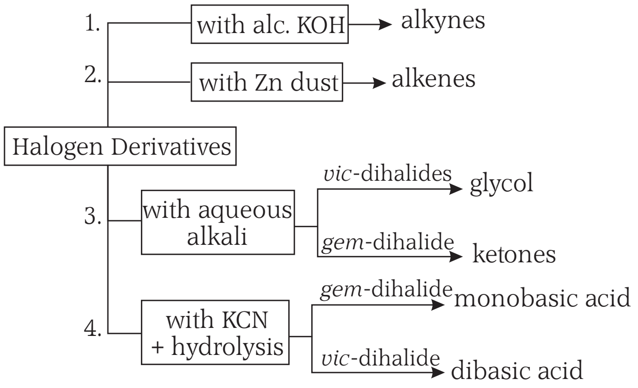
vic-dihalides on the other hand, when subjected to the same procedure give dibasic acid.



$$\begin{matrix}CH_2X\\|\\CH_2X\end{matrix} + 2KCN \xrightarrow[-2KX]{} \begin{matrix}CH_2CN\\|\\CH_2CN\end{matrix} \xrightarrow[\Delta]{H_2O/H^+} \underset{\substack{\text{succinic acid}\\\text{(dibasic acid)}}}{\begin{matrix}CH_2COOH\\|\\CH_2COOH\end{matrix}}$$

(The dibasic acid having —COOH group at successive carbon atoms, do not lose —CO_2 on heating.)

The outlines of their chemical reactions looks as



10.5 Trihaloalkanes

These compounds are commonly called haloforms, *i.e.,* chloroform, bromoform, iodoform etc., and have general formula CHX_3 (where, X = Cl, Br, I). Chloroform is the first discovered haloform.

Methods of Preparation

The important methods used to prepare haloform are as follows

(a) Halogenation of Alkanes

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl \xrightarrow{Cl_2/h\nu} CH_2Cl_2 \xrightarrow{Cl_2/h\nu} \underset{\text{chloroform}}{CHCl_3}$$

It is fully described in the properties of alkanes (halogenation) for mechanism see free radical mechanism chapter 'some basic principles' of organic chemistry.

(b) Reaction of Ethanol or Acetone with Aqueous Na_2CO_3 and KI

$$\text{Ethanol or acetone} + Na_2CO_3 + KI \xrightarrow[60\text{–}70°]{\text{Electrolysis}} \underset{\text{yellow ppt.}}{CHI_3\downarrow}$$

The complete reaction looks like

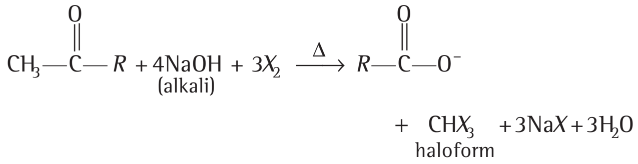
$$CH_3CH_2OH + 4I_2 + 3Na_2CO_3 \longrightarrow \underset{\text{iodoform}}{CHI_3} + HCOO^-Na^+ + 5NaI + 2H_2O + 3CO_2$$

Hot Spot 3

HALOFORM Reaction

This reaction is also important for JEE Main examination. Many times questions is based on it. The level of question vary from easy to average.

When methyl ketone or 2° alcohol having $CH_3\underset{\substack{|\\OH}}{CH}—$ group or ethyl alcohol is treated with halogen, in the presence of alkali, haloform is obtained. The reaction is called haloform reaction.

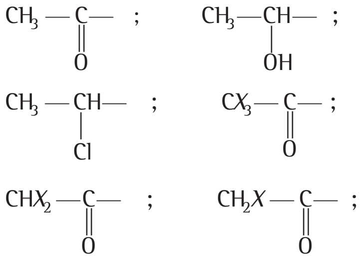


$$CH_3—\overset{\substack{O\\\|}}{C}—R + \underset{\text{(alkali)}}{4NaOH} + 3X_2 \xrightarrow{\Delta} R—\overset{\substack{O\\\|}}{C}—O^- + \underset{\text{haloform}}{CHX_3} + 3NaX + 3H_2O$$

Important facts related to haloform reaction are as

(i) KOH may also be used as alkali.

(ii) The compounds which can give this test must contain either one of these :



$$CH_3—\underset{\substack{\|\\O}}{C}— \;;\quad CH_3—\underset{\substack{|\\OH}}{CH}— \;;$$
$$CH_3—\underset{\substack{|\\Cl}}{CH}— \;;\quad CX_3—\underset{\substack{\|\\O}}{C}— \;;$$
$$CHX_2—\underset{\substack{\|\\O}}{C}— \;;\quad CH_2X—\underset{\substack{\|\\O}}{C}— \;;$$

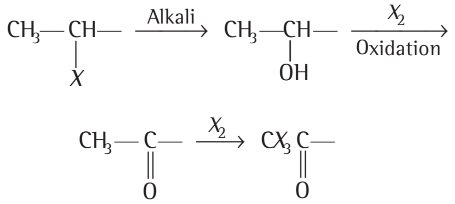
i.e., any compound containing $CH_3CO—$ group or any compound which on oxidation give such group or their halogen derivatives in which halogen is substituted from CH_3 group give this reaction.

(iii) $CH_3CO\underset{\substack{\uparrow\\\text{Active methylene group}}}{CH_2}COOC_2H_5$ does not give haloform reaction inspite of the presence of $CH_3CO—$ group in it. The reason is the presence of active methylene $—CH_2—$ group which prevents the conversion of $CH_3CO—$ to $CX_3CO—$ (a necessity for the reaction).

(iv) The outline of the mechanism is seen as

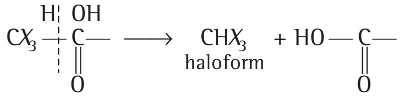
Step I Halogen first oxidises (only in case of alcohols to carbonyl compounds) and then halogenated the compound to get $CX_3\underset{\substack{\|\\O}}{C}—$ group. (If $CH_3—\underset{\substack{|\\X}}{CH}—$ is taken it is first converted to $CH_3—\underset{\substack{|\\OH}}{CH}—$ by alkali and oxidised followed by halogenation)

i.e.,



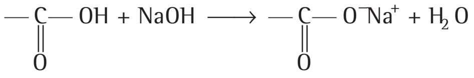
$$CH_3—\underset{\substack{|\\X}}{CH}— \xrightarrow{\text{Alkali}} CH_3—\underset{\substack{|\\OH}}{CH}— \xrightarrow[\text{Oxidation}]{X_2}$$
$$CH_3—\underset{\substack{\|\\O}}{C}— \xrightarrow{X_2} CX_3\underset{\substack{\|\\O}}{C}—$$

Step II This $CX_3—\underset{\substack{\|\\O}}{C}—$ is then hydrolysed by alkali as



$$CX_3 \overset{H\;\vdots\;OH}{—\!\!\!\vdots\!\!\!—}\underset{\substack{\|\\O}}{C}— \longrightarrow \underset{\text{haloform}}{CHX_3} + HO—\underset{\substack{\|\\O}}{C}—$$

Step III The $—\underset{\substack{\|\\O}}{C}—OH$ is further reacts with alkali to give salt and water as



$$—\underset{\substack{\|\\O}}{C}—OH + NaOH \longrightarrow —\underset{\substack{\|\\O}}{C}—O^-Na^+ + H_2O$$

Reaction of Bleaching Powder with Ethyl Alcohol or Acetone

It is a modified form of haloform reaction in which bleaching powder ($CaOCl_2$) works as the source of halogen (Cl_2) and weak base ($Ca(OH)_2$) as

$$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

Rest of the reaction is same, *i.e.*,

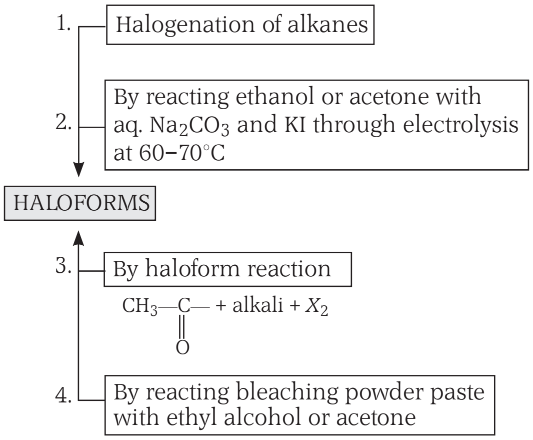
$$CH_3COCH_3 + 3Cl_2 \longrightarrow CCl_3COCH_3 + 3HCl$$

$$2CCl_3COCH_3 + Ca(OH)_2 \xrightarrow{\text{Hydrolysis}} \underset{\text{chloroform}}{2CHCl_3} + (CH_3COO)_2Ca$$

The reaction is used for the preparation of only $CHCl_3$.

Caution Point *Preparation of chloroform from alcohol and bleaching powder involves three steps, viz, oxidation, chlorination and hydrolysis.*

The outline of methods of preparation looks like

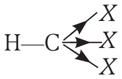


Physical Properties

1. $CHCl_3$ and $CHBr_3$ are sickly smelling liquid, while CHI_3 is in the form of yellow, hexagonal plates.
2. Their boiling point increases with increase in mol. wt. [$CHCl_3$ 334K, $CHBr_3$ 422.5 K and CHI_3 392 K mp].
3. $CHCl_3$ and $CHBr_3$ are sparingly soluble in water but more soluble in organic solvents, CHI_3 is insoluble in H_2O but soluble in ether and ethanol.

Chemical Properties

Before going into detail of reactions, remember the presence of three halogen atoms distort the trihalogen compounds molecule. Their dipole moments are very high and the structure looks like



Thus, here the C—H bond is polar and can be easily broken with the help of any base, resulting to dihalocarbenes as for $CHCl_3$

$$CHCl_3 + \bar{O}H \rightleftharpoons :\bar{C}Cl_3 + H_2O$$

$$:\bar{C}Cl_3 \longrightarrow \underset{\text{dichlorocarbene}}{:CCl_2} + Cl^-$$

This dihalocarbene is a very good electrophile and most of the reaction of trihalogen derivatives are attributed to it. Their reactivity order follows

$$CHI_3 > CHBr_3 > CHCl_3 >> CHF_3$$

This is because the C—I bond is less stable as compared to C— Cl or C—F bond.

(a) Oxidation

Chloroform is so sensitive to oxygen that it autoxidises in the presence of sunlight with air only and result in the formation of phosgene (carbonyl chloride) gas.

$$CHCl_3 + \frac{1}{2}O_2 \longrightarrow COCl_2 + HCl$$

The phosgene gas formed is extremely poisonous. To retard this oxidation we use 1% C_2H_5OH which converts poisonous phosgene to non-poisonous ethyl carbonate.

$$COCl_2 + 2C_2H_5OH \longrightarrow \underset{\text{ethyl carbonate}}{(C_2H_5O)_2CO} + 2HCl$$

(b) Reduction

On using simple reducing agents/molecular H_2 with **catalyst, dihalogen** and **monohalogen derivatives** of alkanes along with **alkanes can** be produced.

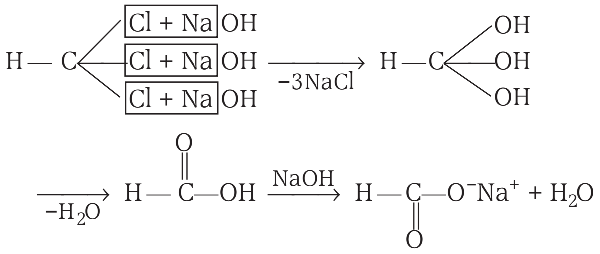
$$CH_4 \xleftarrow[-HCl]{Zn/H_2O} CHCl_3 \xrightarrow{Zn/HCl-C_2H_5OH} CH_2Cl_2$$

(c) Hydrolysis

Sodium or potassium salt of acid is obtained.

$$CHCl_3 + 4NaOH \longrightarrow HCOO^-Na^+ + 3NaCl + 2H_2O$$

The reader can grasp it as



$$\xrightarrow[-H_2O]{} H—\overset{\overset{O}{\|}}{C}—OH \xrightarrow{NaOH} H—\underset{\underset{O}{\|}}{C}—O^-Na^+ + H_2O$$

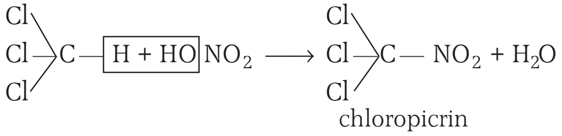
(d) Halogenation

On further halogenation $CHCl_3$ results in the formation of CCl_4.

$$\underset{\text{chloroform}}{CHCl_3} \xrightarrow{Cl_2/h\nu} \underset{\text{tetrachloromethane (pyrene)}}{CCl_4}$$

(e) Nitration

It results in the formation of chloropicrin, which is also called tear gas.



Chloropicrin (nitro chloroform) is used as **insecticide** and **a war gas.**

(f) **With Ag**

(See, Alkynes method of preparation) The reaction looks as

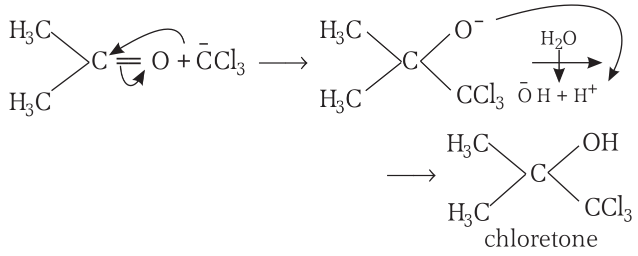
$$CHCl_3 + Ag \longrightarrow \underset{\text{alkyne}}{CH \equiv CH}$$

It is an example of dehalogenation reaction.

(g) With Acetone

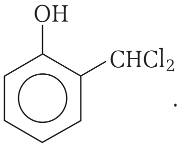
The reaction occurs in alkaline medium and $\bar{C}Cl_3$ attacks at $\rangle C{=}O$ group of acetone as a nucleophile *i.e.,*

$$CHCl_3 + \bar{O}H \longrightarrow \bar{C}Cl_3 + H_2O$$

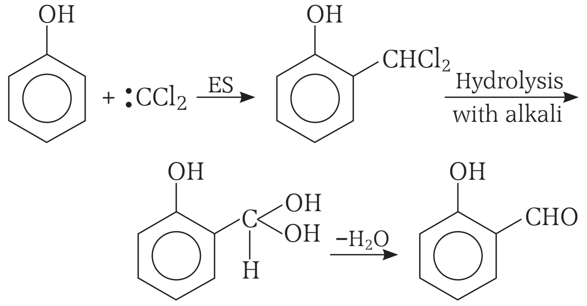


Chloretone is a sleep inducing medicine, (*i.e.,* hypnotic).

(h) **Reimer-Tiemann Reaction**

The attacking electrophile in this reaction is $:CCl_2$ (dichlorocarbene) which attacks itself to benzene ring through electrophilic substitution to give .

This compound undergoes hydrolysis due to the presence of electrophile to give salicylaldehyde. Thus ,



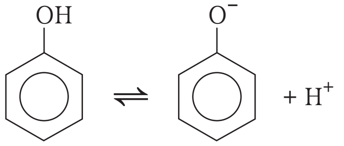
salicylaldehyde

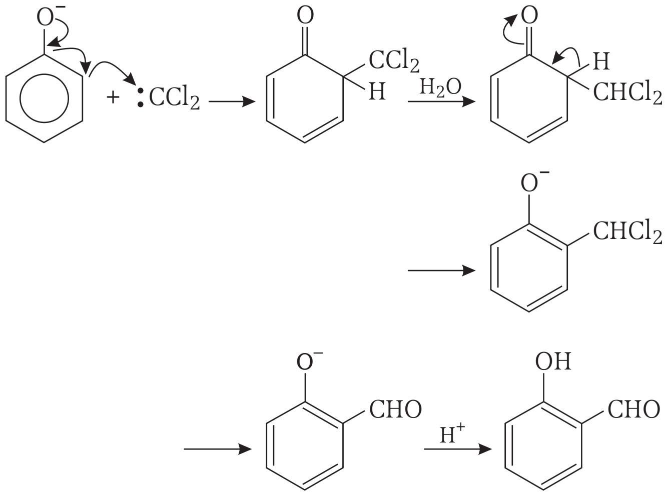
The mechanism of the reaction can be seen as

Step I $CHCl_3 + OH^- \rightleftharpoons :CCl_3^- + H_2O$

$:CCl_3^- \longrightarrow :CCl_2 + Cl^-$

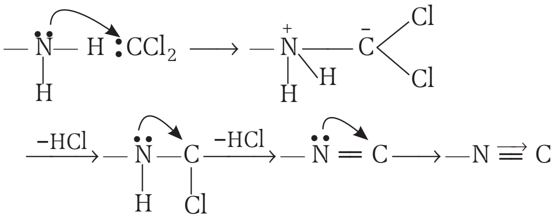
Step II





(i) **Carbylamine Reaction**

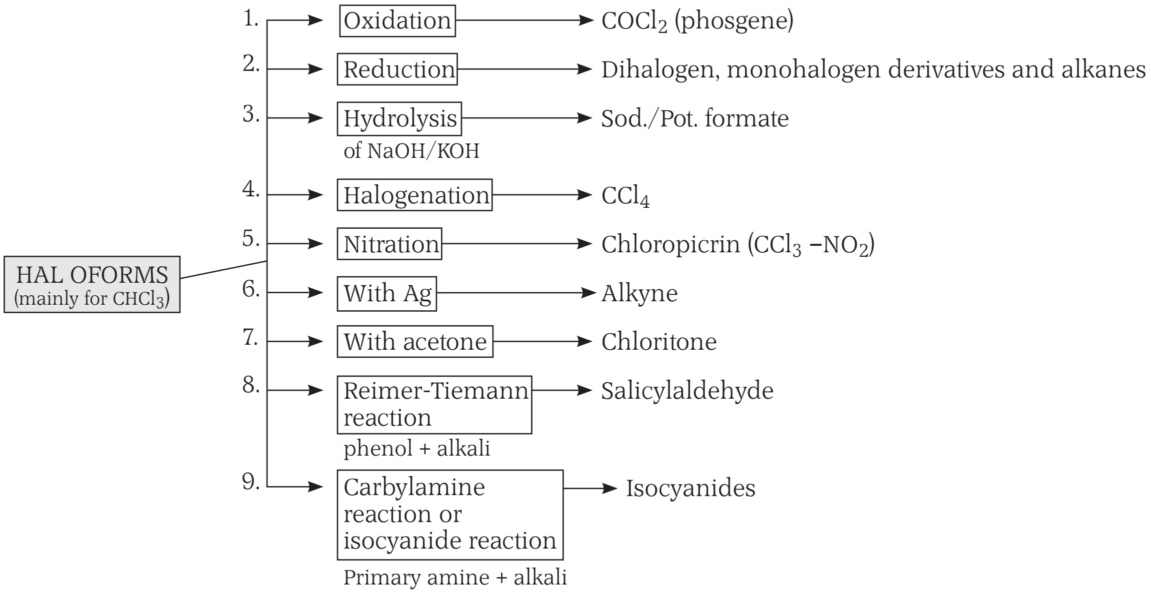
The attacking reagent in this reaction is also $:CCl_2$ which attacks on the lone pair of nitrogen of amino group as



The complete reaction is as

$$CHCl_3 + 3KOH + RNH_2 \xrightarrow{\Delta} \underset{\substack{\text{isocyanide or}\\ \text{carbylamine}}}{RNC} + 3KCl + 3H_2O$$

The outline of their chemical properties can be summarised as



Uses of Haloforms

The important applications of haloforms are as

1. Chloroform is used for the synthesis of drug like chloretone and insecticide like chloropicrin. Moreover, it can be used as an anaesthetic but because of its harmful effects it is not used for this purpose now a days.
2. Chloroform is used as a solvent for fats, waxes, rubber, iodine etc.
3. Iodoform is extensively used as an antiseptic for wounds. Its antiseptic action is due to liberation of free iodine, not because of the iodoform itself.

Environmental Effects of Trihalomethanes (THMs)

THMs (trihalomethanes) are also environmental pollutants, and many are considered **carcinogenic.**

Their adverse effect on environment are as follows

1. **Trifluoromethane** and **chlorodifluoromethane** are both used as **refrigerants** in some applications. Trihalomethanes released to the environment break down faster than **chlorofluorocarbons** (CFCs), thereby doing much less damage to the **ozone layer** (if they contain chlorine). However, fluoroform is not ozone depleting.

   Unfortunately, the breakdown of trihalomethane HCFCs does still result in the creation of some free chlorine radicals in the upper atmosphere and subsequent ozone destruction. Ideally, HCFCs will be phased out entirely in favour of entirely non-chlorinated refrigerants.
2. Chloroform is a very common **solvent** used in organic chemistry. It is a significantly less **polar** solvent than water, well-suited to dissolving many **organic compounds.** Although still toxic and potentially carcinogenic, chloroform is significantly less harmful than **carbon tetrachloride.** Because of the health and regulatory issues associated with the use of carbon tetrachloride, in modern chemistry laboratories. chloroform is used as a cheaper, cleaner alternative wherever possible.
3. **Chloroform** is also formed in **swimming pools** which are disinfected with **chlorine** or **hypochlorite** in the **haloform reaction** with organic substances (**urine, sweat** and **skin** particles). The reaction to **phosgene** under the influence of UV is also possible.
4. Some of the THMs are quite volatile and may easily vaporize into the air. This makes it possible to inhale while showering. In swimmers uptake of THMs is greatest *via* the skin with thermal absorption accounting for 80% of THM uptake. Exercising in chlorinated pool increases the toxicity of a "safe" chlorinated pool atmosphere with toxic effects of chlorine byproducts greater in young swimmers than older swimmers.

10.6 **Polyhaloalkanes**

These are the compounds having more than three halogen atoms, may be same or different.

Some important of such compounds are described below

Carbon Tetrachloride (CCl_4)

It is a covalent molecule so does not have free Cl atoms.

Methods of Preparation

It is prepared by the chlorination of alkane (methane), chloroform, carbondisulphide or propane under different reaction conditions as

$$\underset{\text{methane}}{CH_4} + \underset{\text{(excess)}}{4Cl_2} \xrightarrow{400°C} CCl_4 + 4HCl$$

$$\underset{\text{chloroform}}{CHCl_3} + Cl_2 \xrightarrow{h\nu} CCl_4 + HCl$$

$$\underset{\text{carbon disulphide}}{CS_2} + 3Cl_2 \xrightarrow{AlCl_3 \text{ or } SbCl_3} CCl_4 + \underset{\text{sulphur monochloride}}{S_2Cl_2}$$

$$CS_2 + 2S_2Cl_2 \xrightarrow{AlCl_3} CCl_4 + 6S$$

$$\underset{\text{propane}}{C_3H_8} + 9Cl_2 \xrightarrow[\text{pressure}]{\Delta} \underset{\substack{\text{carbon}\\\text{tetrachloride}\\\text{(liquid)}}}{CCl_4} + \underset{\substack{\text{hexa}\\\text{chloro}\\\text{ethane}\\\text{(solid)}}}{C_2Cl_6} + 8HCl$$

Physical Properties

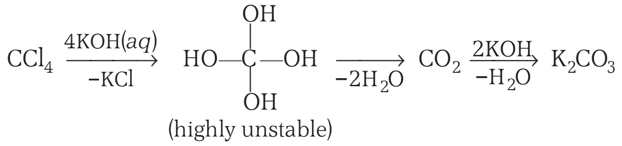
CCl_4 is a colourless, non-inflammable and poisonous liquid with a characteristic odour. Its boiling point is 77°C. It is insoluble in water but soluble in a organic solvents. It is also resistant towards boiling water due to the non-availability of *d*-orbitals in carbon.

Chemical Reactions

(i) **Reduction** With different reducing agents, CCl_4 gives different products as

$$CH_2Cl_2 \xleftarrow{Fe/H_2O} CCl_4 \xrightarrow{Fe/HCl} CHCl_3$$

(ii) **Hydrolysis** This reaction looks like as

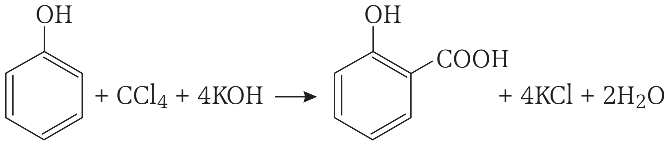


$$CCl_4 \xrightarrow[-KCl]{4KOH(aq)} \underset{\text{(highly unstable)}}{HO-\overset{\displaystyle OH}{\underset{\displaystyle OH}{C}}-OH} \xrightarrow[-2H_2O]{} CO_2 \xrightarrow[-H_2O]{2KOH} K_2CO_3$$

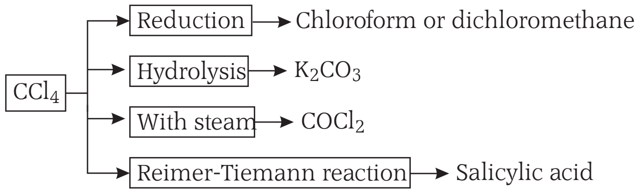
(iii) **With steam** CCl_4 gets oxidised to phosgene when reacts with steam at 500°C.

$$CCl_4 + H_2O \xrightarrow[\text{steam, 500°C}]{\text{Superheated}} COCl_2 + 2HCl$$

(iv) **Reimer-Tiemann reaction** The reaction follows the same mechanism as in case of chloroform and the net reaction looks as



The outlines of chemical properties looks like as



Uses

(i) CCl_4 is used as a fire extinguisher under the name **pyrene**. It is used in medicines as helmenthicide and as a solvent for fats, oils, waxes, greases etc.

(ii) It is also used in the manufacture of refrigerants and propellants for aerosol cans.

(iii) It is also used in the synthesis of CFCs (chloro fluorocarbons) and other chemicals and in pharmaceutical manufacturing.

Harmful Effects

(i) Exposure to CCl_4 may cause irregular heart beat or heart failure. It may irritate the eyes on contact.

(ii) It causes dizzines, light-headedness, nausea, vomitting which can cause permanent damage to nerve cells. Subsequently, these effects may lead to stupor, coma, unconsciousness, or death.

(iii) In air, it depletes the ozone layer which increases the level of ultraviolet rays, causing skin cancer, eye diseases and disruption of the human immune system.

Freons

These are **chlorofluorocarbon** (CFC) *i.e.,* contain, **carbon, chlorine,** and **fluorine** and produced as a **volatile** derivatives of **methane** and **ethane.** A common subclass is the **hydro chloro fluorocarbons** (HCFCs), which contain hydrogen, as well. The most common representative is **dichlorodifluoromethane** (R-12 or Freon-12).

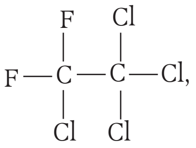
Nomenclature of Freon

(i) **Fron-12** The first number (*e.g.*,1) denotes C atom, whereas the second number (*e.g.*, 2) denotes the number of F atoms and remaining H atoms in CH_4 or C_2H_6 are replaced by Cl atoms. Number of Cl atoms is not mentioned.

(ii) **Freon-22** (These are obtained from ethane, since it contains two C atoms).

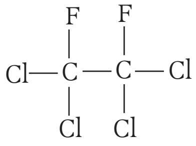
Alkane	Freon
CH_4	Freon-11 $CFCl_3$ (1 C, 1F, 3 Cl)
	Freon-12 CF_2Cl_2 (1 C, 2 F, remaining H atoms are replaced by 2 Cl atoms)
	Freon-13 CF_3Cl (1C, 3F, 1 Cl)
C_2H_6	Freon-22 $C_2F_2Cl_4$ (2C, 2F, remaining 2 H atoms replaced by Cl atoms)
	Freon-23 $C_2F_3Cl_3$ (2 C, 3F, 3Cl)
	Freon-24 $C_2F_4Cl_2$ (2 C, 4F, 2Cl)

Freon derived from ethane can exist in various isomeric forms and the numerals are written according to the number of C and F atoms. *e. g.*, Freon-22 ($C_2F_2Cl_4$) can exist as



$F-\overset{F}{\underset{Cl}{C}}-\overset{Cl}{\underset{Cl}{C}}-Cl$,

freon 1210



$Cl-\overset{F}{\underset{Cl}{C}}-\overset{F}{\underset{Cl}{C}}-Cl$

freon 1111

Methods of Preparation

CFCs and HCFCs are usually produced by halogen exchange starting from chlorinated methanes and ethanes. Illustrative is the synthesis of chlorodifluoromethane from **chloroform.**

$$HCCl_3 + 2HF \longrightarrow HCF_2Cl + 2HCl$$

The brominated derivatives are generated by free-radical reactions of the chlorofluorocarbons, replacing C—H bonds with C—Br bonds. The production of the **anesthetic 2-bromo- 2-chloro-1,1,1-trifluoroethane** ("halothane") is illustrative

$$CF_3CH_2Cl + Br_2 \longrightarrow CF_3CHBrCl + HBr$$

Physical Properties

Their physical properties include

(i) CFCs and HCFCs are colourless, relatively non-toxic liquids and gases with a faintly sweet ethereal odour.

(ii) In general they are volatile, but less so than parent alkane. The decreased volatility is attributed to the molecular polarity induced by the halides and the polarizability of halides, which induces intermolecular interactions. Thus, methane boils at −161°C whereas the fluoromethanes boil between −51.7 (CF_2H_2) and −128°C (CF_4). The CFCs have still higher boiling points because the chloride is even more polarizable than fluoride.

Because of their polarity, the CFCs are useful solvents.

(iii) The CFCs are far less flammable than methane, in part because they contain fewer C—H bonds and in part because, in the case of the chlorides and bromides, the released halides quench the free radicals that sustain flames.

(iv) The densities of CFCS are invariably higher than the corresponding alkanes. In general the density of these compounds correlates with the number of chlorides.

Chemical Reactions

The most important reaction of the CFCs is the **photo-induced cleavage of a C—Cl bond**

$$CCl_3F \longrightarrow CCl_2F^{\bullet} + Cl^{\bullet}$$

The chlorine atom, written often as $Cl^{\bullet}$, behaves very differently from the chlorine molecule (Cl_2). The radical $Cl^{\bullet}$ is long-lived in the upper atmosphere, where it catalyzes the conversion of ozone into O_2. Ozone absorbs UV-radiation better than does O_2, so its depletion allows more of this high energy radiation to reach the Earth's surface. **Bromine** atoms are even more efficient catalysts, hence brominated CFCs are also regulated.

Applications

Their uses include **refrigerants, blowing agents,** propellants in medicinal applications, and degreasing solvents. Billions of kilograms of chlorodifluoromethane are produced annually as a precursor to **tetrafluoroethylene,** the monomer that is converted into **teflon.**

Effect Upon Environment

The decomposition of freons in the atmosphere contributes to the destruction of the ozone layer. Overexposure may cause dizziness, loss of concentration, central nervous system depression and/or cardiac arrhythmia. Vapours displace air and can cause asphyxiation in confined spaces. Although being non-flammable, their combustion products include hydrofluoric acid, phosgene, and related species.

DDT (*p*,*p*'-Dichlorodiphenyl trichloroethane)

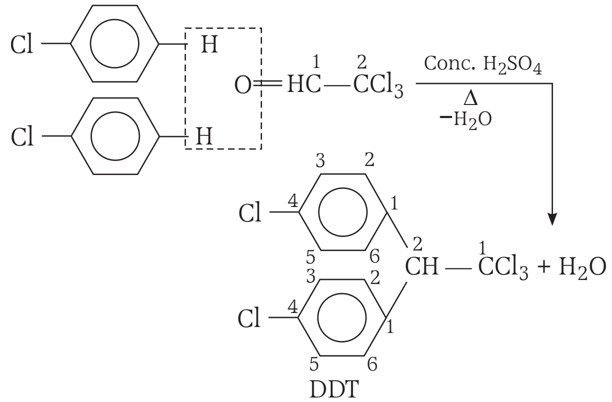
DDT was the first chlorinated organic insecticide and prepared in 1873. But its effectiveness as an insecticide was discovered in 1939 by Paul Muller of Geigy

Pharmaceuticals in Switzerland. In 1948 Paul Muller was awarded the Nobel Prize in medicine and physiology.

Its **IUPAC name** is 2,2-bis (4-chlorophenyl)-1,1,1-trichloroethane.

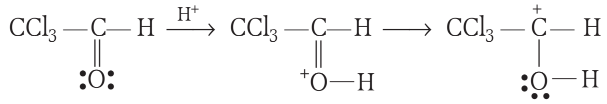
Method of Preparation

It is prepared by heating chloral (trichloro acetaldehyde or 2,2,2-trichloroethanal) with two moles of chlorobenzene in the presence of concentrated H_2SO_4.



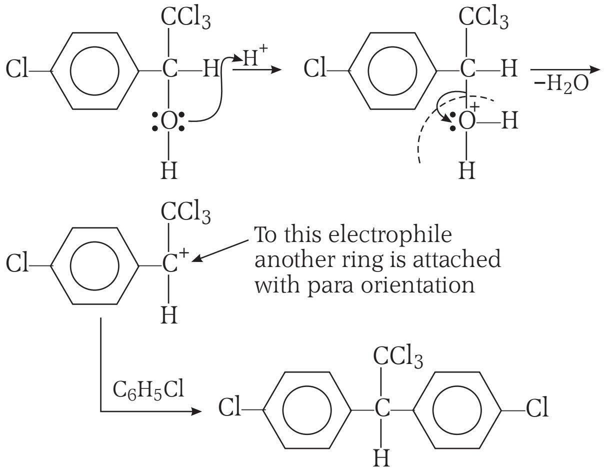
DDT

Mechanism It follows electrophilic substitution in which electrophile is generated as



$$CCl_3-\underset{\underset{:O:}{\|}}{C}-H \xrightarrow{H^+} CCl_3-\underset{\underset{^+O-H}{\|}}{C}-H \longrightarrow CCl_3-\overset{+}{\underset{\underset{:\ddot{O}-H}{|}}{C}}-H$$

After its attachment with one chloro benzene at para position H^+ of acid further takes lone pair from oxygen resulting to removal of water and generation of another electrophile as



Uses

It is a cheap but powerfull insecticide for mosquitoes that spread malaria and lice that carry typhus.

Harmful Effects

Due to its extensive use since 1940s., many species of insects developed resistance to DDT. It has high toxicity towards fish. Due to its stability and fat solubility, it is not metabolised rapidly by animals but is deposited and stored in the fatty tissues. It was banned in the USA in 1973, but is still used in many parts of the word due to the non-availability of any other better and cheaper insecticides.

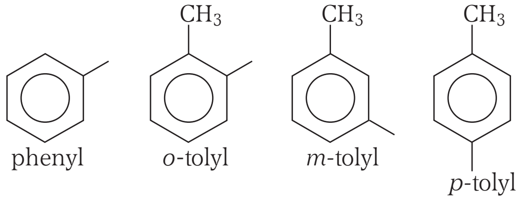
Caution Point *In chloral hydrate two* —OH *groups are present at the same carbon atom but still it is a stable compound. This is because of the existence of intramolecular* H*-bonding between* Cl *and* H *atom (of* OH *group).*

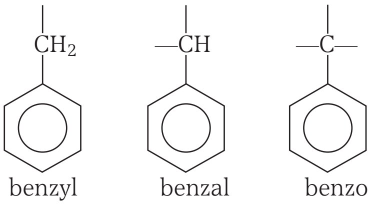
Check Point 2

1. Chloroform is always kept with a little ethyl alcohol in dark coloured bottles. Explain.
2. $CH_2COCH_2COOC_2H_5$ contains CH_3COO— group but does not give positive iodoform test. Explain why?
3. Hydrogen atom of chloroform is definitely acidic in nature. Explain.
4. Iodoform gives yellow precipitate with $AgNO_3$ but chloroform give no precipitate with $AgNO_3$. Explain, why?
5. CCl_4 is used to extinguish fire. Explain.

10.7 Aryl Halides

Aryl halides are the compounds having halogen atom directly attached to the aromatic ring. These compounds are represented by Ar–*X* where Ar represents phenyl, substituted phenyl or any other aryl ring. Before going in detail notice the below written terms and their usage.





Methods of Preparation

General methods used for the preparation of alkyl halide are generally not applied to synthesise **aryl halides.**

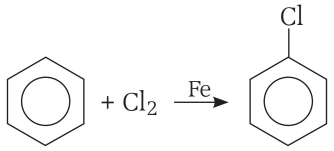
These are prepared by the following methods.

(a) Halogenation

Low temperature and presence of a halogen carrier (Lewis acid) favour this substitution. (The chlorides or bromides of Al, Fe, Sb, Sn, etc, may be used as halogen carriers.) Fe is most commonly used among them as it is converted into Lewis acid.

$$2Fe + 3Cl_2 \longrightarrow 2FeCl_3$$

The reaction looks like

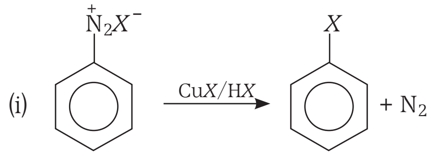


Without halogen carrier halonium ion (X^+) is not formed, thus, the reaction is not possible.

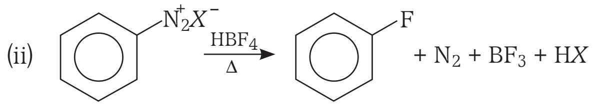
(The mechanism of reaction is given in chapter some basic principles of organic chemistry under electrophilic substitution.)

(b) Decomposition of Diazonium Salt

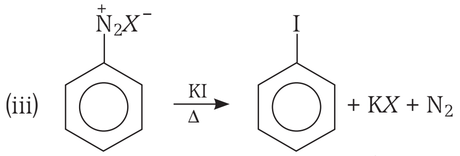
The reaction looks like



(Sandmeyer reaction) [X = Cl, Br]



(Sandmeyer reaction)

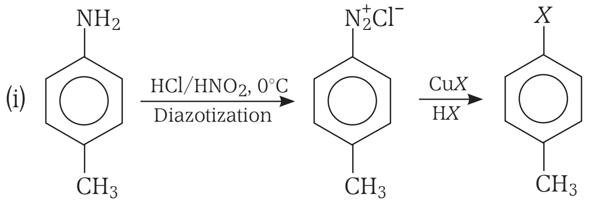


(Gattermann reaction)

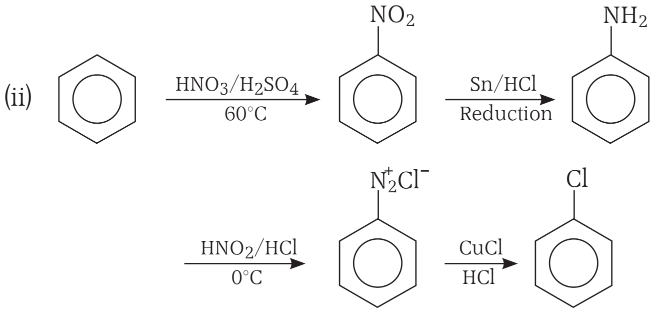
Thus, fluorides, chlorides, bromides and iodides can be prepared with the same method due to their differential reactivity. Above written (i) reaction is used to prepare **chlorides** and **bromides** (ii) reaction is used to prepare **fluorides** and (iii) reaction is used to prepare **aryl iodides.**

(c) From Aromatic Amino and Nitro Compounds

A better yield of aryl halides is obtained through this reaction which is summarised as

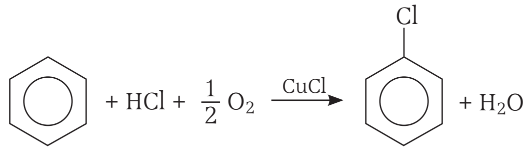


(Laboratory method)



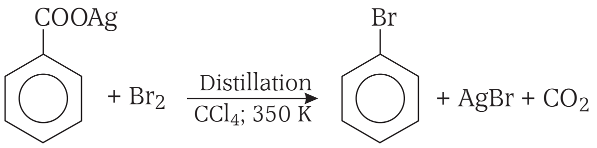
(d) Raschig Process

It is the commercial method of the preparation chlorobenzene. The reaction looks like



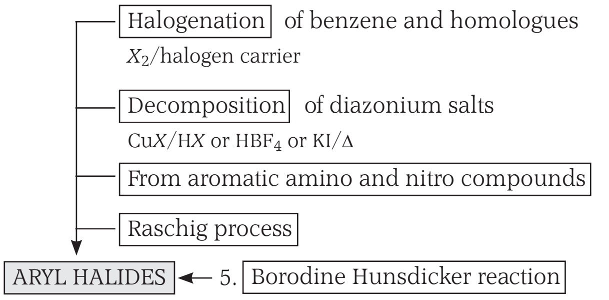
(e) Borodine Hunsdicker Reaction

The reaction looks like as



(Also see methods of preparation of monohalogen derivatives)

The outlines of methods of preparation of aryl halides is as



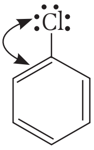
Physical and Chemical Properties

Aryl halides are heavier than water, though polar but immiscible with water (due to incapability of forming H-bonds).

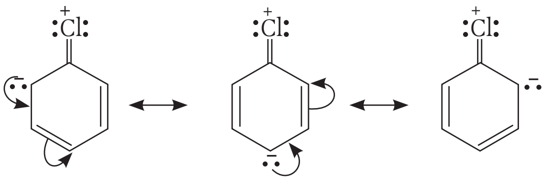
(a) **Nucleophilic Substitution Reactions**

Aryl halides are less reactive towards nucleophilic substitution reactions as compared to alkyl halides due to the following reasons

1. The C–*X* bond in aryl halides have double bond character due to conjugation between lone pair of halogen and benzene ring as :

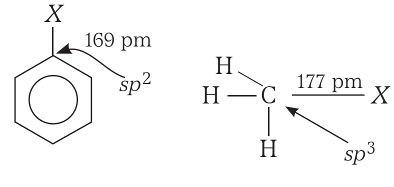


Conjugation resulting to following 3 resonating structures.



Due to the presence of such double bond character, aryl halides does not give the normal reactions of X^- (halides) ions *i.e.*, it is difficult to break C–*X* bond in favour of *X*-atoms. Thus, aryl halides show nucleophilic substitution with difficulty.

2. Moreover in halobenzene, C atom holding the halogen atom is sp^2-hybridised and in methyl halide it is sp^3-hybridised. Since, an sp^2-hydridised orbital is smaller in size as compared to an sp^3-hybridised orbital therefore, the (C—*X*) bond in halobenzene should be shorter and hence stronger than that in CH_3X.



3. The sp^2-hybrid C atom is more electronegative as compared to sp^3-hybrid C atom, therefore, the sp^2-hybrid (of C —*X* bond) in aryl halide is less willing to release electron to the halogen than an sp^3-hybrid C atom in alkyl halide. As a result, (C—*X*) bond in an aryl halide is less polar than in alkyl halides, This is supported by the observation that dipole moment of chlorobenzene is 1.7 D as compared to the dipole moment CH_3Cl *i.e.*, 1.94 D. Consequently, the halogen atom present in aryl halides cannot be easily replaced by nucleophiles.

$$H_5\overset{+\delta}{C_6}—\overset{-\delta}{Cl} \qquad H_3\overset{+\delta}{C}—\overset{-\delta}{Cl}$$

Caution Point *For the same reason, chlorobenzene does not give test for* $Cl^{\ominus}$ *ions when treated with aq.* NaOH *and then with* $AgNO_3$*, whereas* CH_3Cl *gives this test.*

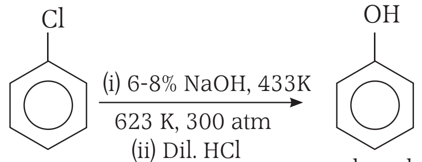
$$C_6H_5Cl + Aq.KOH \xrightarrow{AgNO_3} No.ppt$$

$$CH_3Cl + Aq.KOH \longrightarrow CH_3OH + Cl^{\ominus} \xrightarrow{AgNO_3}$$
$$AgCl \text{ (White ppt., soluble in } NH_4OH)$$

4. Phenyl cation formed as a result of self-ionisation will not be stabilised by resonance, and therefore, S_N1 mechanism is not possible.
5. It is difficult for the electron rich nucleophile to approach electron rich arenes because of repulsion between them.

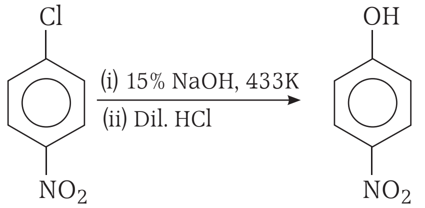
However, aryl halides can be made to undergo nucleophilic substitution either under drastic conditions (such as the use of high temperature, pressure, or very strong nucleophile) or by the presence of electron-withdrawing group (*e.g.*, $—NO_2$, —COOH, etc.) at the *o*-and *p*-positions to the nuclear halogen. *e.g.*,

(i)



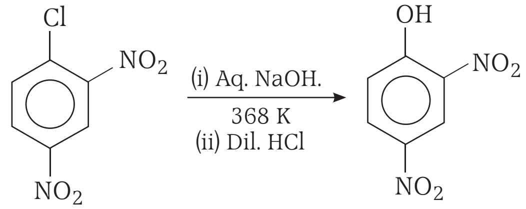
phenol

(ii)



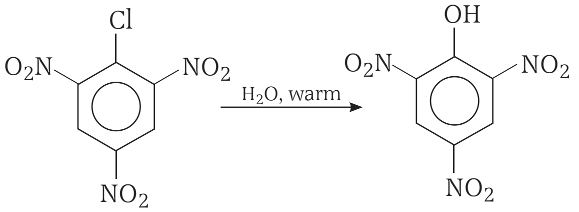
p-nitrophenol

(iii)



2, 4-dinitro-chlorobenzene 2, 4-dinitrophenol

(iv)



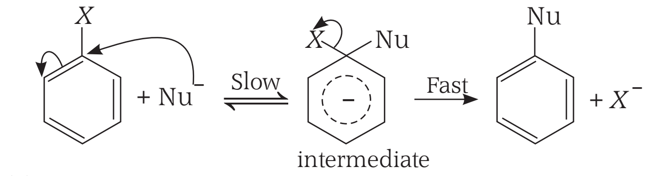
2, 4, 6 trinitro chlorobenzene (picryl chloride)

2, 4, 6-trinitrophenol (picric acid)

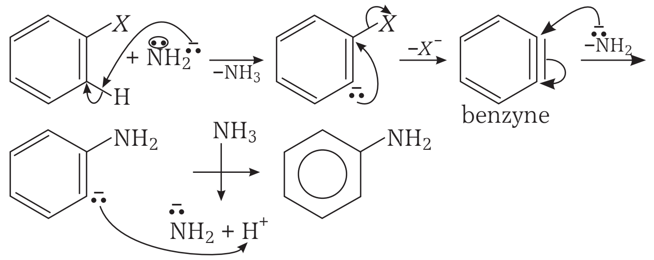
Explanation The presence of nitro group at *ortho*- and *para* positions withdraws the electron density from the benzene ring and thus facilitates the attack of the nucleophile on haloarene. The carbanion thus formed is stabilised through resonance. The negative charge appearing at *ortho*- and *para*-positions with respect to the halogen substituent is stabilised by (—NO_2) group, while in case of *meta*-nitrobenzene, none of the resonating structures bears the negative charge on carbon atom bearing the (—NO_2) group. Therefore, the presence of nitro group at *meta*- position does not stabilise the negative charge and no effect on reactivity is observed by the presence of (—NO_2) group at *meta*-position.

In general **nucleophilic substitution** reactions does not take place through straight S_N mechanism but alternate benzyne or bimolecular mechanisms has been provided which are summarised as

(i) Bimolecular mechanism



(ii) Benzyne mechanism



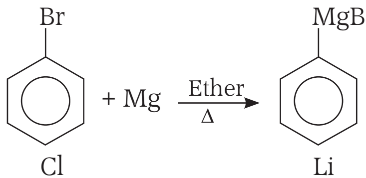
Nucleophilic substitution of NH_2 can also perform by reacting aryl halides with $NaNH_2$ or KNH_2 in liquid NH_3.

Caution Point *In the absence of electron withdrawing groups or in the presence of electron donating groups, the nucleophilic substitution reactions in aryl halides occur by the benzyne mechanism.*

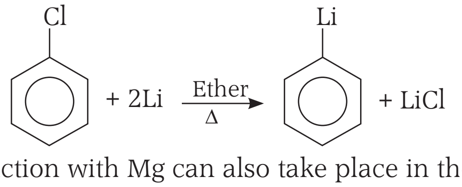
(b) Reaction with Metals

By this reaction, organometallic compounds are formed. The reactions looks like

(i)



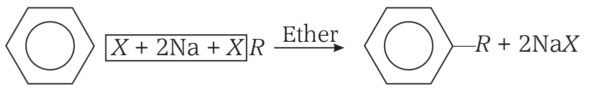
(ii)



The reaction with Mg can also take place in the presence of THF.

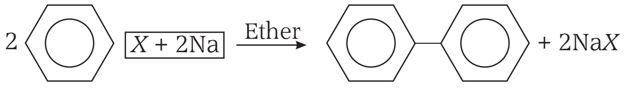
(c) Wurtz-Fittig and Fittig Reaction

These reactions are infact modified form of Wurtz reaction and involves aryl halide in place of alkyl halide as



alkyl benzene

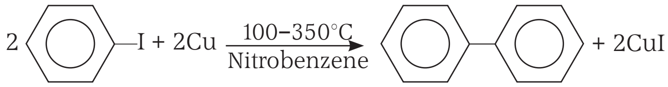
(Wurtz-Fittig reaction)



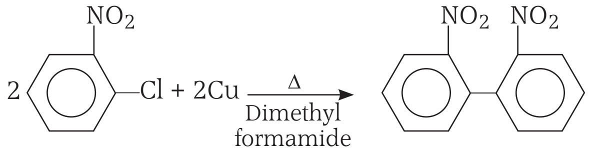
biphenyl (Fittig reaction)

(d) Ullmann Reaction

The reaction is successful with aryl iodides as C—I bond is weakest among all C—*X* bonds in aryl halides and looks like

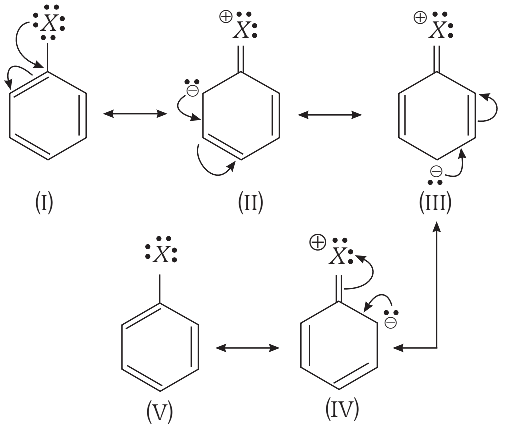


However, aryl chlorides and bromides also react when some electronegative substituent with ability to activate the halogen is present, *e.g.*,



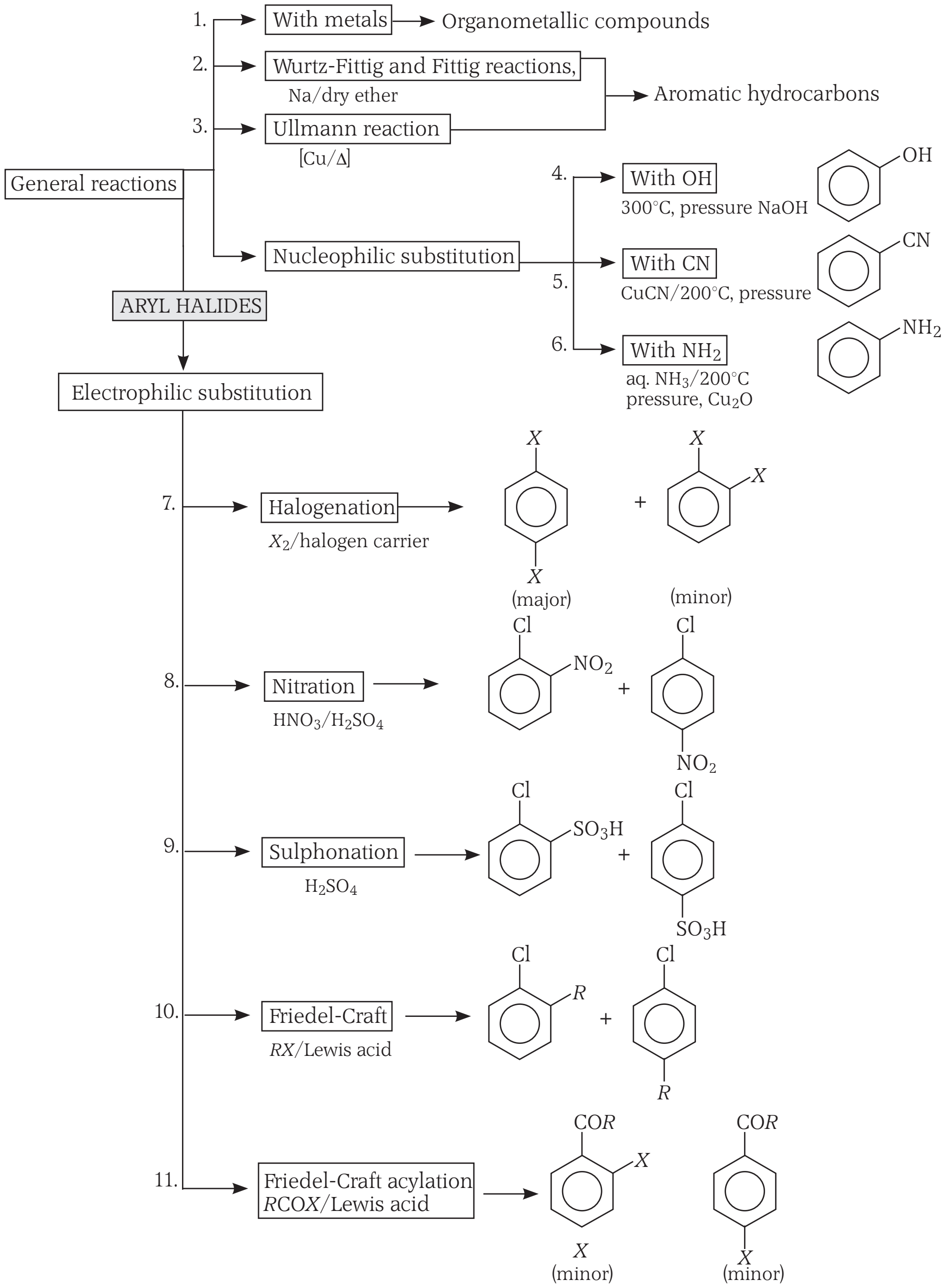
Electrophilic Substitution Reactions

Ar*X* undergoes the usual electrophilic substitution reactions of the benzene ring such as halogenation, sulphonation, nitration, and Friedel-Crafts reactions. Although slightly deactivating (due to–*I* effect), yet they are *o*, *p*-directing. Orientation (*o*-,*p*-directing) influence of halogens is explained by the resonance. Due to + *R* effect, Ar*X* is resonance stabilised as follows



Due to resonance, benzene ring is activated at *o*-and *p*-positions, thereby increasing the electron density more at *o*-and *p*-positions than at *m*-position. Moreover, due to –*I* effect of *X*, there is some tendency to withdraw electron from the benzene ring; as a result the ring gets slightly deactivated as compared to benzene and hence SE reaction in Ar*X* occurs slowly and drastic conditions are required as compared to those in benzene.

The chemical properties of aryl halides looks like



Check Point 3

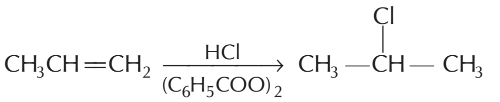
1. Aryl halides do not give the normal reactions of halide ions. Why?
2. In order to prepare chlorobenzene from benzene, presence of a halogen carrier is a necessity. Explain.
3. Chlorobenzene does not give Ullmann reaction but *ortho* nitrochlorobenzene does. Explain why?

WORKED OUT Examples

Example 1 *When hydrochloric acid gas is treated with propene in the presence of benzoyl peroxide, it gives*

(a) *2-chloropropane* (b) *allyl chloride*
(c) *n-propyl chloride* (d) *isopropyl chloride*

Solution (a) Peroxide effect is observed only in case of HBr. Therefore, addition of HCl to propene even in the presence of benzoyl peroxide occurs according to Markownikoff's rule.



$$CH_3CH{=}CH_2 \xrightarrow[(C_6H_5COO)_2]{HCl} CH_3-\overset{\overset{\large Cl}{|}}{C}H-CH_3$$

Example 2 *Identify (C) in*

$$CH_3CH_2CH_2Br \xrightarrow{aq.\ NaOH} A \xrightarrow{Al_2O_3} B \xrightarrow{Cl_2/H_2O} C$$

(a) $CH_3CHOHCH_2Cl$
(b) $CH_3CHClCH_2Cl$
(c) *mixture of* $CH_3CHCl\cdot CH_2Cl$ *and* $CH_3CHOHCH_2Cl$
(d) $CH_3CH_2ClCH_2OH$

Solution (a)

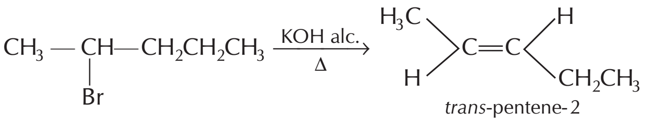
$$CH_3CH_2CH_2Br \xrightarrow{Aq.\ NaOH} CH_3CH_2CH_2OH \xrightarrow[-H_2O]{Al_2O_3,\,\Delta} CH_3CH{=}CH_2$$

$$CH_3CH{=}CH_2 \xrightarrow{Cl_2\,/\,H_2O} CH_3-CHOH-CH_2Cl$$

Example 3 *2-bromopentane is heated with potassium ethoxide in ethanol. The major product obtained is*

(a) *pentene-1*
(b) *2-ethoxypentane*
(c) *trans-pentene-2*
(d) *cis-pentene-2*

Solution (c) Secondary alkyl halides on treatment with alcoholic KOH preferably undergo elimination rather than substitution to give alkenes in accordance with Saytzeff rule. Usually the more stable *trans*-alkenes predominate in this reaction. Thus, 2-bromopentane gives *trans*-pentene-2



trans-pentene-2

Example 4 C—Cl *bond of chlorobenzene in comparison to* C—Cl *bond of methyl chloride is*

(a) *longer and stronger*
(b) *shorter and stronger*
(c) *longer and weaker*
(d) *shorter and weaker*

Solution *(b) Due to resonance* C—Cl *bond of chlorobenzene is shorter but stronger.*

Example 5 *The yield of chlorobenzene obtained by reaction of phenol with* PCl_5 *is less due to the formation of*

(a) *p-chlorophenol*
(b) *o-chlorophenol*
(c) *triphenyl phosphate*
(d) *phosphorus oxychloride*

Solution (c) $C_6H_5OH + PCl_5 \longrightarrow C_6H_5Cl + POCl_3 + HCl$

$$3C_6H_5OH + POCl_3 \longrightarrow (C_6H_5)_3PO_4 + 3HCl$$

The yield of phenol is poor because the main product is triphenyl phosphate.

Example 6 *In which of the following molecules p-electron of halogen is delocalised over the entire structure?*

(a) *Picryl chloride*
(b) *Benzyl chloride*
(c) *Allyl chloride*
(d) *Benzal chloride*

Solution (a) In picryl chloride or 1–chloro-2,4,6-trinitro benzene, the Cl group is directly attached to benzene ring and *p*-electrons are delocalised over the entire structure due to the presence of three deactivating NO_2 groups.

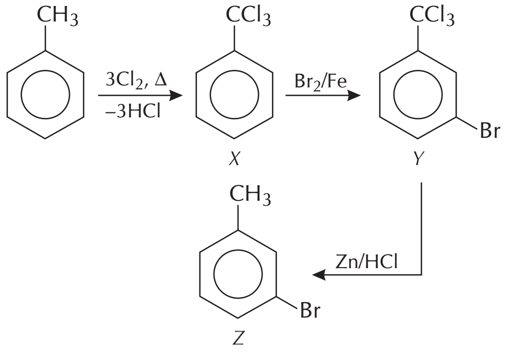
Example 7 *The compound*

$$C_7H_8 \xrightarrow{3Cl_2/\Delta} X \xrightarrow{Br_2/Fe} Y \xrightarrow{Zn/HCl} Z.$$

The compound Z is

(a) *m-bromotoluene*
(b) *p-bromotoluene*
(c) *o-bromotoluene*
(d) *2,4,6-trichlorotoluene*

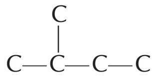
Solution (*a*)



Example 8 *An alkyl chloride (A) on reaction with magnesium in dry ether followed by treatment with ethanol gave 2-methylbutane. Give the possible structure of (A).*

(*a*) $(CH_3)_2C(Cl)CH_2CH_3$
(*b*) $(CH_3)_2CHCH_2CH_2Cl$
(*c*) $CH_3CH_2CH_2CH_2CH_2X$
(*d*) *Both (a) and (b)*

Solution (*d*) Since, the compound gives 2-methyl butane, it must contain the following carbon skeleton.

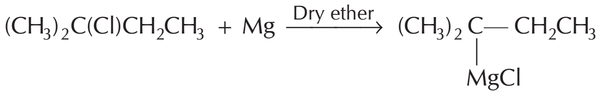


$$\overset{\displaystyle C}{\overset{|}{}}\!\!\!\!\!C—C—C—C$$

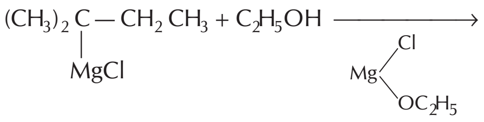
Thus, the structure of chloride may be

$(CH_3)_2C(Cl)CH_2CH_3$ or $(CH_3)_2CHCH_2CH_2Cl$

and reactions are as follows



$$(CH_3)_2C(Cl)CH_2CH_3 + Mg \xrightarrow{\text{Dry ether}} (CH_3)_2\underset{\displaystyle MgCl}{\underset{|}{C}}—CH_2CH_3$$



$$(CH_3)_2\underset{\displaystyle MgCl}{\underset{|}{C}}—CH_2CH_3 + C_2H_5OH \longrightarrow Mg\langle^{Cl}_{OC_2H_5}$$

$$\underset{\text{2-methyl butane}}{(CH_3)_2CHCH_2CH_3}$$

or $(CH_3)_2CHCH_2CH_2Cl + Mg \xrightarrow{\text{Dry ether}}$

$$(CH_3)_2CHCH_2CH_2MgCl$$

$$(CH_3)_2CHCH_2CH_2MgCl + C_2H_5OH \longrightarrow$$

$$\underset{\text{2-methylbutane}}{(CH_3)_2CHCH_2CH_3}$$

Start Practice for JEE Main

Round I (Topically Divided Problems)

General Characteristics and Preparation of Monohaloalkanes

1. The position of —Br in the compound $CH_3CH{=}CHC(Br)(CH_3)_2$ can be classified as [**NCERT** Exemplar]

(a) allyl (b) aryl
(c) vinyl (d) secondary

2. What should be the correct IUPAC name for diethylbromomethane? [**NCERT** Exemplar]

(a) 1-bromo-1, 1-diethylmethane
(b) 3-bromopentane
(c) 1-bromo-1-ethylpropane
(d) 1-bromopentane

3. Which of the following is an example of *vic*-dihalide? [**NCERT** Exemplar]

(a) Dichloromethane (b) 1, 2-dichloroethane
(c) Ethylidene chloride (d) Allyl chloride

4. Alkyl iodides can be prepared by

(a) $RCH_2COOAg + I_2 \xrightarrow[\Delta]{CCl_4} RCH_2I$

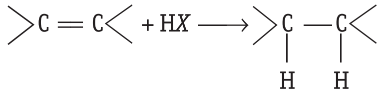
(b) $RCH_2Cl + NaI \xrightarrow[\Delta]{Acetone} RCH_2I + NaCl$

(c) $R - OH + I_2 \longrightarrow RI + H_2O$

(d) $CH_4 + I_2 \longrightarrow CH_3I$

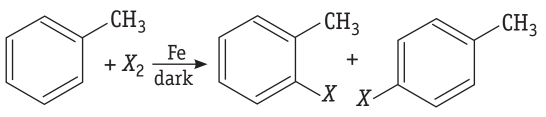
5. Which of the following is halogen exchange reaction? [**NCERT** Exemplar]

(a) $RX + NaI \longrightarrow RI + NaX$

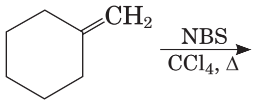
(b)


$>C=C< + HX \longrightarrow >\underset{H}{\underset{|}{C}}-\underset{H}{\underset{|}{C}}<$

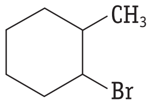
(c) $R{-}OH + HX \xrightarrow{ZnCl_2} R-X + H_2O$

(d)


6. The major product formed in the reaction



is

(a)


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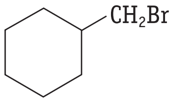

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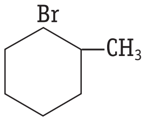

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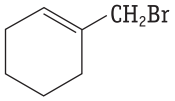
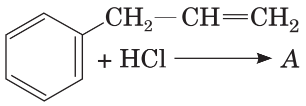
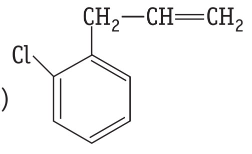


7. What is '*A*' in the following reaction? [**NCERT** Exemplar]



(a)


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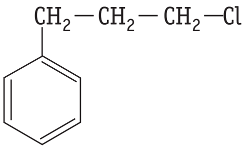

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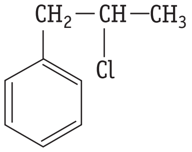

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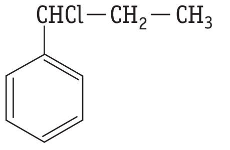
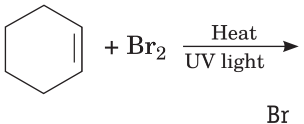
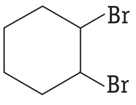


8. Draw the structure of major monohalo product in the following reaction [**NCERT**]



(a)


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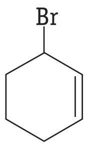
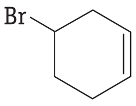
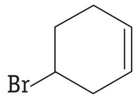
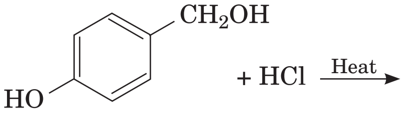


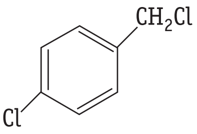
(c)


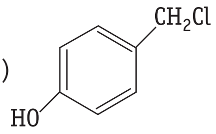
(d)


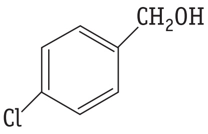
9. Find the structure of the product

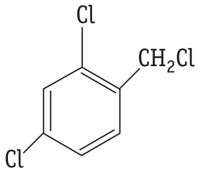


[NCERT]

(a)


(b)


(c)


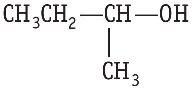
(d)


10. Among the isomeric alkanes of molecular formula C_5H_{12} identify the one that on photochemical chlorination yields 1 four isomeric monochlorides. [NCERT]

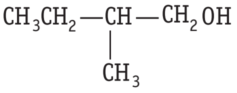
(a) 2-methylbutane (b) 2, 2-dimethylpropane
(c) 3-methylbutane (d) *n*-pentane

11. Which of the following alcohols will yield the corresponding alkyl chloride on reaction with concentrated HCl at room temperature? [NCERT Exemplar]

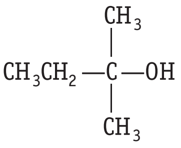
(a) $CH_3CH_2—CH_2—OH$

(b)


$CH_3CH_2—\underset{\substack{|\\CH_3}}{CH}—OH$

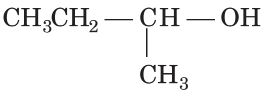
(c)


$CH_3CH_2—\underset{\substack{|\\CH_3}}{CH}—CH_2OH$

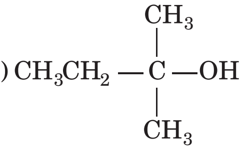
(d)


$CH_3CH_2—\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}—OH$

12. The order of reactivity of the following alcohols with halogen acids is [NCERT Exemplar]

(*A*) $CH_3CH_2—CH_2—OH$ (*B*)


$CH_3CH_2—\underset{\substack{|\\CH_3}}{CH}—OH$

(*C*)


$CH_3CH_2—\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}—OH$

(a) (*A*) > (*B*) > (*C*) (b) (*C*) > (*B*) > (*A*)
(c) (*B*) > (*A*) > (*C*) (d) (*A*) > (*C*) > (*B*)

13. Grignard reagents should be prepared under anhydrous conditions because [NCERT Exemplar]

(a) it is highly reactive towards protonic substances
(b) it reacts with ether
(c) Both (a) and (b)
(d) None of the above

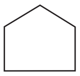
14. Sulphuric acid cannot be used during the reaction of alcohols with KI because it is a [NCERT]

(a) strong oxidant (b) strong reductant
(c) weak oxidant (d) it can be used

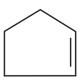
15. The reagents required to obtain 1-iodobutane from but-1-ene is/are [NCERT]

(a) I_2 / red P
(b) KI
(c) HI / H_2O_2
(d) HBr / H_2O_2 and KI/acetone

16. A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound C_5H_9Cl in bright sunlight. Identify the hydrocarbon. [NCERT]

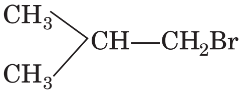
(a)


(b) $CH_3CH_2—CH=CHCH_2Cl$

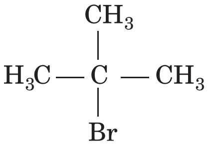
(c) $CH_3CH=CHCH_2CH_2Cl$ (d)


Properties of Monohaloalkanes

17. Arrange the following compounds in the increasing order of their boiling points. [NCERT Exemplar]

(*A*)


(*B*) $CH_3CH_2CH_2CH_2Br$

(*C*)


$H_3C—\overset{\substack{CH_3\\|}}{\underset{\substack{|\\Br}}{C}}—CH_3$

(a) (*B*) < (*A*) < (*C*) (b) (*A*) < (*B*) < (*C*)
(c) (*C*) < (*A*) < (*B*) (d) (*C*) < (*B*) < (*A*)

18. Which is the correct increasing order of boiling points of the following compounds?

1-iodobutane, 1-bromobutane, 1-chlorobutane, Butane [NCERT Exemplar]

(a) Butane < 1-chlorobutane < 1-bromobutane <1-iodobutane
(b) 1-iodobutane < 1-bromobutane < 1-chlorobutane < butane
(c) Butane < 1- iodobutane < 1-bromobutane < 1-chlorobutane
(d) Butane <1-chlorobutane < 1-iodobutane <1-bromobutane

19. The order of reactivities of the following alkyl halides for a S_N2 reaction is

(a) *R*F > *R*Cl > *R*Br > *R*I (b) *R*F > *R*Br > *R*Cl > *R*I
(c) *R*Cl > *R*Br > *R*F > *R*I (d) *R*I > *R*Br > *R*Cl > *R*F

20. A primary alkyl halide would prefer to undergo [**NCERT** Exemplar]

(a) S_N1 reaction (b) S_N2 reaction
(c) α-elimination (d) racemisation

21. The reaction of ethyl bromide and silver cyanide results in the formation of

(a) ethylene (b) ethyl cyanide
(c) ethyl isocyanide (d) ethyl alcohol

22. The alkyl halide that undergoes S_N1 reaction more readily is

(a) ethyl bromide (b) *iso*-propyl bromide
(c) vinyl bromide (d) *t*-butyl bromide

23. Among the following alkyl halides the one having the highest bond polarity is

(a) CH_3Cl (b) CH_3Br
(c) CH_3I (d) CH_3F

24. In the reaction,

$$R-Br + Cl^- \xrightarrow{\text{Dimethyl formamide}} R-Cl + Br^-$$

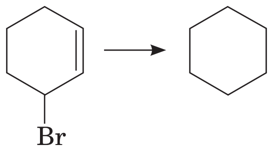
the relative rates of reaction of methyl bromide (I), ethyl bromide (II), *iso*-propyl bromide (III) and tert-butyl bromide (IV) follow the order

(a) I > II > III > IV (b) IV > III > II > I
(c) IV > I > II > III (d) II > III > IV > I

25. The Friedel-Crafts reactions of *n*-propylbromide with benzene in the presence of anhydrous $AlCl_3$ gives

(a) *n*-propyl benzene (b) *iso*-propyl benzene
(c) 1,4-dipropyl benzene (d) 1,2-dipropyl benzene

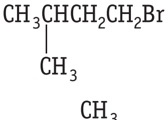
26. The transformation

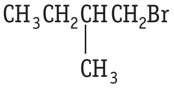


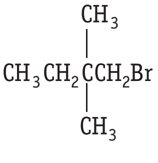
can be brought about using

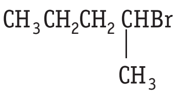
(a) Zn/H^+ (b) CuI
(c) Na (d) $(CH_3)_2CuLi$

27. Which alkyl halide from the following pairs would you expect to react more rapidly by an S_N2 mechanism? [**NCERT**]

(a) 
$CH_3CH(CH_3)CH_2CH_2Br$

(b) 
$CH_3CH_2CH(CH_3)CH_2Br$

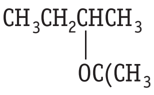
(c) 
$CH_3CH_2C(CH_3)_2CH_2Br$

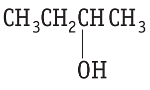
(d) 
$CH_3CH_2CH_2CH(CH_3)Br$

28. In the reaction,

$CH_3CH_2CHBrCH_3 + (CH_3)_3COK \longrightarrow$

the main product is

(a) 
$CH_3CH_2CH(OC(CH_3)_3)CH_3$

(b) 
$CH_3CH_2CH(OH)CH_3$

(c) $CH_3CH_2CH=CH_2$ (d) $CH_3CH=CHCH_3$

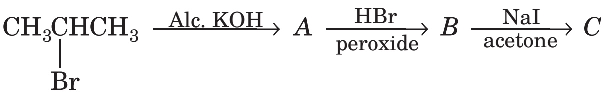
29. Butyronitrile may be prepared by heating

(a) propyl alcohol with KCN
(b) butyl alcohol with KCN
(c) propyl chloride with KCN
(d) butyl chloride with KCN

30. Wet ether is not used as a solvent in Wurtz reaction, because the water present in it

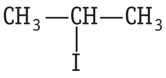
(a) hydrolyses *RX* to *R*OH (b) reduces *RX* to *R*H
(c) destroy the Na metal (d) reacts with *R*–*R*

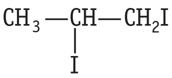
31. In the reaction,


$$CH_3CH(Br)CH_3 \xrightarrow{\text{Alc. KOH}} A \xrightarrow[\text{peroxide}]{\text{HBr}} B \xrightarrow[\text{acetone}]{\text{NaI}} C$$

C is

(a) $CH_3CH_2CH_2I$

(b) 
$CH_3-CH(I)-CH_3$

(c) 
$CH_3-CH(I)-CH_2I$

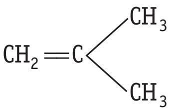
(d) $CH_3CH=CHI$

32. A mixture of 1-chloropropane and 2-chloropropane when treated with alcoholic KOH, gives

(a) *iso*-propylene
(b) 2-propene
(c) 1-propene
(d) a mixture of 1-propene and 2-propene

33. The treatment of tertiary butyl chloride with 80% aqueous ethanol at 140°C gives

(a) $(CH_3)_3C-OH$ (b) $(CH_3)_3C-OCH_2CH_3$

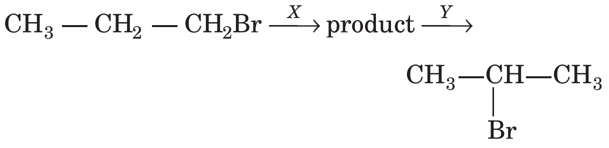
(c) 
$CH_2=C(CH_3)_2$

(d) All of these

34. An alkyl halide with molecular formula, $C_6H_{13}Br$ on treatment with alcoholic KOH gave two isomeric alkenes, *A* and *B*. Ozonolysis of the mixture gave the following compounds.
CH_3COCH_3, CH_3CHO, CH_3CH_2CHO and $(CH_3)_2CHCHO$. The alkyl halide is

(a) 2-bromohexane
(b) 3-bromo-2-methylpentane
(c) 2, 2-dimethyl-1-bromobutane
(d) 2-bromo-2, 3-dimethylbutane

35. Identify the set of reagent/reaction conditions 'X' and 'Y' in the following set of transformations.



$$CH_3-CH_2-CH_2Br \xrightarrow{X} \text{product} \xrightarrow{Y} CH_3-\underset{\substack{|\\ Br}}{CH}-CH_3$$

(a) X = dilute aqueous NaOH, 20°C; Y = HBr/acetic acid, 20°C
(b) X = concentrated alcoholic NaOH, 80°C; Y = HBr/acetic acid, 20°C
(c) X = dilute aqueous NaOH, 20°C; Y = $Br_2/CHCl_3$, 0° C
(d) X = concentrated alcoholic NaOH, 80°C; Y = $Br_2/CHCl_3$, 0°C

Di, tri and Polyhalogen Compounds

36. Which one of the following has the highest dipole moment ? **[NCERT]**
(a) CH_2Cl_2
(b) $CHCl_3$
(c) CCl_4
(d) All have equal dipole moment

37. Chloroform reacts with conc HNO_3 to give
(a) water gas (b) tear gas
(c) laughing gas (d) producer gas

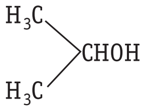
38. The bad smelling substance formed by the reaction of chloroform with methyl amine and alcoholic KOH will be
(a) methyl amine (b) methyl alcohol
(c) methyl cyanide (d) methyl isocyanide

39. If chloroform is left open in air in presence of sun, rays
(a) polymerisation taken place
(b) no reaction takes place
(c) explosion takes place
(d) phosgene gas is formed

40. The trade name of trichloroethylene is
(a) freon (b) westron
(c) westrosol (d) DDT

41. The compound which does not give iodoform with I_2 and alkali is
(a) CH_3CH_2OH (b) CH_3COCH_3

(c)



$(H_3C)_2CHOH$

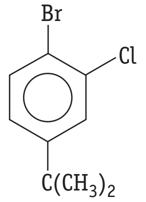
(d) CH_3OH

42. Haloform reaction cannot be used to prepare
(a) CHF_3 (b) $CHCl_3$
(c) $CHBr_3$ (d) CHI_3

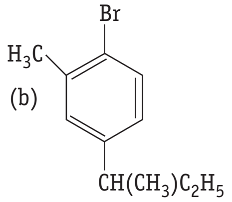
43. Which is not the correct statement ?
(a) Chloretone is an insecticide
(b) $COCl_2$ is called phosgene
(c) Chloropicrin is used as an insecticide
(d) CCl_4 is used as fire extinguisher under the name pyrene

44. Write the structure of the following compounds.
1-bromo-4-*sec*-butyl-2-methylbenzene **[NCERT]**

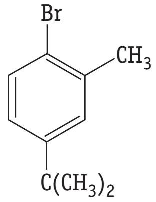
(a)



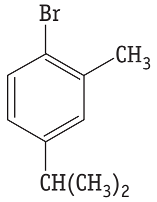
(b)



(c)

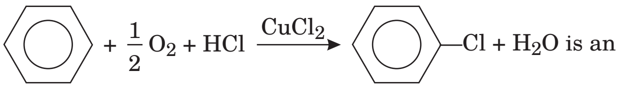


(d)



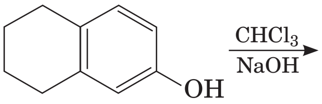
45. Out of $C_6H_5CHClC_6H_5$ and $C_6H_5CH_2Cl$ which is more easily hydrolysed by aqueous KOH? **[NCERT]**
(a) $C_6H_5CHClC_6H_5$
(b) $C_2H_5CH_2Cl$
(c) Both get equally hydrolysed
(d) Unpredictable

46. Conversion of,



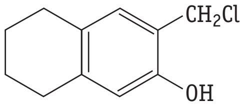
example of which of the following reaction?
(a) Nucleophilic substitution
(b) Electrophilic substitution
(c) Free radical addition
(d) Free radical substitution

47. The product obtained in the reaction,

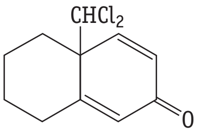


are

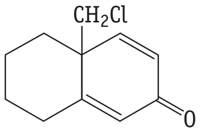
(a)



(b)



(c)



(d) None of these

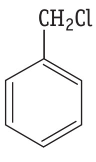
48. Chlorobenzene is formed by reaction of chlorine with benzene in the presence of $AlCl_3$. Which of the following species attacks the benzene ring in this reaction ? **[NCERT Exemplar]**

(a) Cl^- (b) Cl^+

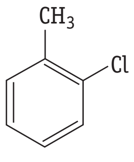
(c) $AlCl_3$ (d) $[AlCl_4]^+$

49. The reaction of toluene with chlorine in the presence of iron and in the absence of light yields. …… **[NCERT Exemplar]**

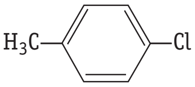
(a)



(b)



(c)



(d) Mixture of (b) and (c)

50. *p*-dichlorobenzene has higher melting point and lower solubility than those of *o*-and *m*-isomers. This is because *p*-isomer is **[NCERT]**

(a) more symmetrical (b) resonance stabilised

(c) stabilised by + *I* effect (d) Both (a) and (b)

51. Aryl halides undergo

(a) the Fittig reaction (b) the Ullmann reaction

(c) the Grignard reaction (d) All of these

52. Arrange *m*-nitrochlorobenzene (I), 2, 4- dinitrochlorobenzene (II) *p*-nitrochlorobenzene (III) according to reactivity with sodium ethoxide.

(a) I > II > III (b) III > I > II

(c) II > III > I (d) II = III > I

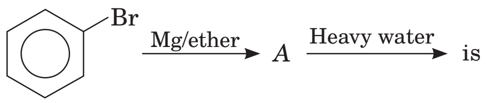
53. Arrange the following in order of increasing ease of nucleophilic substitution reaction

Chlorobenzene (I), 2, 4, 6-trinitrochlorobenzene (II), 2, 4- dinitrochlorobenzene (III) and 4-nitrochlorobenzene (IV)

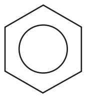
(a) I < IV < III < II (b) I < III < IV < II

(c) II < III < IV < I (d) IV < III < II < I

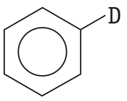
54. The final product obtained in the reaction



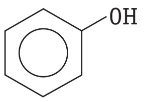
(a)



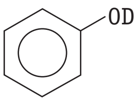
(b)



(c)



(d)



55. Arrange the following compounds in the order of reactivity with alcoholic silver nitrate,

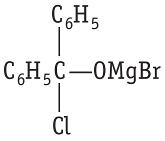
$C_6H_5CH_2CH_2Br$ (I), $C_6H_5CHBrCH_3$ (II) and $C_6H_5CH{=}CHBr$ (III)

(a) II > I > III (b) I > II > III

(c) III > II > I (d) II = I > III

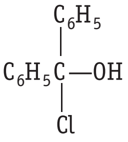
56. Which of the following is the final product in the reaction between benzoyl chloride and phenyl magnesium bromide?

(a)



$C_6H_5\overset{\displaystyle C_6H_5}{\underset{\displaystyle Cl}{C}}{-}OMgBr$

(b)



$C_6H_5\overset{\displaystyle C_6H_5}{\underset{\displaystyle Cl}{C}}{-}OH$

(c) C_6H_5COOH (d) $(C_6H_5)_3COH$

57. Aryl halides are less reactive towards nucleophile than alkyl halides due to

(a) resonance (b) stability of carbonium ion

(c) high boiling point (d) None of these

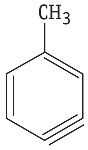
58. A convenient reagent for the conversion of bromobenzene into benzonitrile is

(a) alc KCN alone (b) KCN and pyridine

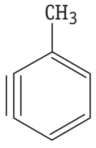
(c) silver cyanide (d) CuCN and pyridine

59. *o*-chlorotoluene reacts with sodamide in liquid NH_3 to give *o*-toluidine and *m*-toluidine. This proceeds through an intermediate

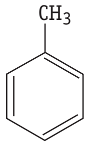
(a)



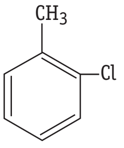
(b)



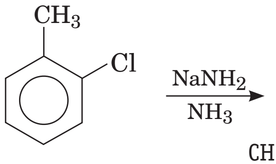
(c)



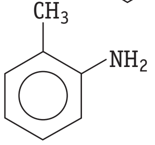
(d)



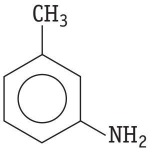
60. What is the product expected in the following reaction?



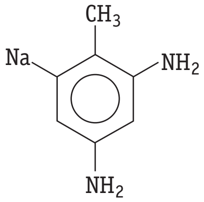
(a)



(b)

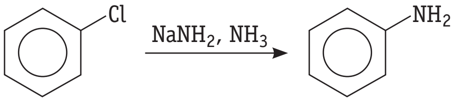


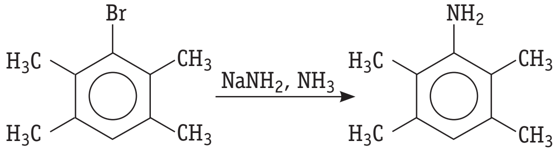
(c)

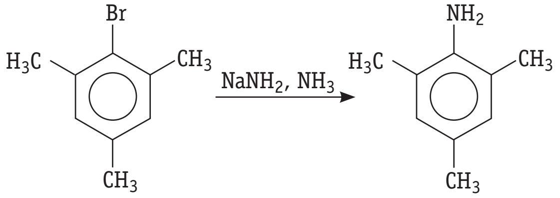


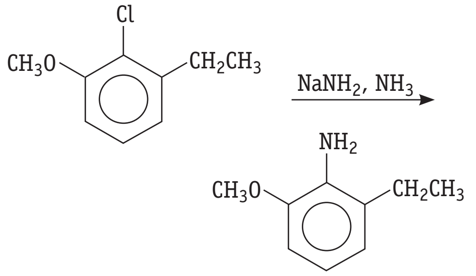
(d) None of these

61. Which of the following reactions is feasible ?

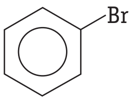
(a) 

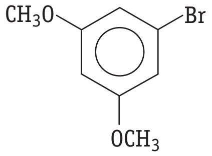
(b) 

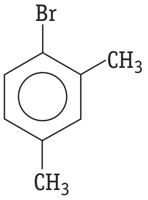
(c) 

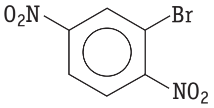
(d) 

62. Which of the following compounds is the most likely to undergo a bimolecular nucleophilic substitution reaction with aqueous NaOH?

(a) 

(b) 

(c) 

(d) 

63. Benzyl chloride ($C_6H_5CH_2Cl$) can be prepared from toluene by chlorination with

$$\underset{\text{I}}{SO_2Cl_2}\ \ \underset{\text{II}}{SOCl_2}\ \ \underset{\text{III}}{Cl_2}\ \underset{\text{IV}}{NaOCl}$$

(a) I, II and III
(b) I and III
(c) II and III
(d) All the four

64. Which of the following sequence of reactions will give 1-bromo-4-trichloromethylbenzene ?

(a) Toluene $\xrightarrow[\text{Fe}]{Br_2}$ *o*-bromotoluene $\xrightarrow[h\nu \text{ or heat}]{Cl_2}$

(b) Toluene $\xrightarrow[\text{Fe}]{Br_2}$ *p*-bromotoluene $\xrightarrow[h\nu \text{ or heat}]{Cl_2}$

(c) Toluene $\xrightarrow[h\nu \text{ or heat}]{Cl_2}$ trichloromethyl benzene $\xrightarrow[\text{Fe}]{Br_2}$

(d) None of the above

Miscellaneous

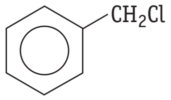
65. Chlorine is the most reactive towards aqueous NaOH in

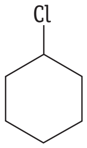
(a) methyl chloride
(b) chlorobenzene
(c) vinyl chloride
(d) ethyl chloride

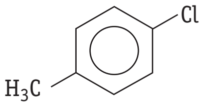
66. Which of the following reagents can be used to distinguish chlorobenzene from chlorocyclohexane ?

(a) $AgNO_3/C_2H_5OH$
(b) $Ag(NH_3)_2OH$
(c) Na fusion; HNO_3; $AgNO_3$
(d) Br_2/CCl_4

67. Which of the following will be the least reactive towards nucleophilic substitution ?

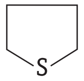
(a) 

(b) 

(c) 

(d) C_2H_5Cl

68. 1, 4-dibromobutane is treated with Na_2S in aqueous ethanol. The product formed is

(a) $BrCH_2CH_2CH_2CH_2OH$
(b) $HSCH_2CH_2CH_2SH$
(c) $BrCH_2CH_2CH_2S^-Na^+$
(d) 

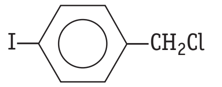
69. The reactivity of the compounds

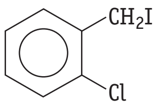
(i) MeBr (ii) $PhCH_2Br$ (iii) MeCl (iv) *p*-$MeOC_6H_4Br$ decreases as

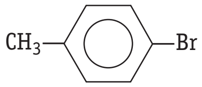
(a) (i) > (ii) > (iii) > (iv)
(b) (iv) > (ii) > (i) > (iii)
(c) (iv) > (iii) > (i) > (ii)
(d) (ii) > (i) > (iii) > (iv)

70. Which of the following will give yellow precipitate on shaking with an aqueous solution of NaOH followed by acidification with dil HNO_3 and addition of $AgNO_3$ solution ?

(a) C_2H_5I

(b) 

(c) 

(d) 

Round II (Mixed Bag)

1. Which reagent will you use for the following reaction ?

$$CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$$

[NCERT]

(a) Cl_2 / UV light
(b) $NaCl + H_2SO_4$
(c) Cl_2 gas in dark
(d) Cl_2 gas in the presence of iron in dark

2. An alkyl halide (RX) reacts with Na to form 4, 5-diethyloctane. Compound RX is

(a) $CH_3(CH_2)_3Br$
(b) $CH_3(CH_2)_2CH(Br)CH_2CH_3$
(c) $CH_3(CH_2)_3CH(Br)CH_3$
(d) CH_3Br

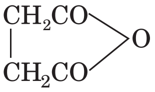
3. Reaction of $C_6H_5CH_2Br$ with aqueous sodium hydroxide follows **[NCERT Exemplar]**

(a) S_N1 mechanism
(b) S_N2 mechanism
(c) any of the above two depending upon the temperature of reaction
(d) Saytzeff rule

4. Among the following the most reactive towards alcoholic KOH is

(a) $CH_2{=}CHBr$
(b) $CH_3COCH_2CH_2Br$
(c) CH_3CH_2Br
(d) $CH_3CH_2CH_2Br$

5. The product of which of the following reactions on dehydration gives



(a) 1,2-dibromoethane $\xrightarrow{KCN} \xrightarrow[\Delta]{H_3O^+}$

(b) 1,1,-dibromoethane $\xrightarrow{KCN} \xrightarrow[\Delta]{H_3O^+}$

(c) 1,1,1-trichloroethane $\xrightarrow[\text{hydrolysis}]{\text{Alkaline}}$

(d) None of the above

6. The hydrogen atoms in chloroform are

(a) acidic
(b) basic
(c) neutral
(d) unpredictable

7. The main product of the reaction,

2-butene + chloroform $\xrightarrow{NaOH}$ would be

(a) butanoic acid
(b) 2-methylbutanoic acid
(c) 1,1,1-trichloro-2-methylbutane
(d) 1,4-butanediol

8. Chloroform with alcoholic KOH gives

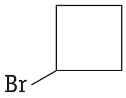
(a) potassium acetate
(b) potassium formate
(c) potassium chloride
(d) potassium chlorate

9. 1, 2-dibromoethane reacts with alcoholic KOH to yield a product X. The hybridisation state of the carbons present in X respectively, are

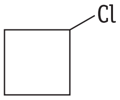
(a) sp, sp
(b) sp^3, sp^3
(c) sp^3, sp^2
(d) sp^3, sp^2

10. What would be the product formed when 1-bromo-3-chlorocyclobutane reacts with two equivalents of metallic sodium in ether?

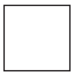
(a)



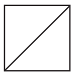
(b)



(c)



(d)



11. The product of which of the following reaction gives the acid catalysed elimination most readily?

(a) $(CH_3)_3COMgBr \xrightarrow{H_3O^+}$

(b) $CH_3CH_2CH_2OMgBr \xrightarrow{H_3O^+}$

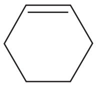
(c) $(CH_3)_2CHOMgBr \xrightarrow{H_3O^+}$

(d) $CH_3CH_2OMgBr \xrightarrow{H_3O^+}$

12. Identify Z in the following sequence of reactions

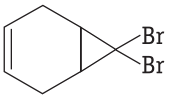
$$C_3H_7I \xrightarrow{\text{Alc KOH}} X \xrightarrow[\Delta]{\text{NBS}, h\nu} Y \xrightarrow{\text{Alc KCN}} Z$$

(a) $(CH_3)_2CH{-}CN$
(b) $Br{-}CH{=}CH{-}CN$
(c) $CH_2{=}CH{-}CH_2CN$
(d) $CH_2{=}CH{-}CHBr{-}CN$

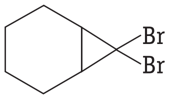
13. CBr_4 + MeLi +  $\longrightarrow$?

Identify the end product.

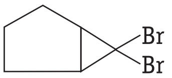
(a)



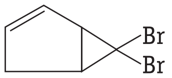
(b)



(c)



(d)

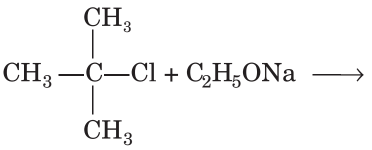


14. A new carbon-carbon bond formation is possible in
- (a) Cannizzaro reaction
- (b) Reimer-Tiemann reaction
- (c) Clemmensen reduction
- (d) None of the above

15. A compound obtained by the hydrolysis of the substance *A*, on reduction forms 2-hexanol. Hence, the substance *A* is
- (a) 3,3-dichlorohexane (b) 2,3-dichlorohexane
- (c) 2,2-dichlorohexane (d) 1,1-dichlorohexane

16. A dihaloalkane '*X*', having formula $C_3H_6Cl_2$, on hydrolysis gives a compound, that can reduce Tollen's reagent. The compound '*X*' is
- (a) 1, 2-dichloropropane (b) 1, 1-dichloropropane
- (c) 1, 3-dichloropropane (d) 2, 2-dichloropropane

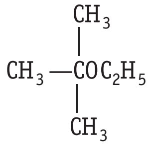
17.



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-Cl + C_2H_5ONa \longrightarrow$$

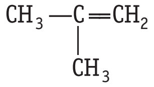
Major product of this reaction is

(a)



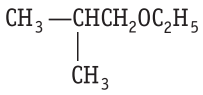
$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}OC_2H_5$

(b)



$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$

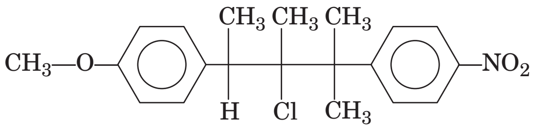
(c)



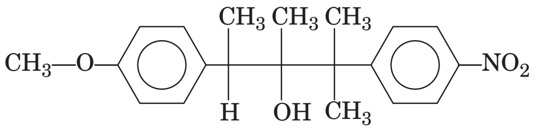
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2OC_2H_5$

(d) None of these

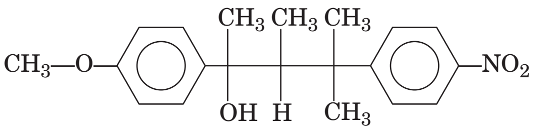
18. The following compound on hydrolysis in aqueous acetone will give



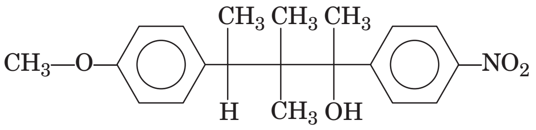
(K)



(L)



(M)

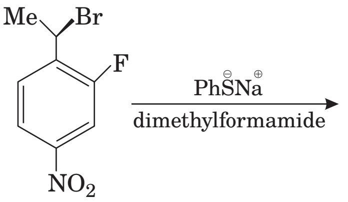


- (a) mixture of (K) and (L) (b) mixture of (K) and (M)
- (c) only (M) (d) only (K)

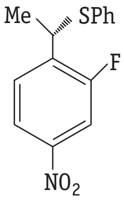
19. Primary alkyl halide $C_4H_9Br(A)$ reacted with alcoholic KOH to give compound (*B*). Compound (*B*) is reacted with HBr to give (*C*) which is an isomer of (*A*). When (*A*) is reacted with sodium metal, it gives compound (*D*), C_8H_{18} which is different from the compound formed when *n*-butyl bromide is reacted with sodium. Give the name of (*A*). **[NCERT Exemplar]**
- (a) 2-methylbromopropane
- (b) 1-bromobutane
- (c) 2-bromobutane
- (d) 1-bromo-2-dimethyl propane

20. A hydrocarbon of molecular mass 72 g mol^{-1} gives a single monochloro derivative and two dichloro derivatives on photochlorination. Give the name of the hydrocarbon. **[NCERT]**
- (a) *n*-pentane (b) 2, 2-dimethyl propane
- (c) 2, 2-dimethyl pentane (d) *iso*-pentane

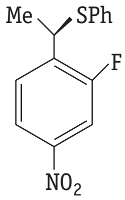
21. The major product of the following reaction is



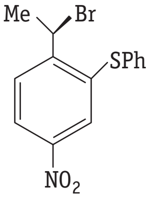
(a)



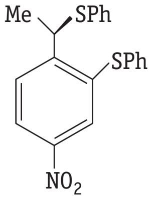
(b)



(c)

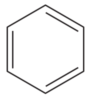


(d)

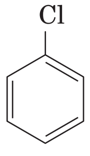


22. Arrange the following compounds in the increasing order of their densities. **[NCERT]**

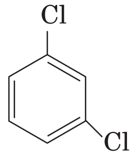
(*A*)



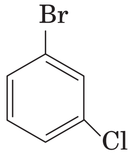
(*B*)



(*C*)



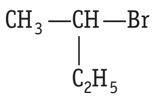
(*D*)

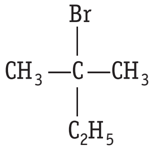


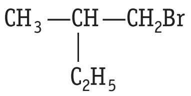
(a) (*A*) < (*B*) < (*C*) < (*D*) (b) (*A*) < (*C*) < (*D*) < (*B*)
(c) (*D*) < (*C*) < (*B*) < (*A*) (d) (*B*) < (*D*) < (*C*) < (*A*)

23. Which of the following compounds will give racemic mixture on nucleophilic substitution by OH^- ion ?

[NCERT Exemplar]

(*A*) 
$CH_3-\underset{\displaystyle C_2H_5}{\underset{|}{CH}}-Br$

(*B*) 
$CH_3-\underset{\displaystyle C_2H_5}{\underset{|}{\overset{\displaystyle Br}{\overset{|}{C}}}}-CH_3$

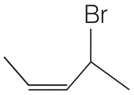
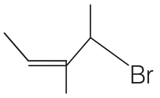
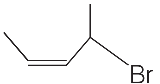
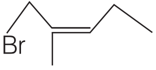
(*C*) 
$CH_3-\underset{\displaystyle C_2H_5}{\underset{|}{CH}}-CH_2Br$

(a) (*A*) (b) (*A*), (*B*), (*C*)
(c) (*B*), (*C*) (d) (*A*), (*C*)

24. The dihalogen derivative '*X*' of a hydrocarbon with three carbon atoms reacts with alcoholic KOH and produces another hydrocarbon which forms a red precipitate with ammoniacal Cu_2Cl_2. '*X*' gives an aldehyde on reaction with aqueous KOH. The compound '*X*' is

(a) 1, 3-dichloropropane (b) 1, 2-dichloropropane
(c) 2, 2-dichloropropane (d) 1, 1-dichloropropane

25. Match the structures given in Column I with the names in Column II.

	Column I		Column II
(A)		(p)	4-bromopent-2-ene
(B)		(q)	4-bromo-3-methylpent-2-ene
(C)		(r)	1-bromo-2-methylbut-2-ene
(D)		(s)	1-bromo-2-methylpent-2-ene

	A	B	C	D		A	B	C	D
(a)	p	q	r	s	(b)	q	p	r	s
(c)	p	q	p	s	(d)	p	q	p	p

26. Match the items of Column I and Column II

	Column I		Column II
(A)	S_N1 reaction	(p)	*vic*-dibromides
(B)	Chemicals in fire extinguisher	(q)	*gem*-dihalides
(C)	Bromination of alkenes	(r)	Racemisation
(D)	Alkylidene halides		
(E)	Elimination of HX from alkyl halide	(s)	Saytzeff rule
		(t)	Chlorobromocarbons

	A	B	C	D	E		A	B	C	D	E
(a)	r	t	q	p	s	(b)	r	t	p	q	s
(c)	t	r	p	q	s	(d)	r	t	p	s	q

More than One Correct Option

27. Haloalkanes contain halogen atom(s) attached to the sp^3 hybridised carbon atom of an alkyl group. Identify haloalkane from the following compounds.

(a) 2-bromopentane **[NCERT Exemplar]**
(b) Vinyl chloride (chloroethene)
(c) 2-chloroacetophenone
(d) Trichloromethane

28. Reagent which cannot be used to distinguish allyl bromide from *n*-propyl bromide are

(a) Br_2/CCl_4
(b) shaking with an aqueous solution of $AgNO_3$
(c) boiling with aqueous KOH solution followed by acidification with dil. HNO_3 and addition of $AgNO_3$ solution
(d) fusion with Na followed by acidification with dilute HNO_3 and addition of $AgNO_3$ solution

29. In the reaction,

$CHCl_3 + 4OH^- \longrightarrow HCOO^- + 3Cl^- + 2H_2O,$ the intermediate species formed is/are

(a) $CH(OH)_3$ (b) $:CCl_2$ (c) CCl_3^- (d) $COCl_2$

30. Which of the following compounds will give haloform test ?

(a) $C_6H_5COCH_3$ (b) CH_3CH_2Br
(c) $CH_3-CHCl-CH_3$ (d) CH_3COCH_2I

31. Alkyl fluorides are synthesised by heating an alkyl chloride/bromide in presence of …… or …… .

[NCERT Exemplar]

(a) CaF_2 (b) CoF_2 (c) Hg_2F_2 (d) NaH

32. The products formed when bromocyclohexane and sodium propynide are heated together are

(a) 2-cyclohexyl propyne (b) 1-cyclohexyl propyne
(c) propyne (d) cyclohexene

Assertion and Reason

Directions (Q. No. 33 to 37) Each of these questions contains two statements : Statement I (Assertion) and Statement II (Reason). Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c) and (d) given below :

(a) Statement I is true; Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true; Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

33. **Statement I** Nucleophilic substitution reaction on an optically active alkyl halide gives a mixture of enantiomers.

Statement II The reaciton follows $S_N 1$ mechanism.

34. **Statement I** Polar solvents are required in $S_N 2$ reactions.

Statement II Ionic reagents are not sufficiently soluble in non-polar solvents to give a high enough concentration of the nucleophile to allow the reaction to occur at a rapid rate.

35. **Statement I** It is difficult to replace chlorine by —OH in chlorobenzene in comparison to that in chloroethane.

Statement II Chlorine-carbon (C—Cl) bond in chlorobenzene has a partial double bond character due to resonance. **[NCERT Exemplar]**

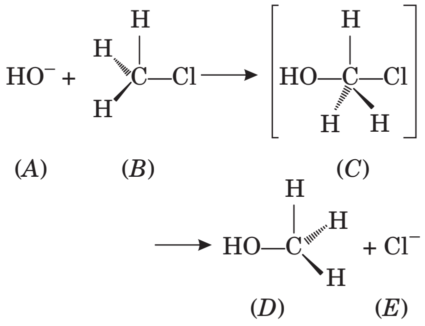
36. Hydrolysis of (–)-2-bromooctane proceeds with inversion of configuration.

Statement II This reaction proceeds through the formation of a carbocation. **[NCERT Exemplar]**

37. **Statement I** In monohaloarenes, further electrophilic substitution occurs at ortho and para positions.

Statement II Halogen atom is a ring deactivator. **[NCERT Exemplar]**

Directions (Q. 38 to 40) Consider the following reactions,



38. Which of the statements are correct about the above reaction? **[NCERT Exemplar]**

(a) (*A*) and (*E*) both are nucleophiles

(b) In (*C*) carbon atom is sp^3 hybridised

(c) In (*C*) carbon atom is sp^2 hybridised

(d) (*A*) and (*C*) both are electrophiles

39. Which of the following statements are correct about this reaction ?

(a) The given reaction follows $S_N 2$ mechanism

(b) (*B*) and (*D*) have opposite configuration

(c) (*B*) and (*D*) have same configuration

(d) The given reaction follows $S_N 1$ mechanism

40. Which of the following statements are correct about the reaction intermediate ?

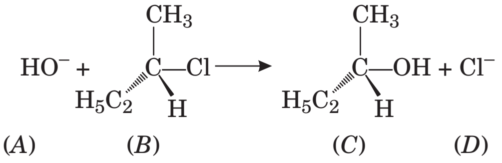
(a) Intermediate (*C*) is unstable because in this carbon is attached to 5 atoms

(b) Intermediate (*C*) is unstable because carbon atom is sp^2 hybridised

(c) Intermediate (*C*) is stable because carbon atom is sp^2 hybridised

(d) Intermediate (*C*) is less stable than the reactant (*B*)

Directions (Q. Nos. 41 and 42) Consider the following nucleophilic substitution reaction.



41. Which of the following statements are correct about the mechanism of this reaction ? **[NCERT Exemplar]**

(a) A carbocation will be formed as an intermediate in the reaction

(b) OH^- will attach the substrate (*B*) from one side and Cl^- will have it simultaneously from other side

(c) An unstable intermediate will be formed in which OH^- and Cl^- will be attached by weak bonds

(d) Reaction proceeds through $S_N 1$ mechanism

42. Which of the following statements are correct about the kinetics of this reaction ?

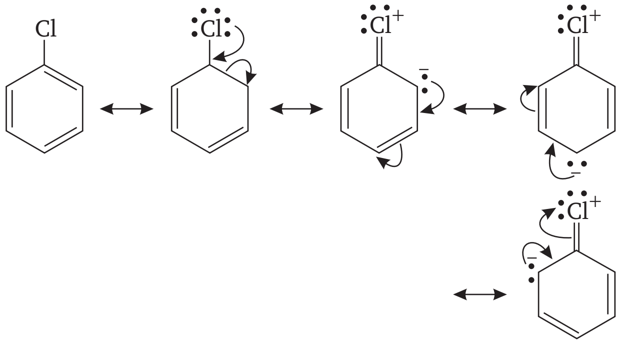
(a) The rate of reaction depends on the concentration of only (*B*)

(b) The rate of reaction depends on concentration of both (*A*) and (*B*)

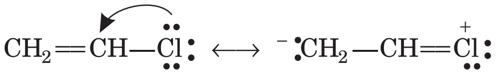
(c) Molecularity of the reaction is one

(d) Molecularity of the reaction is two

Directions (Q. Nos. 43 to 45) Due to sp^2-hybridisation of C-atom holding the halogen atom, resonance effect and smaller polarity of the C—*X* bond, aryl halides do not undergo nucleophilic substitution reactions. Chlorobenzene can be written as a resonance hybrid of the following structures :



Due to resonance, chlorobenzene gets stabilised. In chlorobenzene, the C—Cl bond acquires some double bond charater and hence, it is difficult to break it as compared to C—Cl bond in alkyl halides. Similarly vinyl halides due to resonance are less reactive towards nucleophilic substitution reactions.



$$CH_2{=}CH{-}\ddot{\underset{\cdot\cdot}{Cl}}: \longleftrightarrow {}^{-}:CH_2{-}CH{=}\overset{+}{\underset{\cdot\cdot}{Cl}}:$$

43. Which of the following is most reactive towards nucleophilic substitution reactions?

(a) $ClCH_2CH{=}CH_2$ (b) $CH_3CH{=}CHCl$
(c) C_6H_5Cl (d) None of these

44. Vinyl chloride on treatment with aqueous KOH gives

(a) acetylene (b) acetaldehyde
(c) vinyl alcohol (d) None of these

45. In chlorobenzene, all the six C—C bonds have the same length because of

(a) inductive effect (b) isomerism
(c) tautomerism (d) sp^2-hybridisation

Directions (Q. 46 to 48) The majority of haloalkanes have a dipole moment. This is a result of the electron withdrawing ability of halogen atoms. The halogen atom carries a slight negative charge, with the remainder of the molecule having a slight positive charge. The carbon atom bonded to the halogen can act as a centre of attraction of nucleophiles. Atoms or molecules with lone pairs of electrons and/or a negative charge make good nucleophiles. However, equally important as far as a successful reaction is concerned is that the halogen atom makes a good leaving group. The majority of haloalkanes fit the same pattern in their reactions.

46. The following reaction,

$$C_2H_5Br + KOH \longrightarrow C_2H_5OH + KBr \text{ is}$$

(a) electrophilic substitution
(b) nucleophilic addition
(c) free radical substitution
(d) nucleophilic substitution

47. A solution of (+) 1-chloro-1-phenylethane in toluene racemises slowly in the presence of a small amount of $SbCl_5$, due to the formation of

(a) carbocation (b) carbanion
(c) free radical (d) carbene

48. The rate of S_N2 reaction is maximum when the solvent is

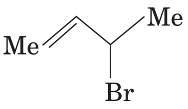
(a) CH_3OH (b) H_2O
(c) DMSO (d) benzene

Previous Years' Questions

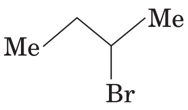
49. Consider the following bromides

(*A*)

(*B*)



(*C*)



The correct order of S_N1 reactivity is [AIEEE 2010]

(a) (*B*) > (*C*) > (*A*)
(b) (*B*) > (*A*) > (*C*)
(c) (*C*) > (*B*) > (*A*)
(d) (*A*) > (*B*) > (*C*)

50. The organic chloro compound, which shows complete stereochemical inversion during an S_N2 reaction is [AIEEE 2008]

(a) $(C_2H_5)_2CHCl$ (b) $(CH_3)_3CCl$
(c) $(CH_3)_2CHCl$ (d) CH_3Cl

51. *Trans*-2-phenyl-1-bromocyclopentane on reaction with alcoholic KOH produces [AIEEE 2006]

(a) 4-phenylcyclopentene
(b) 2-penylcyclopentene
(c) 1-phenylcyclopentene
(d) 3-phenylcyclopentene

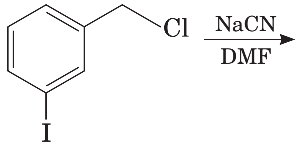
52. $CH_3Br + Nu^- \longrightarrow CH_3{-}Nu + Br^-$

The decreasing order of the rate of the above reaction with nucleophile (Nu^-) *A* and *D* is

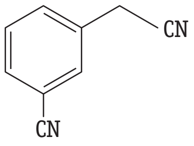
$[Nu = (A)\ PhO^-, (B) AcO^-, (C) HO^-, (D)\ CH_3O^-]$ [AIEEE 2006]

(a) *D* > *C* > *A* > *B* (b) *D* > *C* > *B* > *A*
(c) *A* > *B* > *C* > *D* (d) *B* > *D* > *C* > *A*

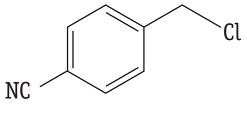
53. The structure of the major product formed in the following reaction is [AIEEE 2006]



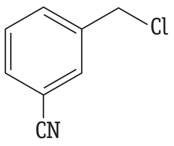
(a)



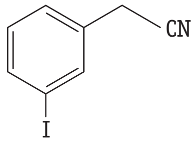
(b)



(c)



(d)



54. Alkyl halides react with dialkyl copper reagents to give [AIEEE 2005]

(a) alkenyl halides (b) alkanes
(c) alkyl copper halides (d) alkenes

55. On mixing ethyl acetate with aqueous sodium chloride, the composition of the resultant solution is [AIEEE 2004]

(a) $CH_3COOC_2H_5 + NaCl$
(b) $CH_3COONa + C_2H_5OH$
(c) $CH_3COCl + C_2H_5OH + NaOH$
(d) $CH_3Cl + C_2H_5COONa$

56. Acetyl bromide reacts with excees of CH_3MgI followed by treatment with a saturated solution of NH_4Cl gives [AIEEE 2004]

(a) acetone (b) acetamide
(c) 2-methyl-2-propanol (d) acetyl ioide

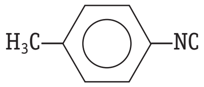
57. The compound formed on heating chlorobenzene with chloral in the presence of concentrated sulphuric acid is [AIEEE 2004]

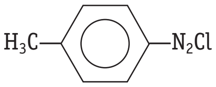
(a) gammexane (b) DDT
(c) freon (d) hexachloroethane

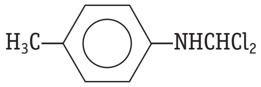
58. Bottles containing C_6H_5I and $C_6H_5CH_2I$ lost their original labels. They were labelled *A* and *B* for testing. *A* and *B* were separately taken in test tubes and boiled with NaOH solution. The end solution in each tube was made acidic with dilute HNO_3 and then some $AgNO_3$ solution was added. Substance *B* gave a yellow precipitate. Which one of the following statements is true for this experiment ? [AIEEE 2003]

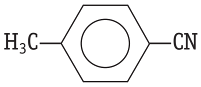
(a) *A* was C_6H_5I
(b) *A* was $C_6H_5CH_2I$
(c) *B* was C_6H_5I
(d) Addition of HNO_3 was unnecessary

59. The reaction of chloroform with alcoholic KOH and *p*-toluidine form [AIEEE 2003]

(a) 

(b) 

(c) 

(d) 

60. CH_3MgI is an organometallic compound due to [AIEEE 2002]

(a) Mg—I bond (b) C—I bond
(c) C—Mg bond (d) C—H bond

Answers

Round I

1. (a)	**2.** (b)	**3.** (b)	**4.** (b)	**5.** (a)	**6.** (d)	**7.** (d)	**8.** (b)	**9.** (b)	**10.** (a)
11. (d)	**12.** (b)	**13.** (a)	**14.** (a)	**15.** (d)	**16.** (a)	**17.** (c)	**18.** (a)	**19.** (d)	**20.** (b)
21. (c)	**22.** (d)	**23.** (a)	**24.** (a)	**25.** (b)	**26.** (a)	**27.** (a)	**28.** (d)	**29.** (c)	**30.** (c)
31. (a)	**32.** (c)	**33.** (b)	**34.** (b)	**35.** (b)	**36.** (a)	**37.** (b)	**38.** (d)	**39.** (d)	**40.** (c)
41. (d)	**42.** (a)	**43.** (a)	**44.** (b)	**45.** (a)	**46.** (b)	**47.** (c)	**48.** (b)	**49.** (d)	**50.** (a)
51. (d)	**52.** (c)	**53.** (a)	**54.** (b)	**55.** (a)	**56.** (d)	**57.** (a)	**58.** (d)	**59.** (b)	**60.** (a)
61. (a)	**62.** (d)	**63.** (b)	**64.** (b)	**65.** (a)	**66.** (a)	**67.** (c)	**68.** (d)	**69.** (d)	**70.** (c)

Round II

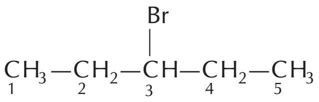
1. (a)	**2.** (b)	**3.** (a)	**4.** (d)	**5.** (a)	**6.** (a)	**7.** (b)	**8.** (b)	**9.** (a)	**10.** (d)
11. (a)	**12.** (c)	**13.** (b)	**14.** (b)	**15.** (c)	**16.** (b)	**17.** (b)	**18.** (a)	**19.** (d)	**20.** (b)
21. (a)	**22.** (a)	**23.** (a)	**24.** (d)	**25.** (c)	**26.** (b)	**27.** (a,d)	**28.** (c,d)	**29.** (b,c)	**30.** (a,b,c,d)
31. (b,c)	**32.** (c,d)	**33.** (a)	**34.** (a)	**35.** (a)	**36.** (c)	**37.** (b)	**38.** (a,b)	**39.** (a,b)	**40.** (a,d)
41. (a,d)	**42.** (a,c)	**43.** (a)	**44.** (d)	**45.** (d)	**46.** (d)	**47.** (a)	**48.** (c)	**49.** (a,b)	**50.** (d)
51. (d)	**52.** (a)	**53.** (d)	**54.** (b)	**55.** (a)	**56.** (c)	**57.** (b)	**58.** (a)	**59.** (a)	**60.** (c)

the Guidance

Round I

1. —$CH_2CH{=}CH_2$ is called allyl group, so here Br occupy allylic position.

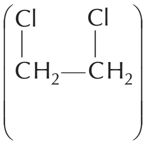
2. Correct IUPAC name for diethylbromomethane is 3-bromopentane.



$$\overset{1}{C}H_3-\overset{2}{C}H_2-\overset{3}{C}H(Br)-\overset{4}{C}H_2-\overset{5}{C}H_3$$

3-bromopentane

3. 1, 2-dichloroethane



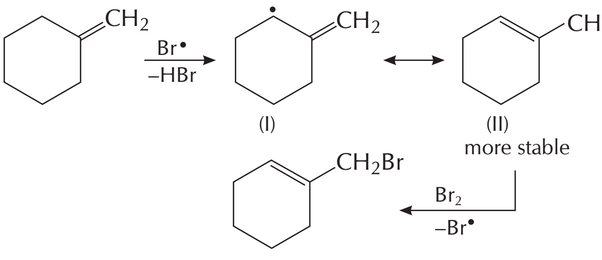
$$\left(\begin{matrix}Cl & & Cl\\ | & & |\\ CH_2 & - & CH_2\end{matrix}\right)$$

is an example of *vic*-dihalide because two halogen atoms occupy successive positions.

4. $RCH_2Cl + NaI \xrightarrow[\Delta]{Acetone} RCH_2I + NaCl$

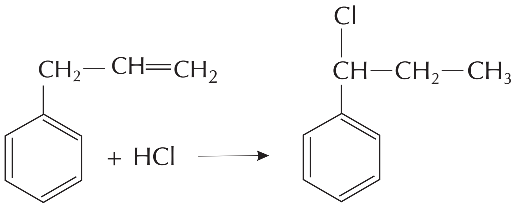
All other reactions are not feasible.

6. The mechanism of allylic bromination is



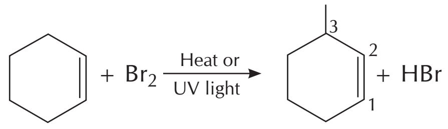
Since, endocyclic double bond is more stable than exocyclic double bond, therefore initially formed less stable free radical (I) gets converted into the more stable free radical (II) which then reacts with Br_2 to give the product.

7.



It is an addition reaction and addition occurs according to Markownikoff's rule.

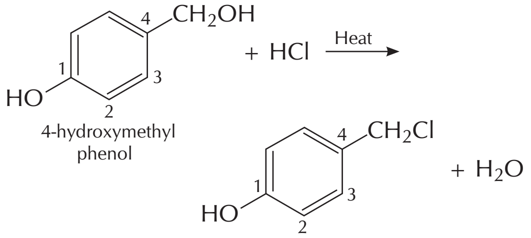
8.



cyclohexene 3-bromocyclohexene

Note Under above specified conditions allylic halogenation takes place. Addition reaction can take place only if reaction is at room temperature.

9.

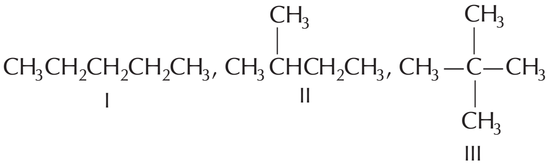


4-hydroxymethyl phenol

4-chloromethyl phenol

Note Phenolic —OH group is not replaced by —Cl group.

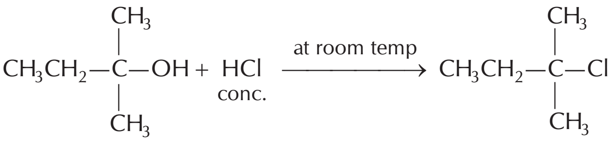
10. The possible isomers of C_5H_{12} are



$$\underset{I}{CH_3CH_2CH_2CH_2CH_3},\quad \underset{II}{CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH_3},\quad \underset{III}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3}$$

Isomer [II] has four groups of equivalent hydrogen atoms. Therefore, it can produce four isomeric monochlorides.

11.

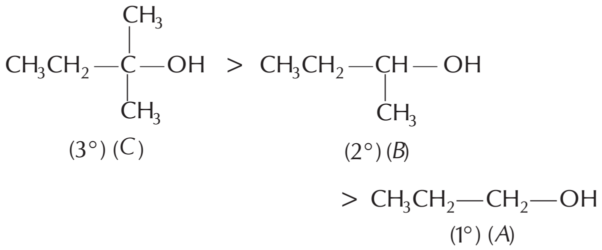


$$CH_3CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH + \underset{conc.}{HCl} \xrightarrow{\text{at room temp}} CH_3CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Cl$$

(2-methylbutan-2-ol)
(because it is a 3° alcohol)

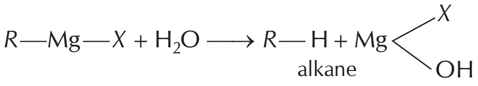
2-chloro-2-methylbutane

12. The order of reactivity of alcohols wih halogen acid is



$$\underset{(3°)\,(C)}{CH_3CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH} > \underset{(2°)\,(B)}{CH_3CH_2-\underset{\underset{CH_3}{|}}{C}H-OH} > \underset{(1°)\,(A)}{CH_3CH_2-CH_2-OH}$$

13. Grignard reagents (R—Mg —X) are readily decomposed by water to produce alkanes. That is why they should be prepared under anhydrous conditions. Instead, ether is used as a solvent during the preparation of Grignard reagent as these are inert towards it.



$$R-Mg-X + H_2O \longrightarrow \underset{\text{alkane}}{R-H} + Mg\begin{matrix}X\\ OH\end{matrix}$$

14. When KI reacts with H_2SO_4, It produces HI. In order to produce alkyl iodides (*R*—I), this HI should react with alcohols (*R*—OH). But the reaction does not take place in this manner as H_2SO_4 oxidises HI to I_2 which in turn does not react with alcohol.

$$KI + H_2SO_4 \xrightarrow{Heat} KHSO_4 + HI$$
$$H_2SO_4 \longrightarrow H_2O + SO_4 + [O]$$
$$2HI + [O] \longrightarrow H_2O + I_2$$

Note Instead of H_2SO_4; H_3PO_4 can be used to produce alkyl iodides.

15. Alkene is first reacted with HBr to form alkyl bromide.

$$CH_3CH_2CH=CH_2 \xrightarrow[H_2O_2]{HBr} CH_3CH_2CH_2—CH_2Br$$

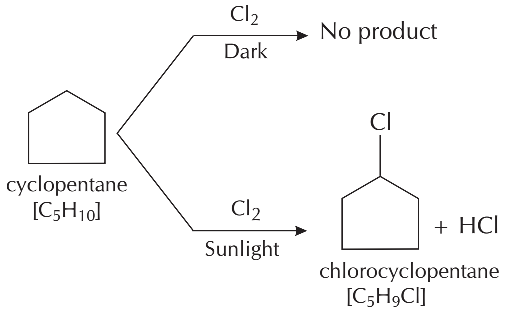
Alkyl bromide formed reacts with potassium iodide to form alkyl iodide.

$$CH_3CH_2CH_2CH_2Br \xrightarrow[Acetone]{KI} CH_3CH_2CH_2CH_2I + KBr$$

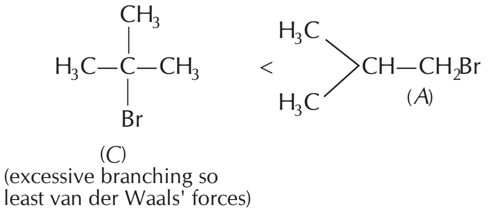
16. Molecular formula C_5H_{10} can be either alkene or cycloalkane.

Since, the hydrocarbon does not react with chlorine in dark, it is not an alkene. So, it is a cycloalkane, *i.e.*, cyclopentane.

Since, it forms only single monochloro derivative in bright sunlight, all the H-atoms should be identical. So, it is cyclopentane.



17. Increasing order of the boiling points of the compounds are



$$H_3C-\underset{Br}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3 < \begin{matrix}H_3C\\H_3C\end{matrix}\!\!>CH-CH_2Br$$

(*C*)
(excessive branching so least van der Waals' forces)

(*A*)

$< CH_3CH_2CH_2CH_2Br$
(*B*)
(no branching)

18. The correct increasing order of boiling points of the compounds are

butane < 1-chlorobutane < 1-bromobutane < 1-iodobutane because boiling point increases with increase in the size of halogen atom.

20. A primary alkyl halide would prefer to undergo S_N2 reaction as transition state is more stable for unhindered halide.

21. Alkyl halides react with silver cyanide to give isocyanides.

$$CH_3CH_2Br + AgCN \longrightarrow \underset{\text{ethyl isocyanide}}{CH_3CH_2NC} + AgBr$$

22. S_N1 mechanism involves formation of carbocation intermediate. Hence, the species which gives the most stable carbocation readily undergoes S_N1 mechanism. *t*-butyl bromide gives the most stable carbocation, *i.e.*, 3° carbocation, so it readily undergoes S_N1 reaction.

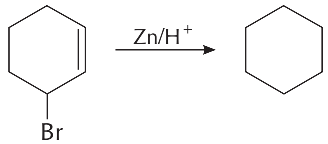
24. Haloalkanes are highly reactive and here, mainly show bimolecular nucleophilic substitution reaction. Hence, the correct order of reactivity of haloalkanes is

$$CH_3Br > CH_3CH_2Br > C_3H_7Br > C_4H_9Br$$

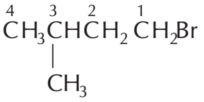
25. $C_6H_6 + C_3H_7Br \xrightarrow{AlCl_3} C_6H_5CH(CH_3)_2 + HBr$

The 1° carbonium ion isomerizes to the more stable 2° carbonium ion, which in turn reacts with benzene in the Friedel-Crafts reaction to give *iso*-propyl benzene.

26.

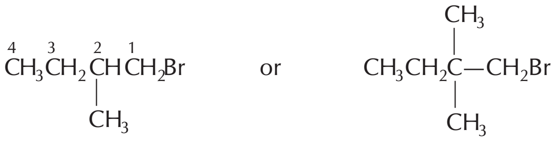


27.



$$\overset{4}{C}H_3\overset{3}{\underset{CH_3}{\underset{|}{C}}}H\overset{2}{C}H_2\overset{1}{C}H_2Br$$

Out of the give compounds three are primary halides. The presence of methyl group closer to halide group increases the steric hindrance and decreases rate in

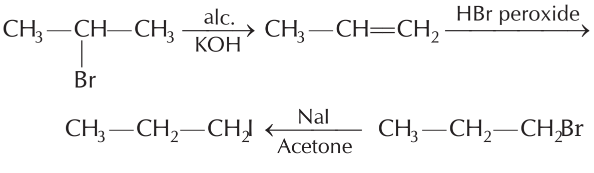


$$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{\underset{CH_3}{\underset{|}{C}}}H\overset{1}{C}H_2Br \quad \text{or} \quad CH_3CH_2\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2Br$$

29. $\underset{\text{propylchloride}}{CH_3CH_2CH_2Cl} \xrightarrow[-\,KCl]{KCN} \underset{\text{butanenitrile}}{CH_3CH_2CH_2CN}$

30. In Wurtz reaction, wet ether is not used because wet ether destroy the sodium metal.

31.

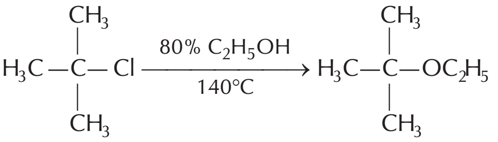


$$CH_3-\underset{Br}{\underset{|}{CH}}-CH_3 \xrightarrow[KOH]{alc.} CH_3-CH=CH_2 \xrightarrow{HBr\ peroxide}$$
$$CH_3-CH_2-CH_2I \xleftarrow[Acetone]{NaI} CH_3-CH_2-CH_2Br$$

32. $CH_3CH_2CH_2Cl \xrightarrow{KOH\ (alc)} CH_3CH=CH_2$

$$CH_3CHClCH_3 \xrightarrow{KOH\ (alc)} \underset{\text{1-propene}}{CH_3CH=CH_2}$$

33.



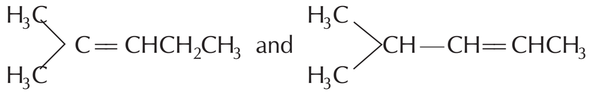
$$H_3C-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-Cl \xrightarrow[140°C]{80\%\ C_2H_5OH} H_3C-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OC_2H_5$$

34. Out of CH_3COCH_3, CH_3CHO, CH_3CH_2CHO and $(CH_3)_2CHCHO$ two pairs containing a total six carbon atoms are

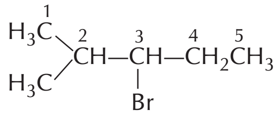
(i) $CH_3COCH_3 + CH_3CH_2CHO$

(ii) $CH_3CHO + (CH_3)_2CHCHO$

The alkenes which will give these pairs of compound on ozonolysis are

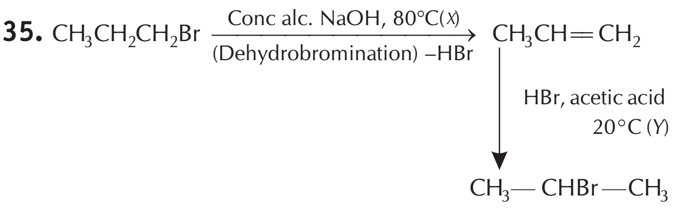


These two alkenes can be obtained on dehydrogenation if the alkyl halide is $(CH_3)_2CHCH(Br)CH_2CH_3$



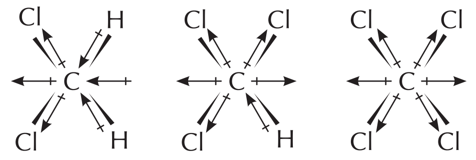
3-bromo-2-methyl pentane

35.



$$CH_3CH_2CH_2Br \xrightarrow[\text{(Dehydrobromination) –HBr}]{\text{Conc alc. NaOH, 80°C}(X)} CH_3CH{=}CH_2 \xrightarrow{\text{HBr, acetic acid, 20°C }(Y)} CH_3-CHBr-CH_3$$

36.



$\mu = 1.62$ D $\quad \mu = 1.03$ D $\quad \mu = 0.0$ D

CCl_4 (tetrachloromethane) is a symmerical molecule so, it has zero dipole moment.

In $CHCl_3$ (trichloromethane/chloroform), the resultant of two C—Cl dipole moments is opposed by the resultant of C—H and C—Cl bond. Since, the letter resultant dipole moment is smaller than the former, $CHCl_3$ has a dipole moment = 1.03D.

In CH_2Cl_2 (dichloromethane), the resultant of two C—Cl dipole moments is reinforced by the resultant ot two C—H bonds. Thus, CH_2Cl_2 has a dipole moment = 1.62 D.

Therefore, CH_2Cl_2 has the highest dipole moment amongst the above three molecules.

37. Chloroform reacts with conc. HNO_3 to give chloropicrin or tear gas.

$$\underset{\text{chloroform}}{CHCl_3} + \underset{\text{conc}}{HNO_3} \longrightarrow \underset{\text{chloropicrin or tear gas}}{CCl_3NO_2} + H_2O$$

38. $$\underset{\text{methyl amine}}{CH_3NH_2} + \underset{\text{chloroform}}{CHCl_3} + 3KOH \longrightarrow \underset{\text{methyl isocyanide}}{CH_3N \overset{\rightarrow}{\equiv} C} + 3KCl + 3H_2O$$

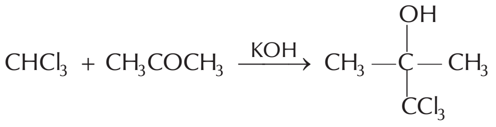
39. Chloroform undergoes oxidation in the presence of light and air to form phosgene gas.

$$2CHCl_3 + \frac{1}{2}O_2 \longrightarrow \underbrace{COCl_2}_{\text{phosgene gas}} + 2HCl$$

41. On heating with I_2 and NaOH, methanol (CH_3OH) does not give yellow compound.

42. F_2 reacts with NaOH to give oxygen difluoride (OF_2) and not hypofluorite ion (OF^-) needed for haloform reaction. Hence, CHF_3 cannot be prepared.

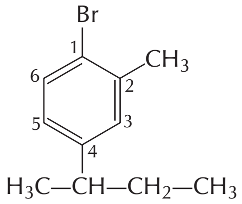
43. When acetone reacts with chloroform in alkaline solution, chloretone is obtained which is used as a hypnotic drug.



$$CHCl_3 + CH_3COCH_3 \xrightarrow{KOH} CH_3-\underset{CCl_3}{\overset{OH}{C}}-CH_3$$

chloretone

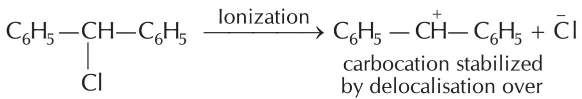
44.



1-bromo-4-sec-butyl-2-methylbenzene

Note After drawing the structures, count the valencies of every element and complete them by using H-atoms, (if incomplete.)

45.



$$C_6H_5-\underset{Cl}{CH}-C_6H_5 \xrightarrow{\text{Ionization}} C_6H_5-\overset{+}{C}H-C_6H_5 + \overset{-}{Cl}$$

1-chloro-1, 1-diphenyl methane (2°)

carbocation stabilized by delocalisation over C_6H_5 rings (more stable)

$$\underset{\text{benzyl chloride (°)}}{C_6H_5CH_2Cl} \xrightarrow{\text{Ionization}} C_6H_5\overset{+}{C}H_2 + Cl^-$$

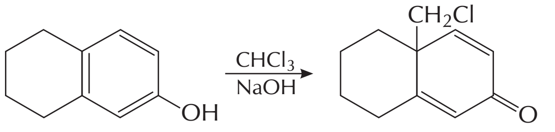
carbocation stabilized by delocalisation over one C_6H_5 ring (less stable)

In S_N1 reaction, reactivity depends upon the stability of carbocations. $C_6H_5-\overset{+}{C}H-C_6H_5$ carbocation is more stable as compared to $C_6H_5\overset{+}{C}H_2$. Therefore, $C_6H_5CHClC_6H_5$ gets hydrolysed more easily than $C_6H_5CH_2Cl$.

46. Replacement of H of benzene by any atom/group is called electrophilic substitution reaction. The electrophile in this reaction is Cl^+. The Cl^+ is produced as a result of redox reaction,

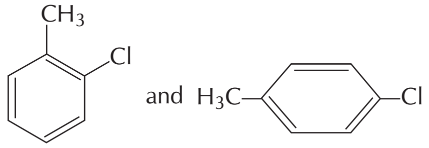
$$O_2 + 2Cl^- + 4H^+ \longrightarrow 2H_2O + 2Cl^+$$

47.

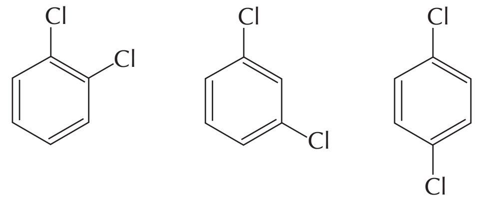


48. $AlCl_3 + Cl_2 \longrightarrow AlCl_4^- + \underset{\text{electrophile}}{Cl^+}$

49. The reaction of toluene with chlorine in the presence of iron and in the absence of light yields the mixture of



50. Symmetry of the molecule is related to its crystal littice structure and hence, to its melting point and solubility. A highly symmetrical structure has a higher melting point.

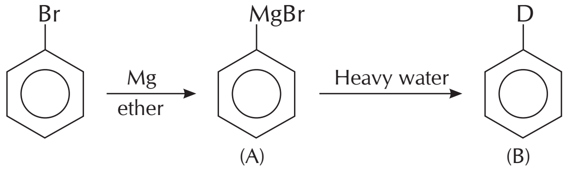


o-dichlorobenzene *m*-dichlorobenzene *p*-dichlorobenzene

Out of the above three isomers of dichlorobenzene, the *p*-isomer is more symmetrical than other two isomers. *i.e.*, it has more closely packed arrangement of molecules in its crystal lattice. So, *p*-dichlorobenzene has a higher melting point and lower solubility as compared to *ortho* and *meta* isomers.

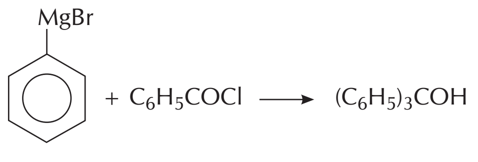
52. *m*-nitrochlorobenzene is however less reactive than the *p*-nitrochlorobenzene since the NO_2 group at *m*-position can't stabilize the intermediate carbanion by resonance. Thus, the correct option is II > III > I.

53. Reactivity decreases as the number of NO_2 groups at *o* and *p*-position with respect to chlorine decreases. Thus, the correct order is II > III > IV > I.

54. 

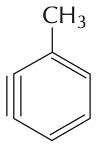
55. The reactivity of an aryl halide towards alcoholic $AgNO_3$ depends on the ability of the aryl halide to ionise.

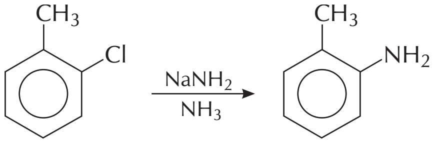
$$C_6H_5CHBrCH_3 > C_6H_5CH_2CH_2Br > C_6H_5CH{=}CHBr$$

56. 

57. Aryl halides are less reactive towards nucleophile than alkyl halides due to resonance.

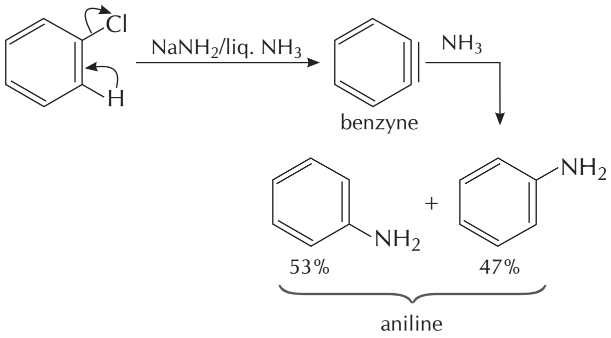
59. The formation of a mixture of *ortho* and *meta*-toluidine certainty suggests that the triple bond in benzyne is between *o*- and *m*-positions and hence the structure of intermediate is

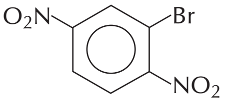


60. 

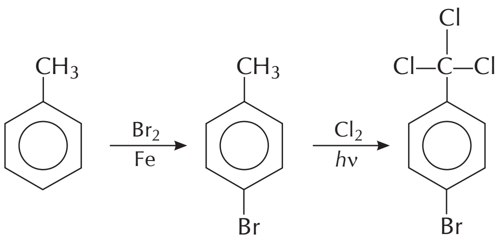
For the formation of benzyne intermediate, it is essential that an hydrogen should be available at an *ortho* position to the halogen.

61. When chlorobenzene is treated with sodamide in liquid ammonia at 196 K, the reaction occurs through the intermediate benzyne formation and finally gives aniline.



62. The reactivity of substance for Ar S_N2 reaction depends on the $-R$ and $-I$ powers of the group present at *o*-and/ or *p*-position. Thus,  is most reactive for S_N2 reaction.

63. $C_6H_5CH_3 \xrightarrow[\text{or } Cl_2/h\nu]{SO_2Cl_2/\text{peroxide}} C_6H_5CH_2Cl$

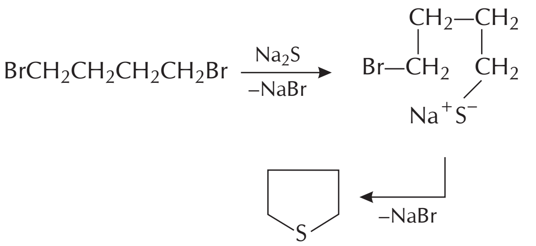
64. 

65. Bulky groups cause steric hinderance in the formation of transition state. Therefore, higher homologues are less reactive than lower homologues.

66. Chlorocyclohexane behaves like an aliphatic halogen substituted hydrocarbon and can, therefore reacts with alcoholic $AgNO_3$.

67. ArS_N reactions are accelerated by electron withdrawing groups, especially at the *o*-and *p*-positions to the leaving group and retarded by electron-donating groups.

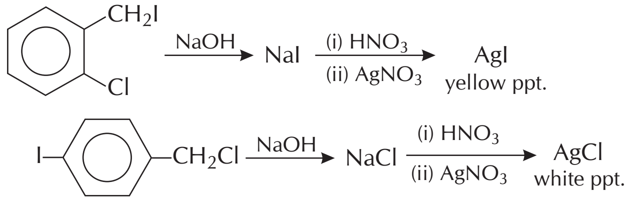
68.



69. The order of reactivity follows the sequence, benzyl halides > alkyl halides > aryl halides. Out of chlorides and bromides, bromides are more reactive. Therefore, the correct order of reactivity is

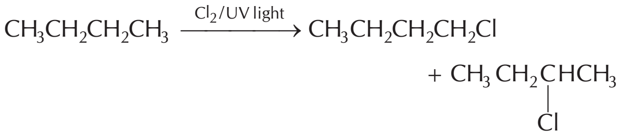
$$PhCH_2Br > MeBr > MeCl > p\text{-}MeOC_6H_4Br$$

70. Only benzyl halide, *i.e.*, *p*-iodobenzyl chloride and *o*-chlorobenzyl iodide undergo hydrolysis on shaking with an aqueous solution of NaOH.



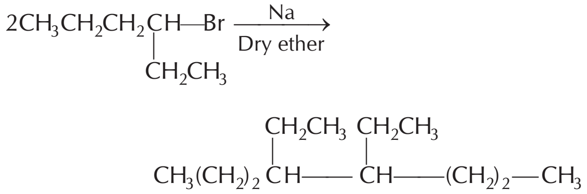
Round II

1.



$$CH_3CH_2CH_2CH_3 \xrightarrow{Cl_2/\text{UV light}} CH_3CH_2CH_2CH_2Cl + CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3$$

2. Since, the alkyl halide *RX* gives 4, 5-diethyloctane, when reacts with Na, it must be $CH_3(CH_2)_2CH(Br)CH_2CH_3$.



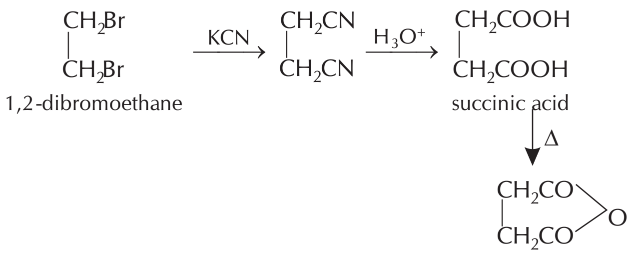
$$2CH_3CH_2CH_2\underset{\displaystyle CH_2CH_3}{\underset{|}{C}}H\text{—}Br \xrightarrow[\text{Dry ether}]{Na} CH_3(CH_2)_2\overset{\displaystyle CH_2CH_3}{\overset{|}{C}}H\text{——}\overset{\displaystyle CH_2CH_3}{\overset{|}{C}}H\text{——}(CH_2)_2\text{—}CH_3$$

This reaction is known as Wurtz reaction.

3. Reaction of $C_6H_5CH_2Br$ with aqueous sodium hydroxide follows S_N1 mechanism as $C_6H_5CH_2^+$ is a more stable carbocation which is involved as intermediate.

4. The polarity between the C—*X* bond increases by increasing +*I* effect. The +*I* effect also increases by increasing the alkyl group, therefore in $CH_3CH_2CH_2Br$ the polarity is maximum than CH_3CH_2Br. While in rest the polarity decreases due to the presence of $=$ bond and $\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}$ group.

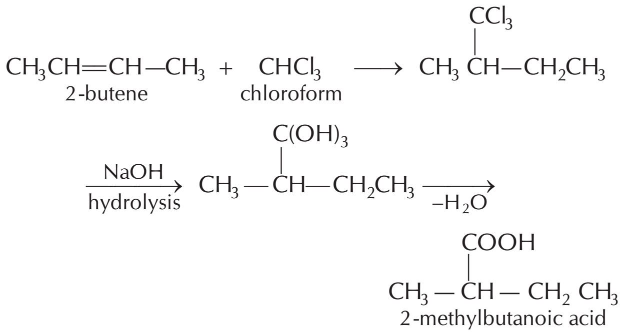
5.



$$\underset{\text{1,2-dibromoethane}}{\begin{matrix}CH_2Br\\|\\CH_2Br\end{matrix}} \xrightarrow{KCN} \begin{matrix}CH_2CN\\|\\CH_2CN\end{matrix} \xrightarrow{H_3O^+} \underset{\text{succinic acid}}{\begin{matrix}CH_2COOH\\|\\CH_2COOH\end{matrix}} \xrightarrow{\Delta} \begin{matrix}CH_2CO\\|\\CH_2CO\end{matrix}\!\!>O$$

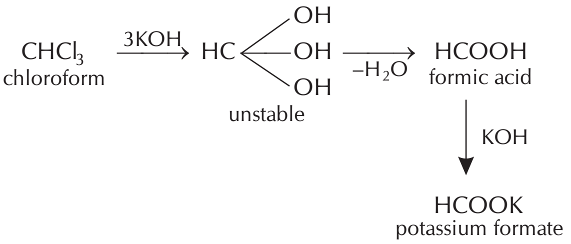
6. The hydrogen of chloroform is acidic in nature.

7.



$$\underset{\text{2-butene}}{CH_3CH{=}CH\text{—}CH_3} + \underset{\text{chloroform}}{CHCl_3} \longrightarrow CH_3\overset{\displaystyle CCl_3}{\overset{|}{C}}H\text{—}CH_2CH_3 \xrightarrow[\text{hydrolysis}]{NaOH} CH_3\text{—}\overset{\displaystyle C(OH)_3}{\overset{|}{C}}H\text{—}CH_2CH_3 \xrightarrow[-H_2O]{} \underset{\text{2-methylbutanoic acid}}{CH_3\text{—}\overset{\displaystyle COOH}{\overset{|}{C}}H\text{—}CH_2CH_3}$$

8. Chloroform with alcoholic KOH gives potassium formate.

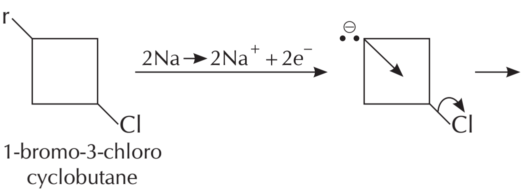


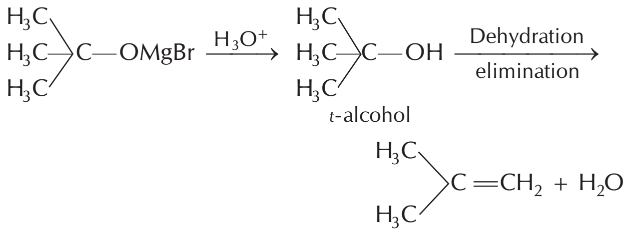
$$\underset{\text{chloroform}}{CHCl_3} \xrightarrow{3KOH} \underset{\text{unstable}}{HC(OH)_3} \xrightarrow[-H_2O]{} \underset{\text{formic acid}}{HCOOH} \xrightarrow{KOH} \underset{\text{potassium formate}}{HCOOK}$$

9. Alkyl halides give elimination reaction with alcoholic KOH and yield an alkene or alkyne (from dihalides) *e.g.*,

$$\underset{\text{1, 2-dibromoethane}}{Br\text{—}CH_2\text{—}CH_2\text{—}Br} \xrightarrow[\Delta]{\text{alc. KOH}} \underset{\text{acetylene}}{\overset{sp}{CH}\equiv\overset{sp}{CH}}$$

10.



11. 

Order of elimination (dehydration) of alcohol is

T > S > P

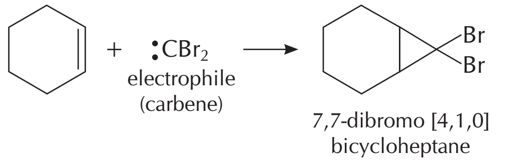
12. $CH_3CH_2CH_2I \xrightarrow{\text{alc KOH}} \underset{(X)}{CH_3CH=CH_2}$

$\xrightarrow[\Delta]{\text{NBS}, h\nu} \underset{(Y)}{CH_2Br-CH=CH_2}$

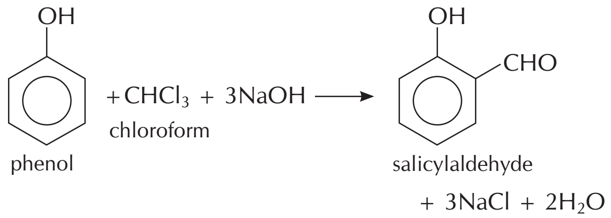
$\xrightarrow{\text{Alc KCN}} \underset{(Z)}{CH_2CN-CH=CH_2}$

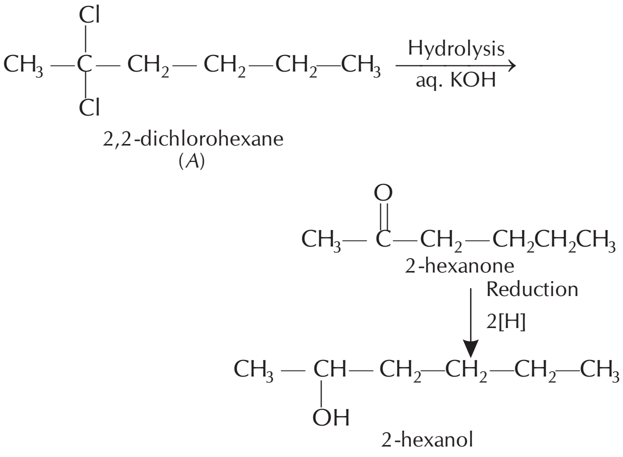
13. $CBr_4 + MeLi \longrightarrow MeBr + LiCBr_3$

$LiCBr_3 \longrightarrow LiBr + :CBr_2$

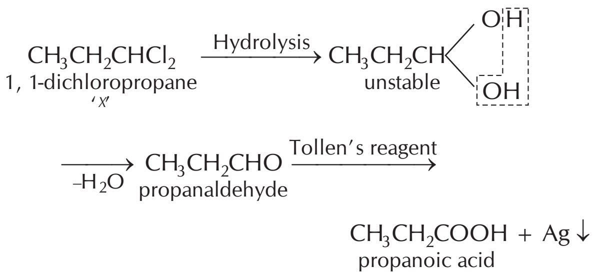


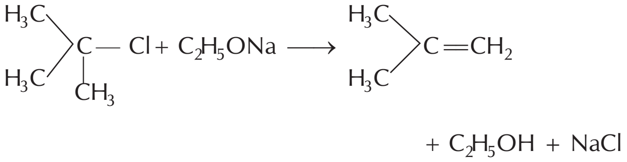
14. In the Reimer-Tiemann reaction, new C—C bond is formed between the carbon of benzene ring and —CHO group.



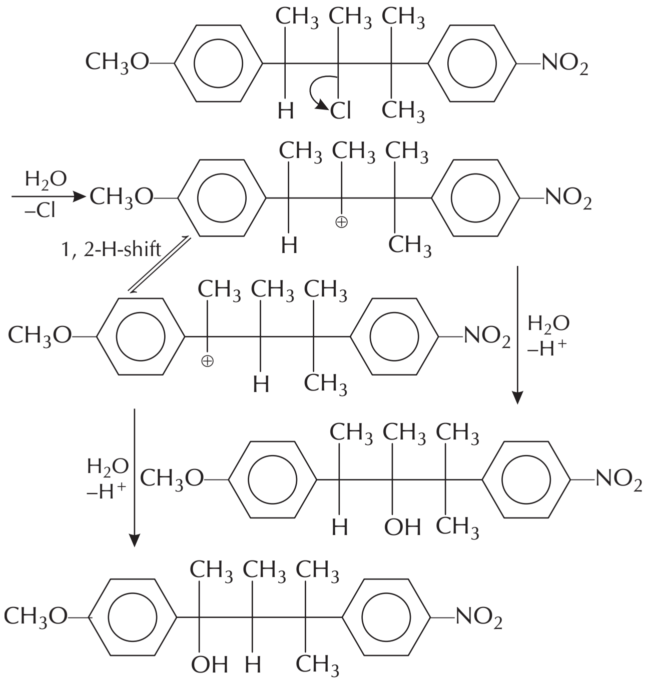
15. 

16. Since, the obtained compound reduces Tollen's reagent, it must be an aldehyde. Thus, it is obvious that both the —Cl atoms are present at C_1. Hence, the compound 'X' is 1,1-dichloropropane and the reactions are as follows

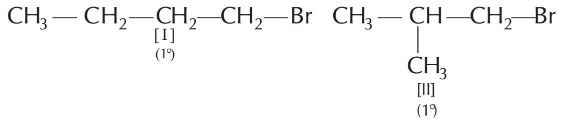


17. 

18. The product (K) is formed through simple nucleophilic substitution while major product (L) is formed through H^- shift *via* S_N1 reaction and methoxy group stabilises the carbocation intermediate of product (L).



19. Two possible isomers of C_4H_9Br are

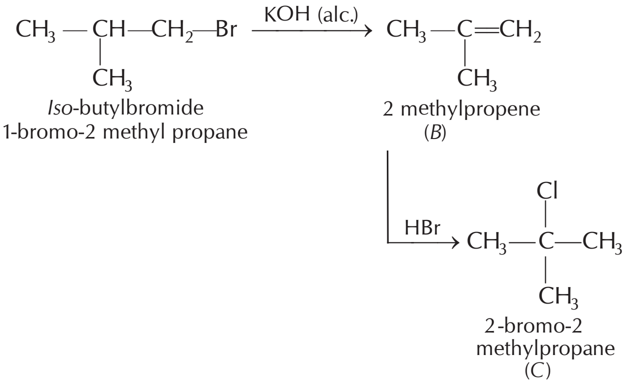


According to the question, compound (*A*) on reaction with sodium does not give the same product produced by *n*-butyl bromide. So, (*A*) cannot be [I].

$$2\,\underset{n\text{–butylbromide}}{CH_3-CH_2-CH_2-CH_2-Br} + 2\,Na \xrightarrow{\text{Ether}}$$

$$\underset{\underset{C_8H_{18}}{n\text{–octane(not formed in the reaction)}}}{CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3}$$

Now [II] must be the correct isomer.


Iso-butylbromide
1-bromo-2 methyl propane

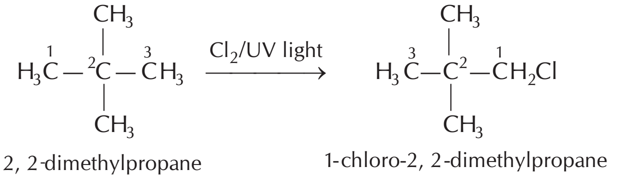
2 methylpropene
(B)

2-bromo-2 methylpropane
(C)

20. Hydrocarbon C_5H_{12} has molecular mass 72 g mol. It has three isomers.

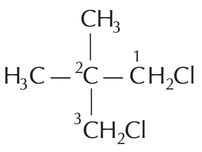
$$\underset{\substack{n\text{-pentane}\\ [I]}}{CH_3—CH_2—CH_2—CH_2—CH_3}$$

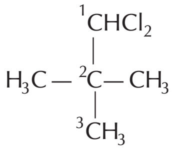
$$\underset{II}{CH_3CH_2CH(CH_3)_2}, \qquad \underset{III}{(CH_3)_4C}$$


2, 2-dimethylpropane
[IV]

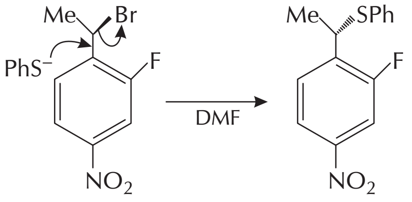
1-chloro-2, 2-dimethylpropane
[monochloro derivative]
[V]

Out of the three isomers [V] structure is correct. Its two dichloroderivatives are

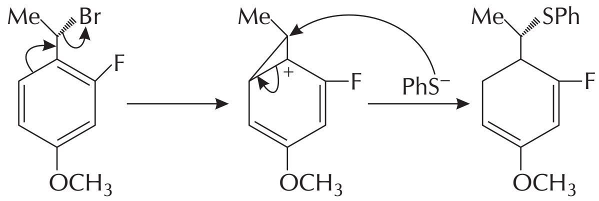

1, 3-dichloro-2, 2-dimethylpropane
[A]


1, 1-dichloro-2, 2-dimethylpropane
[B]

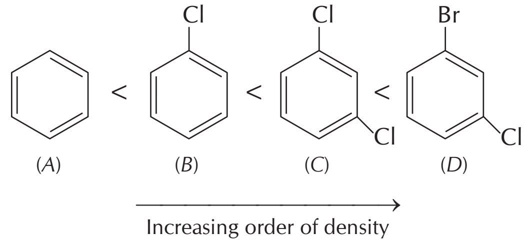
21. PhS^- is a strong nucleophile and dimethylformamide (DMF) is a highly polar aprotic solvent. Condition indicates that nucleophilic substitution (S_N2) takes place at 2° benzylic place, stereochemically. It involves inversion of configuration.



Aryl group can exhibit neighbouring group or can show anchimeric assistance but not possible here due to deactivity imparted by $—NO_2$ and —F., It can be possible if $—OCH_3$ could have been instead of $—NO_2$.

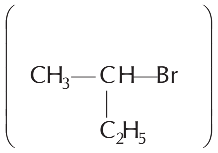

retention of configuration

22. Increasing order of the density of the compounds are



Because density increases with increase in mass (molar mass) or size.

23. 'A' 2-bromobutane



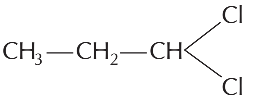
$$\left(\underset{\substack{|\\ C_2H_5}}{CH_3—CH—Br}\right)$$

gives racemic mixture on nucleophilic substitution by OH^- ion. 'B' also gives racemic mixture but 'C' gives inverted product.

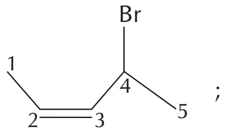
24. 'X' is a three carbon compound with two halogen atom, so its molecular formula is $C_3H_6Cl_2$. Only terminal alkynes give red ppt with ammoniacal Cu_2Cl_2, so the hydrocarbon produced by the reaction of 'X' with alc KOH must be a terminal alkyne (*i.e.*, $CH_3C\equiv CH$).

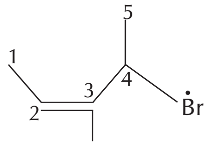
$$C_3H_6Cl_2 \xrightarrow{\text{Alc KOH}} CH_3C\equiv CH \xrightarrow{\text{Amm } Cu_2Cl_2} \underset{\text{red ppt}}{CH_3C\equiv CCu\downarrow}$$

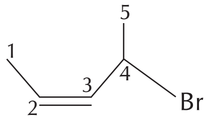
Compound (X) gives an aldehyde when reacts with aqueous KOH. This suggests that both the halogens are present on same terminal carbon atom. Thus, the formula of compound (X) is

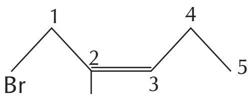

1, 1-dichloropropane

25.


4-bromo-pent-2-ene (p) ;


4-bromo-3-methylpent-2-ene (q)


4-bromopent-2-ene (p) ;


1-bromo-2-methylpent-2-ene(s)

26. (A) S_N1 reaction results in racemisation as well as inversion because of the formation of planar carbocation intermediate.

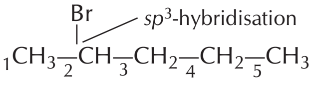
(B) Chlorobromocarbons are used to extinguish fire.

(C) Bromination of alkene result in the formation of *vic* bromide

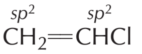
(D) Alkylidine halides are *gem*-dihalides

(E) Elimination of H*X* from alkyl halide occur in accordance with Saytzeff rule.

27.

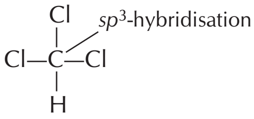


2-bromopentane

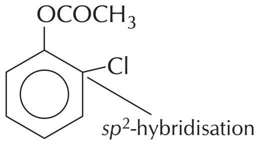


$\overset{sp^2}{CH_2}=\overset{sp^2}{CHCl}$

vinyl chloride



trichloromethane



Thus, 2-bromopentane and trichloromethane haloalkanes contain halogen atom (s)attached to the sp^3-hybridised carbon atom of an alkyl group.

28. Br_2 / CCl_4 can be used as allyl bromide being unsaturated will discharge its colour while *n*-propyl bromide does not. On shaking with aq. $AgNO_3$, allyl bromide being more reactive will give pale yellow ppt. of AgBr but *n*-propyl bromide will not.

On boiling with aq. KOH, both will undergo hydrolysis, hence give ppt. of AgBr. Fusion with Na also converts the Br of both the compounds into NaBr, thus both give ppt with $AgNO_3$. Hence, reagents given in option (c) and (d) cannot be used to distinguish between allyl bromide and *n*-propyl bromide.

29. $CHCl_3 + OH^- \longrightarrow :CCl_3^-$

$$:CCl_3^- \rightleftharpoons :CCl_2 + Cl^-$$

$$:CCl_2 \xrightarrow{OH^-} HO-\bar{C}Cl_2 \xrightarrow[-OH^-]{H_2O} HO-CHCl_2 \xrightarrow{OH^-,\,-2Cl^-} HCOO^-$$

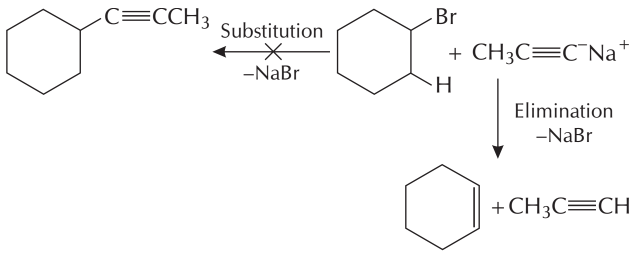
30. $CH_3COCH_2I \xrightarrow[NaOH]{I_2} CHI_3$

$$C_6H_5COCH_3 \xrightarrow[NaOH]{I_2} CHI_3$$

Further under the basic conditions of the reaction, both $CH_3CHClCH_3$ and CH_3CH_2Br will undergo hydrolysis to give $CH_3CHOHCH_3$ and CH_3CH_2OH respectively which will give iodoform test.

31. Alkyl fluorides are synthesised by heating an alkyl chloride/bromide in presence of CoF_2 or Hg_2F_2.

32. 2° alkyl halides preferably undergo elimination rather than substitution.



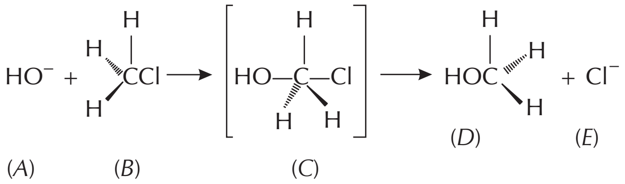
33. Statement II is the correct explanation of statement I.

34. A polar aprotic solvent dissolves ionic compounds and it slovates by orienting the negative end of the dipole around the cation. It is unable to solvate the anion through positive end of its dipole.

35. It is difficult to replace chlorine by —OH in chlorobenzene (C_6H_5Cl) in comparison to that in chloroethane (C_2H_5Cl) because chlorine -carbon (C — Cl) bond in chlorobenzene (C_6H_5Cl) has a partial double bond character due to resonance.

36. Hydrolysis of (–) -2- bromooctane proceeds with inversion of configuration because this reaction does not proceeds through the formation of a carbocation.

37. It involves the formation of transition state. *X* is –*I* showing atom due to which these deactivate benzene nucleus. However due to their electron donating *R* effect, these increases electron density at *ortho* and *para* positions and make them more reactive for electrophilic substitution reaction.



38. In the above reaction molecules HO^- (*A*) and Cl^- (*E*) are nucleophiles. The carbon atom of molecule (*C*) is sp^3 hybridised.

39. Above reaction follows S_N2 mechanism and the compound (*B*) and (*D*) have opposite configuration.

40. Intermediate (*C*) is unstable because in this intermediate carbon is attached to 5 atoms. The intermediate (*C*) is less stable than the reactant (*B*).

41. Since the product have same configuration as the reactant , the reaction must involve carbocation as intermediate. Thus, the reaction involve S_N1 mechanism.

42. Since reaction is S_N1,

rate $= k\,[(CH_3)\cdot CH(C_2H_5)\,Cl]$ or rate $\propto [B]$

It is a unimolecular reaction.

43. Allyl halides (*i.e.,* $ClCH_2CH=CH_2$) are more reactive than vinyl, (*i.e.*, $CH_3CH=CHCl$) and aryl (*i.e.*, C_6H_5Cl) halides towards nucleophilic substitution reactions.

44. $CH_2=CH—Cl \xrightarrow{\text{aq. KOH}}$ No reaction

45. Each sp^2-hybridised carbon atom has a *p*-orbital, these six *p*-orbitals overlap to form a π-molecular orbital in which the electrons are completely delocalized. Due to delocalization of these π-electrons, all the six C—C bonds are equal.

46. Alkyl halides undergo nucleophilic substitution reaction.

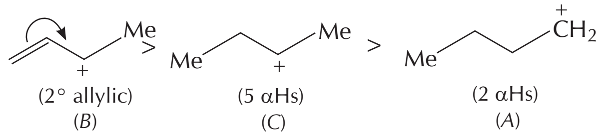
47. In the presence of $SbCl_5$, 1-chloro-1-phenylethane forms a carbocation as follows

$$CH_3CHClC_6H_5 + SbCl_5 \longrightarrow [CH_3\overset{+}{C}H—C_6H_5] + SbCl_6^-$$

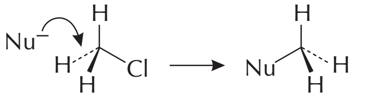
Carbocation is a planar species, therefore, it can be attacked by $SbCl_6^-$ either from the top or the bottom face with equal ease.

48. Polar aprotic solvents such as DMSO increase the rate of the S_N2 reactions.

49. Higher the stability of carbocation, faster is the reaction because S_N1 reactions involve the formation of carbocation intermediate.



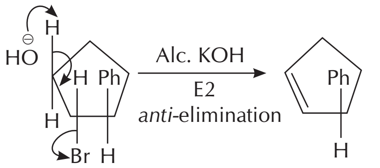
50. Nucleophilic substitution bimolecular (S_N2) prefers less sterically hindered site to attack. Lesser the steric hindrance, faster the S_N2 reaction. So, ease of reaction is 1° > 2° > 3°.



S_N2 involves inversion of configuration stereo chemically.

(**Remember!** if molecule is optically active, optical inversion, also called Walden inversion is known.)

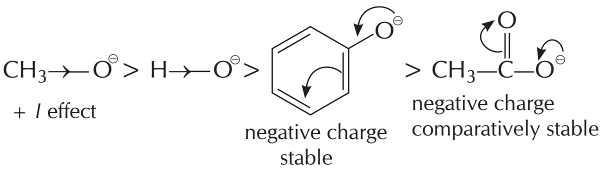
51.



3-phenylcyclopentene

Anti-elimination, means —H and the —Br both departing group must be present at dihedral angle of 180° (*anti*).

52. Nucleophilicity order is



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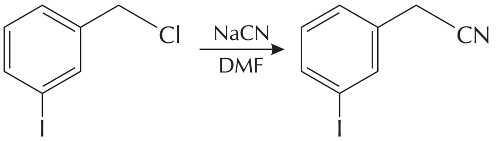
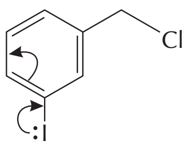


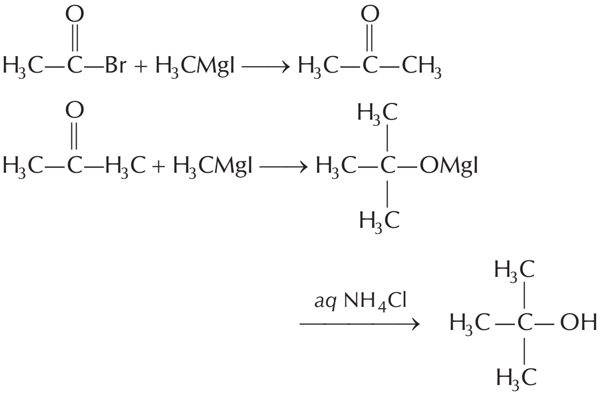
Chloride is on 1° aliphatic carbon which is substituted easier in comparison to iodide which is arylic and more stable due to delocalisation, hence difficult to substitute.



54. It is Corey-House synthesis of alkanes.

55. Aqueous NaCl is neutral hence, there is no reaction between ethyl acetate and aqueous NaCl.

56.



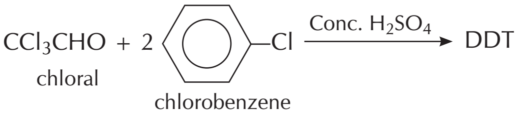
$$H_3C—\overset{\overset{O}{\|}}{C}—Br + H_3CMgI \longrightarrow H_3C—\overset{\overset{O}{\|}}{C}—CH_3$$

$$H_3C—\overset{\overset{O}{\|}}{C}—H_3C + H_3CMgI \longrightarrow H_3C—\underset{H_3C}{\overset{H_3C}{C}}—OMgI$$

$$\xrightarrow{aq\ NH_4Cl} H_3C—\underset{H_3C}{\overset{H_3C}{C}}—OH$$

2-methyl-2-propanol

57.



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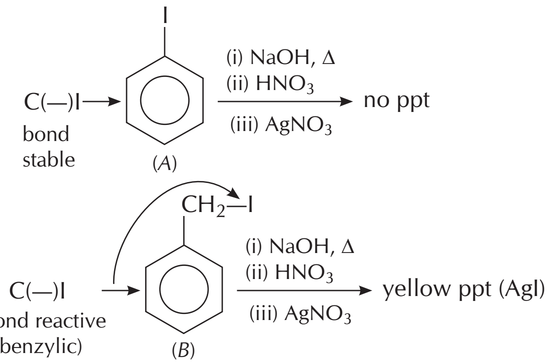

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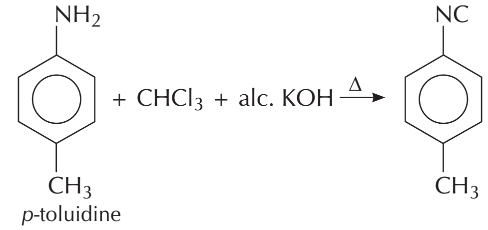


This is carbylamine reaction.

60. CH_3MgI contains carbon-metal (C—Mg) bond, so, classified as organometallic compound.

11

Organic Compounds Containing Oxygen

JEE Main MILESTONE

- Alcohols
- Phenols
- Ethers
- Aldehydes and Ketones
- Carboxylic Acids

11.1 Alcohols

The hydroxy derivatives of aliphatic hydrocarbons are called alcohols. They are obtained by replacing one or more hydrogen atoms of a hydrocarbon by the —OH group.

Alcohols may be classified on the following basis

On the Basis of Position of —OH Group

Alcohols fall into different classes depending on how the —OH group is positioned on the chain of carbon atoms.

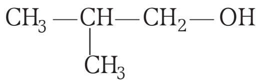
These classes are as

Alcohols, phenols, ethers, aldehydes, ketones and carboxylic acid are included in this group as all of these have O *atom as a part of their functional group. Although these are quite different from each other in structure and chemical properties.*

(a) **Primary Alcohols**

In a primary (1°) alcohol, the carbon, which carries the —OH group, is attached with only one alkyl group, *i.e.*, they contain $—CH_2OH$ group. *e.g.*,

$CH_3—CH_2—OH$
ethanol



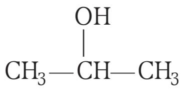
$$CH_3—\underset{\substack{|\\CH_3}}{CH}—CH_2—OH$$

2-methylpropan-1-ol

Methanol, CH_3OH *is an exception to this. It is counted as a primary alcohol even though there is no alkyl group which is attached to the carbon carrying* —OH *group.*

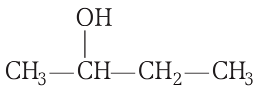
(b) **Secondary Alcohols**

In a secondary (2°) alcohol, the carbon carrying —OH group is joined directly to **two** alkyl groups, which may or may not be same. In other words, they have $\rangle$CHOH group. *e.g.*,



$$CH_3—\overset{\substack{OH\\|}}{CH}—CH_3$$

propan-2-ol

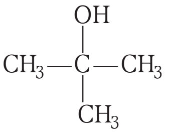


$$CH_3—\overset{\substack{OH\\|}}{CH}—CH_2—CH_3$$

butan-2-ol

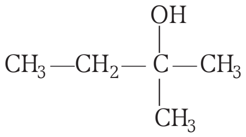
(c) Tertiary Alcohols

In these alcohols (3°), the carbon atom holding the —OH group is attached directly to **three** alkyl groups, which may or may not be same. In other words, they have $\gtrdot$C—OH group. *e.g.*,



$$CH_3-\overset{\overset{\large OH}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-CH_3$$

2-methylpropan-2-ol



$$CH_3-CH_2-\overset{\overset{\large OH}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-CH_3$$

2-methylbutan-2-ol

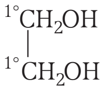
On the Basis of Number of —OH Group Present

However, depending upon the number of —OH group present, the alcohols may be monohydric (*i.e.*, have one —OH group), dihydric (have two —OH groups), trihydric (have three —OH groups).

Some examples of monohydric, dihydric and trihydric alcohols are given below

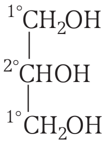
CH_3OH
methanol
(monohydric alcohol)

C_2H_5OH
ethanol
(monohydric alcohol)



$$\begin{array}{l} ^{1°}CH_2OH \\ \quad | \\ ^{1°}CH_2OH \end{array}$$

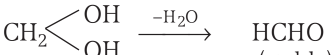
ethylene glycol
(dihydric alcohol)



$$\begin{array}{l} ^{1°}CH_2OH \\ \quad | \\ ^{2°}CHOH \\ \quad | \\ ^{1°}CH_2OH \end{array}$$

glycerol
(trihydric alcohol)
(mixed alcohol)

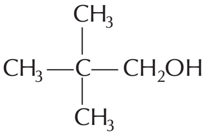
Remember! The two or more —OH groups must be present at different carbon atoms as they if present at same carbon atom, lead to the removal of water molecule *e.g.*,



$$CH_2\begin{matrix} \diagup OH \\ \diagdown OH \end{matrix} \xrightarrow{-H_2O} HCHO$$

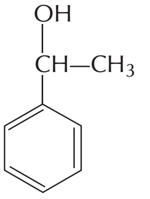
(unstable) (stable) formaldehyde

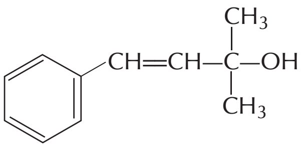
Sample **Problem 1** *Which of the following is a tertiary alcohol?* **[NCERT]**

(a) 

$$CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-CH_2OH$$

(b) $H_2C{=}CH-CH_2OH$

(c) 

(d) 

Interpret (*d*) If —CH_2OH group is present, alcohol is primary (1°), if $\gtrdot$CHOH group is present, it is secondary (2°) and if $\gtrdot$COH group is present, alcohols is (3°), so classification of given alcohols is as follow

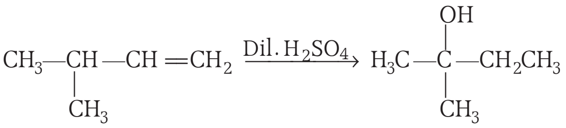
(a) *primary* (b) *primary*
(c) *secondary* (d) *tertiary*

Preparation of Monohydric Alcohols

Important methods used to prepare alcohols are as follows

(i) From Alkenes

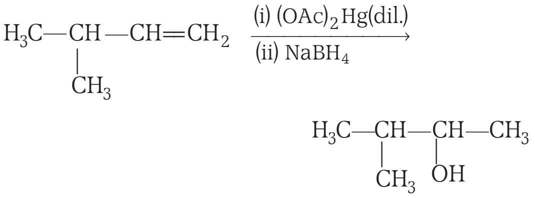
(a) **By acid catalysed hydration** It takes place in the presence of dilute H_2SO_4.



$$CH_3-\underset{\underset{\large CH_3}{|}}{CH}-CH{=}CH_2 \xrightarrow{\text{Dil. }H_2SO_4} H_3C-\overset{\overset{\large OH}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-CH_2CH_3$$

In this reaction intermediate carbocation is formed and rearrange, therefore —OH gets attached at maximum degree of carbon.

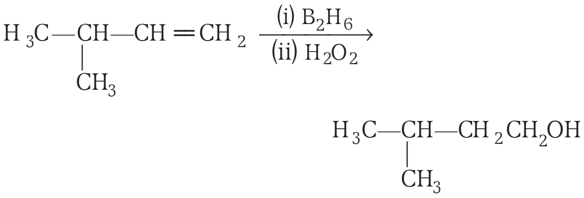
(b) **By oxymercuration-demercuration reaction**



$$H_3C-\underset{\underset{\large CH_3}{|}}{CH}-CH{=}CH_2 \xrightarrow[\text{(ii) NaBH}_4]{\text{(i) (OAc)}_2\text{Hg(dil.)}} H_3C-\underset{\underset{\large CH_3}{|}}{CH}-\underset{\underset{\large OH}{|}}{CH}-CH_3$$

Intermediate carbocation does not form and alcohol is formed according to Markownikoff's rule.

(c) **By hydroboration oxidation reaction**



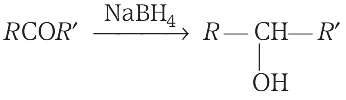
$$H_3C-\underset{\underset{\large CH_3}{|}}{CH}-CH{=}CH_2 \xrightarrow[\text{(ii) }H_2O_2]{\text{(i) }B_2H_6} H_3C-\underset{\underset{\large CH_3}{|}}{CH}-CH_2CH_2OH$$

Intermediate carbocation does not form and alcohol is formed according to anti-Markownikoff's rule.

(ii) By Reduction of Carbonyl Compounds

Aldehydes on reduction give primary alcohols and ketones give secondary alcohols in the presence of weak reducing agent ($NaBH_4$).

$$RCHO \xrightarrow{NaBH_4} RCH_2OH$$



$$RCOR' \xrightarrow{NaBH_4} R-\underset{\underset{\large OH}{|}}{CH}-R'$$

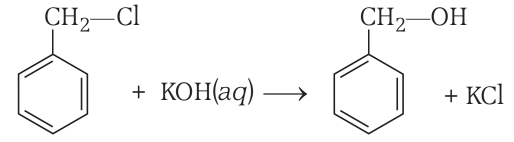
(iii) By Reduction of Acids and Esters

Carboxylic acids and esters on reduction in the presence of strong reducing agent ($LiAlH_4$) give primary alcohols.

$$RCOOH \xrightarrow{LiAlH_4} RCH_2—OH$$

$$CH_3COOCH_2CH_2CH_3 \xrightarrow{LiAlH_4} CH_3CH_2OH + CH_3CH_2CH_2OH$$

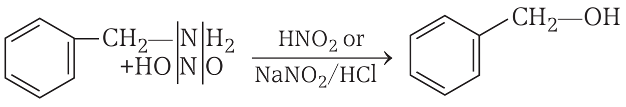
(iv) By Hydrolysis of Alkyl Halides



benzyl chloride

$$CH_3—CH_2Br + NaOH(aq) \longrightarrow CH_3—CH_2—OH + NaBr$$

(v) From Primary Aliphatic Amines

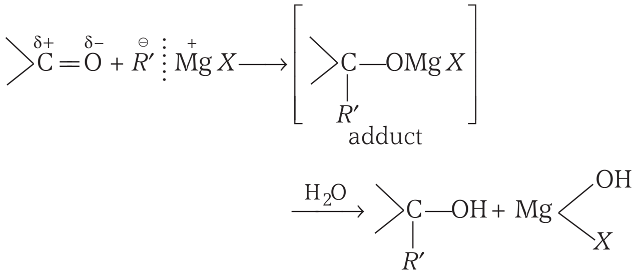


benzyl amine benzyl alcohol

(vi) From Grignard Reagent

Grignard reagent ($R'MgX$) on reaction with aldehydes/ketones followed by hydrolysis gives alcohols.

The nature of alcohol formed depends upon the aldehyde or ketone taken, *e.g.*, if in the reaction aldehyde is formaldehyde, primary alcohol $—CH_2OH$ is obtained while other aldehydes give secondary alcohol ($>CHOH$) with Grignard reagents. Ketones give tertiary alcohol ($\gt COH$) with Grignard reagents.

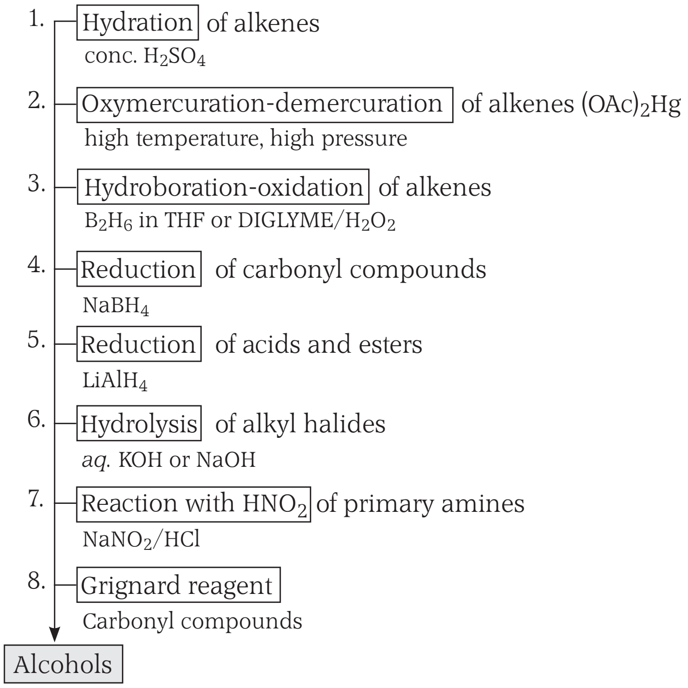


Sample Problem 2 *Propan-1-ol can be prepared from propene by*

(a) H_2O/H_2SO_4
(b) $Hg(OA)_2/H_2O$ *followed by* $NaBH_4$
(c) B_2H_6 *followed by* H_2O_2
(d) CH_3CO_2H / H_2SO_4

Interpret (c) Alkenes undergo addition reaction with diborane. The addition compounds on hydrolysis with H_2O_2 / OH^- yieds alcohols.

$$CH_3—CH=CH_2 \xrightarrow[H_2O_2]{B_2H_6} CH_3—CH_2—CH_2OH$$



1. Hydration of alkenes
   conc. H_2SO_4
2. Oxymercuration-demercuration of alkenes $(OAc)_2Hg$
   high temperature, high pressure
3. Hydroboration-oxidation of alkenes
   B_2H_6 in THF or DIGLYME/H_2O_2
4. Reduction of carbonyl compounds
   $NaBH_4$
5. Reduction of acids and esters
   $LiAlH_4$
6. Hydrolysis of alkyl halides
   aq. KOH or NaOH
7. Reaction with HNO_2 of primary amines
   $NaNO_2/HCl$
8. Grignard reagent
   Carbonyl compounds

Alcohols

Physical Properties of Monohydric Alcohols

(i) Boiling Points

Alcohols have higher boiling point than haloalkanes of comparable molecular mass because alcohols have intermolecular hydrogen bonding.

As the number of carbon atoms increases, boiling point increases. The boiling point decreases with increase of branching in carbon chain.

(ii) Solubility

Alcohols are soluble in water due to ability to form hydrogen bonds with water.

As the number of carbon atoms increases, solubility decreases.

Chemical Properties of Monohydric Alcohols

Order of reactivity of alcohols is as follows

1° alcohol > 2° alcohol > 3° alcohol

The reactions of alcohols may be due to cleavage of O—H bond or C—H bond. The former case shows its acidic behaviour.

(i) Reactions Involving Cleavage of O—H Bond

(a) **Reaction with metals**

$$2R{-}OH + 2Na \longrightarrow 2R{-}O{-}Na + H_2$$

Acidity of alcohols in decreasing order

Primary alcohols > secondary alcohols > tertiary alcohols

Electron releasing group decreases the polarity of —OH bond. Thus, decreases the acid strength.

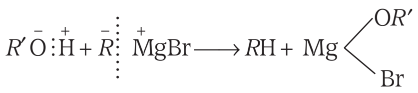
(b) **Reaction with acid and acid derivatives**

Alcohols when react with carboxylic acids, acid chlorides and acid anhydrides, form esters. This reaction is called **esterification.**

$$R'\overset{-}{O}\vdots\overset{+}{H} + R'\overset{+}{C}O\vdots\overset{-}{O}H \xrightleftharpoons{H^+} R'COOR + H_2O$$

(c) **With Grignard reagent**

Alcohols when react with Grignard reagent give alkanes.



$$R'\overset{-}{O}\vdots\overset{+}{H} + \overset{-}{R}\vdots\overset{+}{MgBr} \longrightarrow RH + Mg\begin{cases}OR'\\ Br\end{cases}$$

(ii) Reactions Involving Cleavage of Carbon Oxygen (C—O) Bond

Reaction with hydrogen halides

$$ROH + HX \longrightarrow R{-}X + H_2O$$

Reactivity in decreasing order 3° > 2° > 1°

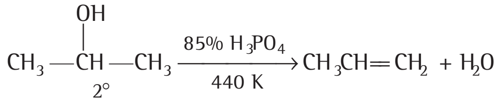
Hot Spot 1

DEHYDRATION

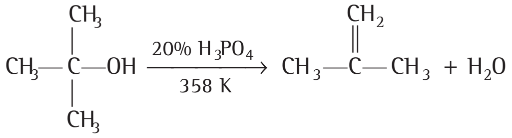
It is an important topic for JEE Main examination. Questions may be asked on the basis of mechanism of dehydration of alcohols.

Dehydration is carried in the presence of protic acids like conc. H_2SO_4 or H_3PO_4 or in presence of catalysts such as anhy. $ZnCl_2$ or Al_2O_3.

$$\underset{1°}{C_2H_5OH} \xrightarrow[443K]{H_2SO_4} CH_2{=}CH_2 + H_2O$$



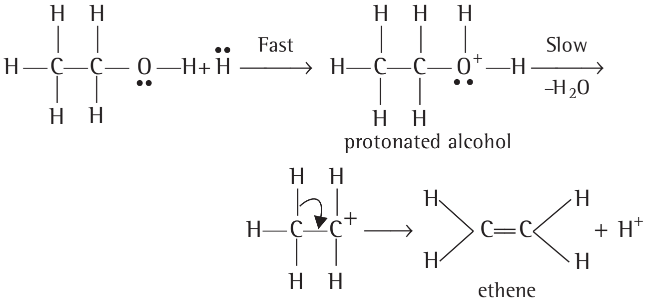
$$\underset{2°}{CH_3{-}\overset{OH}{\overset{|}{C}H}{-}CH_3} \xrightarrow[440\ K]{85\%\ H_3PO_4} CH_3CH{=}CH_2 + H_2O$$



$$CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}OH \xrightarrow[358\ K]{20\%\ H_3PO_4} CH_3{-}\overset{CH_2}{\overset{\|}{C}}{-}CH_3 + H_2O$$

Ease of dehydration of alcohols is as follows 3° > 2° > 1°

Mechanism of dehydration



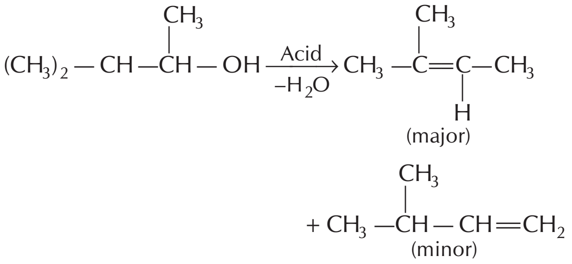
Sample **Problem 3** $(CH_3)_2CHCH(CH_3)OH \xrightarrow[-H_2O]{Acid} X$

The major product obtained in this reaction is

(a) $(CH_3)_2CHCH{=}CH_2$ (b) $(CH_3)_2C{=}CH{-}CH_3$

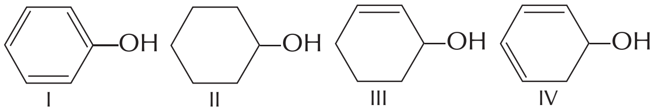
(c) 1 : 1 *mixture of* (a) *and* (b) (d) *None of these*

Interpret (b) Many a time unexpected products result during dehydration of alcohols.



$$(CH_3)_2{-}CH{-}\overset{CH_3}{\overset{|}{C}H}{-}OH \xrightarrow[-H_2O]{Acid} \underset{(major)}{CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}\underset{H}{\underset{|}{C}}{-}CH_3} + \underset{(minor)}{CH_3{-}\overset{CH_3}{\overset{|}{C}H}{-}CH{=}CH_2}$$

Sample **Problem 4** *Dehydration of the following in increasing order is*



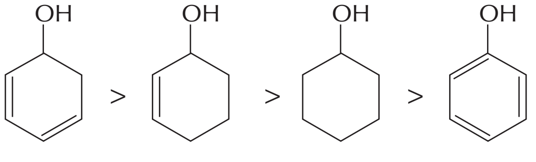
(a) I < II < III < IV

(b) II < III < IV < I

(c) I < III < II < IV

(d) I < IV < II < III

Interpret (a) Greater the chance of conjugation, greater the stability due to resonance and easier the dehydration. Thus, the correct order of dehydration is



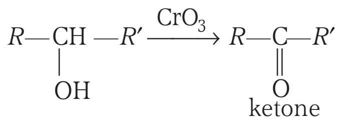
Oxidation

Different reagents are used to oxidise alcohol. The oxidation products are carbonyl compounds generally.

$$R\text{CH}_2\text{OH} \xrightarrow[\text{acidified KMnO}_4]{[\text{O}]} R\text{CHO} \xrightarrow{[\text{O}]} R\text{COOH}$$

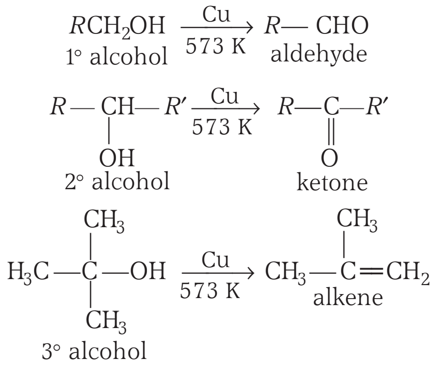
$$R\text{CH}_2\text{OH} \xrightarrow{\text{CrO}_3} R\text{CHO}$$

$$\text{CH}_3\text{—CH=CH—CH}_2\text{OH} \xrightarrow{\text{PCC}} \text{CH}_3\text{—CH=CH—CHO}$$



$$R\text{—}\underset{\text{OH}}{\text{CH}}\text{—}R' \xrightarrow{\text{CrO}_3} \underset{\text{ketone}}{R\text{—}\underset{\text{O}}{\overset{}{\text{C}}}\text{—}R'}$$

Tertiary alcohols do not undergo oxidation reaction. In the presence of strong oxidising agent ($KMnO_4$) and at high temperature cleavage of C—C bond takes place and a mixture of carboxylic acids containing lesser number of carbon atoms is formed.



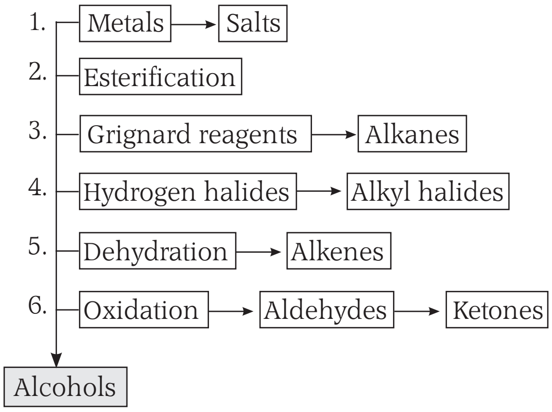
$$\underset{1^\circ\ \text{alcohol}}{R\text{CH}_2\text{OH}} \xrightarrow[573\ \text{K}]{\text{Cu}} \underset{\text{aldehyde}}{R\text{— CHO}}$$

$$\underset{2^\circ\ \text{alcohol}}{R\text{—}\underset{\text{OH}}{\text{CH}}\text{—}R'} \xrightarrow[573\ \text{K}]{\text{Cu}} \underset{\text{ketone}}{R\text{—}\underset{\text{O}}{\overset{}{\text{C}}}\text{—}R'}$$

$$\underset{3^\circ\ \text{alcohol}}{\text{H}_3\text{C—}\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\text{—OH}} \xrightarrow[573\ \text{K}]{\text{Cu}} \underset{\text{alkene}}{\text{CH}_3\text{—}\overset{\text{CH}_3}{\text{C}}\text{=CH}_2}$$

MnO_2 selectively oxidises the —OH group of allylic and benzylic 1° and 2° alcohols to aldehydes and ketones respectively. N_2O_4 in $CHCl_3$ oxidises 1° and 2° benzyl alcohol.

Flow chart showing reactions of alcohols



Uses of Monohydric Alcohols

1. Ethanol, C_2H_5OH, is used for drinking purposes.
2. Ethanol is usually sold as industrial methylated spirits which is ethanol with a small quantity of methanol added and possibly some colour. Methanol is poisonous and so the industrial methylated spirits is unfit to drink.
3. Ethanol burns to give carbon dioxide and water and thus, can be used as a fuel in its own right or in mixtures with petrol (gasoline). "Gasohol" is a petrol/ethanol mixture containing about 10-20% ethanol.
4. Methanol also burns to form carbon dioxide and water.

   $$2CH_3OH + 3O_2 \longrightarrow 2CO_2 + 4H_2O$$

   Thus, it can be used a petrol additive to improve combustion.
5. Ethanol can be produced by fermentation, so this is a useful way for countries without an oil industry to reduce import of petrol.

   $$CH_3CH_2OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O$$
6. Ethanol is widely used as a solvent. It is relatively safe and can be used to dissolve many organic compounds which are insoluble in water. It is used, *e.g.*, in many perfumes and cosmetics.
7. Most methanol is used to make other things *e.g.*, methanal (formaldehyde), ethanoic acid, and methyl esters of various acids. In most cases, these are in turn converted into further products.
8. Propan-2-ol is widely used in an amazing number of different situations as a solvent.

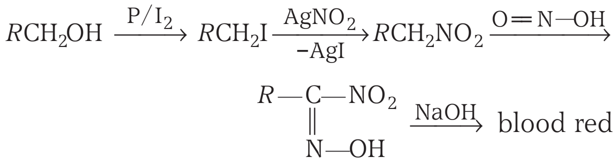
Identification of Primary, Secondary and Tertiary Alcohols

1°, 2° *and* 3° *alcohols can be identified by following tests.*

(a) Victor-Meyer's Test

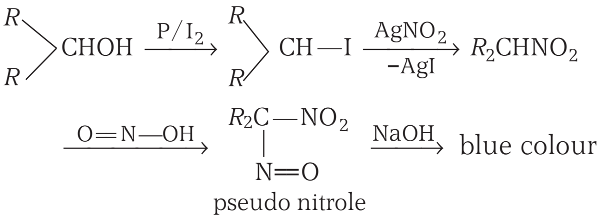
In this test, first the given alcohol is treated with P/ I_2 and then with $AgNO_2$ and HNO_2. The final product obtained gives different (or no) colour with NaOH. By identifying the colour produced, the alcohols are identified. In this test,

(i) Primary alcohols give blood red colour as



$$R\text{CH}_2\text{OH} \xrightarrow{\text{P/I}_2} R\text{CH}_2\text{I} \xrightarrow[-\text{AgI}]{\text{AgNO}_2} R\text{CH}_2\text{NO}_2 \xrightarrow{\text{O=N—OH}} R\text{—}\underset{\text{N—OH}}{\text{C}}\text{—NO}_2 \xrightarrow{\text{NaOH}} \text{blood red}$$

(ii) Secondary alcohols give blue colour as



$$R_2CHOH \xrightarrow{P/I_2} R_2CH-I \xrightarrow[-AgI]{AgNO_2} R_2CHNO_2 \xrightarrow{O=N-OH} R_2C(NO_2)-N=O \xrightarrow{NaOH} \text{blue colour}$$

pseudo nitrole

(iii) Tertiary alcohols produce no colour as

$$R_3C-OH \xrightarrow{P/I_2} R_3C-I \xrightarrow{AgNO_2} R_3CNO_2 \xrightarrow{HNO_2} \text{no reaction} \xrightarrow{NaOH} \text{no colour}$$

(b) Lucas Test

An equimolar mixture of anhydrous $ZnCl_2$ and concentrated HCl is called Lucas reagent. When alcohols are treated with it,

(i) tertiary alcohols produce turbidity immediately.
(ii) secondary alcohols produce turbidity after 5 min.
(iii) primary alcohols do not produce turbidity at room temperature.

(c) Dehydrogenation

Cu or Ag are used for this purpose. In this reaction

(i) primary alcohols give aldehydes as

$$RCH_2OH \xrightarrow{Cu/573K} RCHO + H_2$$

(ii) secondary alcohols give ketones as

$$R_2CHOH \xrightarrow{Cu/573K} R_2C=O$$

(iii) tertiary alcohols are not dehydrogenated. They are rather dehydrated as

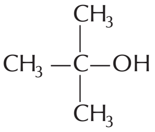
$$(CH_3)_3C-OH \xrightarrow[-H_2O]{Cu/573K} (CH_3)_2C=CH_2$$

(d) Oxidation Method

Oxidation reaction is also used to distinguish between 1°, 2° and 3° alcohols. These reactions have been discussed in chemical properties of alcohols.

Sample **Problem 5** *On treatment with a concentrated solution of zinc chloride in concentrated* HCl *at room temperature, an alcohol immediately gives, an oily product. The alcohol can be*

(*a*) $C_6H_5CH_2OH$ (*b*) $CH_3CHOHCH_3$

(*c*) 

$CH_3-C(CH_3)_2-OH$

(*d*) *Any of these*

Interpret (*c*) In Lucas test, when alcohol is mixed with conc. HCl and anhydrous $ZnCl_2$ at room temperature, if oily product is formed immediately, the alcohol can be tertiary.

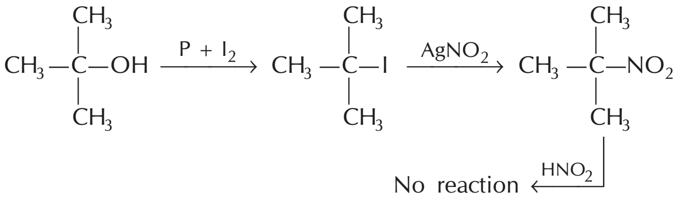
Sample **Problem 6** *In the following reaction sequence*

$$R-OH \xrightarrow{P+I_2} R-I \xrightarrow{AgNO_2} RNO_2 \xrightarrow{HNO_2} \text{no reaction}$$

The alcohol is a

(*a*) *primary alcohol* (*b*) *secondary alcohol*
(*c*) *tertiary alcohol* (*d*) *phenol*

Interpret (*c*) In the given sequence of reaction, the alcohol is tertiary.



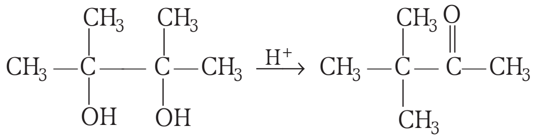
$$(CH_3)_3C-OH \xrightarrow{P+I_2} (CH_3)_3C-I \xrightarrow{AgNO_2} (CH_3)_3C-NO_2 \xrightarrow{HNO_2} \text{No reaction}$$

Alcoholometry

It is the process of determination of alcohol in a given sample. An alcohol water mixture containing 57.1% C_2H_5OH (by volume) or 49.3% C_2H_5OH (by weight) is called **proof spirit.** If the percentage of ethyl alcohol is higher, in comparison to proof spirit, it is called **over proof spirit** and if lower, it is called **under proof spirit.**

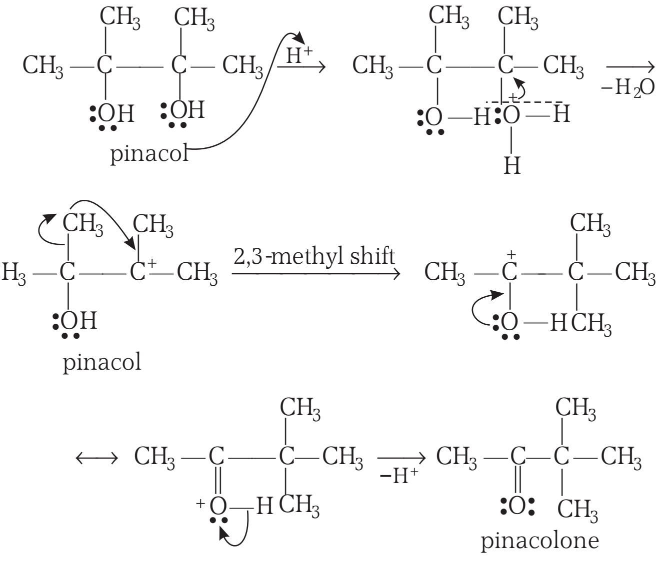
Pinacols

Completely substituted 1,2-diols are called pinacols. Pinacols behave very differently in the presence of acids and the reaction is called pinacol—**pinacolone rearrangement.** The simplest representation of the reaction is



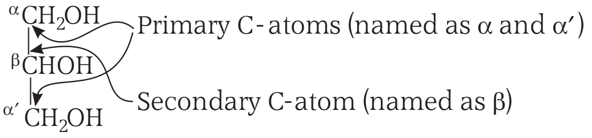
$$CH_3-C(CH_3)(OH)-C(CH_3)(OH)-CH_3 \xrightarrow{H^+} CH_3-C(CH_3)_2-C(=O)-CH_3$$

The reaction proceeds as



Glycerol or Propane -1, 2, 3-triol

Compounds containing three —OH groups at successive C-atoms are called triols. The introduction of third —OH group in a diol makes alcohol more sweet, raises the b.p. by about 100°C (due to enhancement in intermolecular H-bonding) and increases viscocity. Glycerol is the first member of this series with structural formula

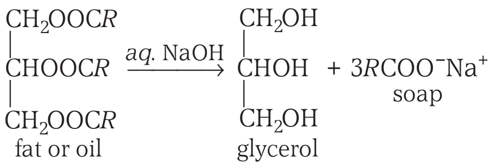


Methods of Preparation

Following methods are used to synthesised alcohols.

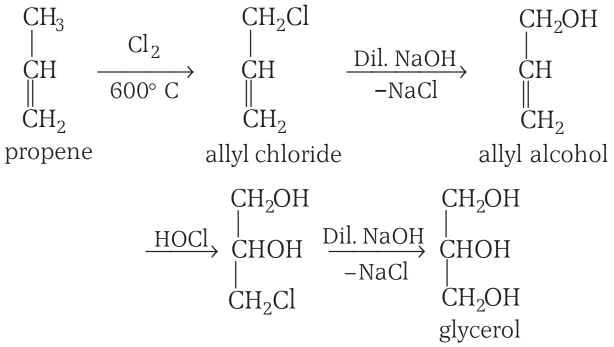
(i) From Fats and Oils

Fats and oils are infact triglycerides (triesters of glycerol with long chain fatty acids or carboxylic acids). Their hydrolysis in alkaline medium produces Na salts of these long chain fatty acids (soap) and glycerol (as **sweet lye** in mother liquor). The reaction (hydrolysis) is called, thus, saponification.

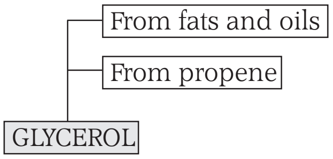


Actually glycerol is the byproduct of saponification reaction.

(ii) From Propene



The outline of methods of preparation looks like



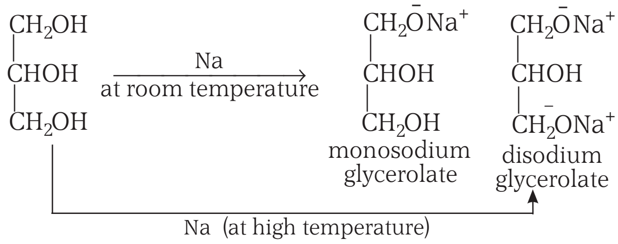
Physical Properties of Glycerol

It is a colourless, odourless, sweet tasting syrupy liquid with b.p. 290°C. It is non-toxic, miscible with water and ethanol but immiscible with ether. It is hygroscopic in nature.

Chemical Properties of Glycerol

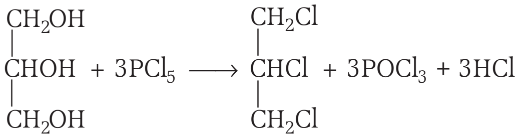
(i) With Na

Disodium salt is obtained.



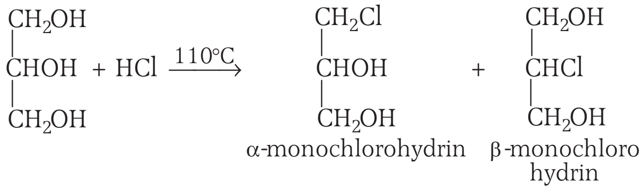
It is seen that the secondary alcoholic group does not react at all.

(ii) With PX_5

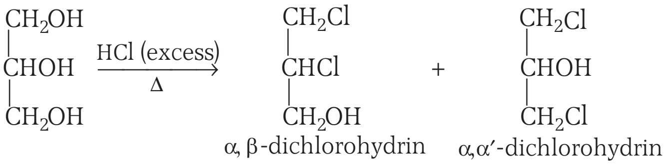


Caution Point *The pentahalides as* Br_2 *and* I_2 *are not known and* PF_5 *is unstable.*

(iii) With HX

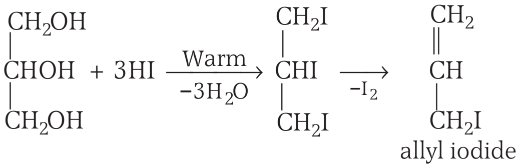


Long exposure to HCl at higher temperature gives,

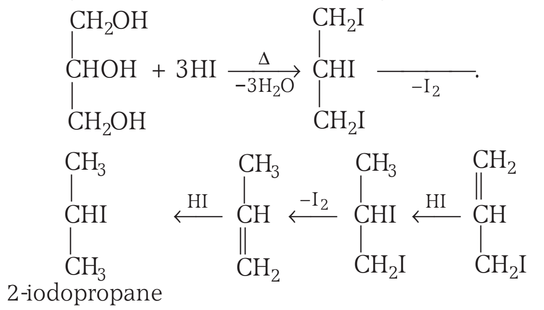


HBr behaves similarly but reaction with HI takes place differently as,

(a) With small amount of HI on warming,



(b) With large amount of HI on heating,

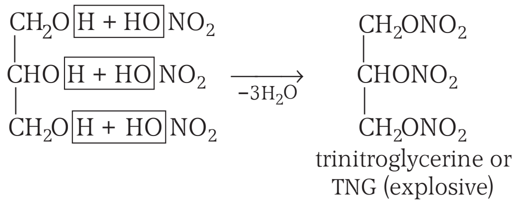


$$\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array} + 3HI \xrightarrow[-3H_2O]{\Delta} \begin{array}{l}CH_2I\\|\\CHI\\|\\CH_2I\end{array} \xrightarrow[-I_2]{} .$$

$$\underset{\text{2-iodopropane}}{\begin{array}{l}CH_3\\|\\CHI\\|\\CH_3\end{array}} \xleftarrow{HI} \begin{array}{l}CH_3\\|\\CH\\\|\\CH_2\end{array} \xleftarrow{-I_2} \begin{array}{l}CH_3\\|\\CHI\\|\\CH_2I\end{array} \xleftarrow{HI} \begin{array}{l}CH_2\\\|\\CH\\|\\CH_2I\end{array}$$

(iv) With HNO_3

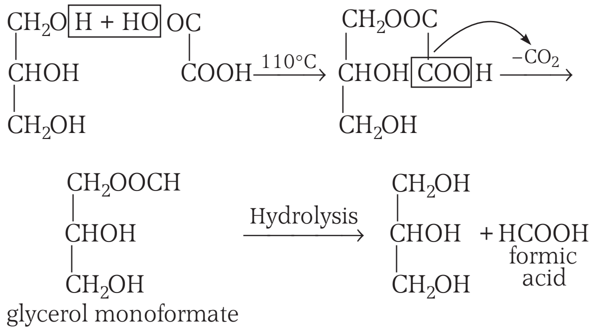
With nitric acid, it yields an explosive compound compound TNG.



$$\begin{array}{l}CH_2O\boxed{H+HO}NO_2\\|\\CHO\boxed{H+HO}NO_2\\|\\CH_2O\boxed{H+HO}NO_2\end{array} \xrightarrow[-3H_2O]{} \underset{\text{trinitroglycerine or TNG (explosive)}}{\begin{array}{l}CH_2ONO_2\\|\\CHONO_2\\|\\CH_2ONO_2\end{array}}$$

(v) With Oxalic Acid

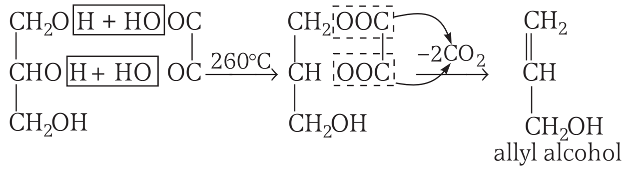
At 110°C



$$\begin{array}{ll}CH_2O\boxed{H+HO}&OC\\|&|\\CHOH&COOH\\|&\\CH_2OH&\end{array} \xrightarrow{110°C} \begin{array}{l}CH_2OOC\\|\qquad\;|\\CHOH\boxed{COO}H\\|\\CH_2OH\end{array} \xrightarrow{-CO_2}$$

$$\underset{\text{glycerol monoformate}}{\begin{array}{l}CH_2OOCH\\|\\CHOH\\|\\CH_2OH\end{array}} \xrightarrow{\text{Hydrolysis}} \begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array} + \underset{\text{formic acid}}{HCOOH}$$

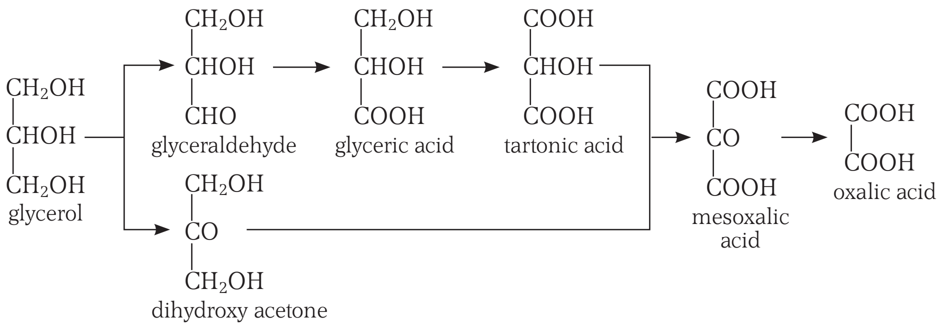
At 260°C



$$\begin{array}{ll}CH_2O\boxed{H+HO}&OC\\|&|\\CHO\boxed{H+HO}&OC\\|&\\CH_2OH&\end{array} \xrightarrow{260°C} \begin{array}{l}CH_2OOC\\|\qquad|\\CH\;OOC\\|\\CH_2OH\end{array} \xrightarrow{-2CO_2} \underset{\text{allyl alcohol}}{\begin{array}{l}CH_2\\\|\\CH\\|\\CH_2OH\end{array}}$$

(vi) Oxidation

Glycerol can give rise to variety of oxidation products which are summarised as,



$$\underset{\text{glycerol}}{\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array}} \longrightarrow \underset{\text{glyceraldehyde}}{\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CHO\end{array}} \longrightarrow \underset{\text{glyceric acid}}{\begin{array}{l}CH_2OH\\|\\CHOH\\|\\COOH\end{array}} \longrightarrow \underset{\text{tartonic acid}}{\begin{array}{l}COOH\\|\\CHOH\\|\\COOH\end{array}} \longrightarrow \underset{\text{mesoxalic acid}}{\begin{array}{l}COOH\\|\\CO\\|\\COOH\end{array}} \longrightarrow \underset{\text{oxalic acid}}{\begin{array}{l}COOH\\|\\COOH\end{array}}$$

$$\underset{\text{glycerol}}{\begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array}} \longrightarrow \underset{\text{dihydroxy acetone}}{\begin{array}{l}CH_2OH\\|\\CO\\|\\CH_2OH\end{array}} \longrightarrow \underset{\text{mesoxalic acid}}{\begin{array}{l}COOH\\|\\CO\\|\\COOH\end{array}}$$

(i) With dil. HNO_3 ⟶ Glyceric acid + Tartonic acid

(ii) With conc. HNO_3 ⟶ Glyceric acid.

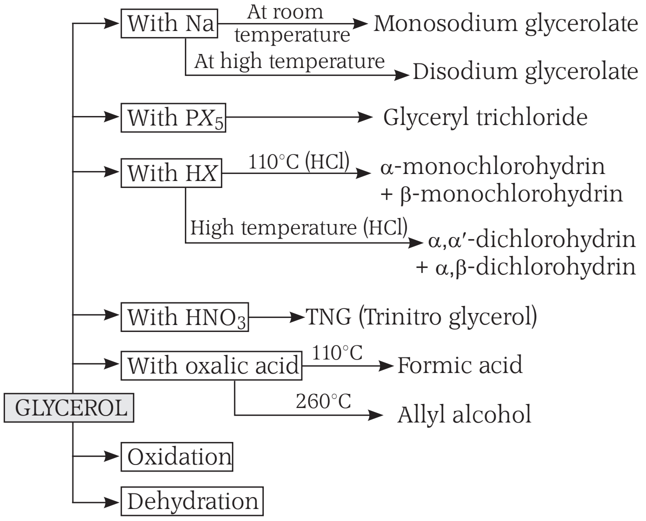
(iii) With bismuth nitrate ⟶ Mesoxalic acid.

(iv) With Br_2 water, sodium hypobromite or Fenton's reagent ($FeSO_4 + H_2O_2$) ⟶ A mixture of glyceraldehyde and dihydroxy acetone (glycerose).

(v) With **periodic acid** ⟶ Formaldehyde + Formic acid.

Chemical Properties

The outline of chemical properties of glycerol looks like

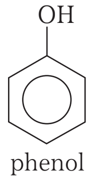


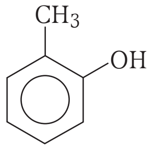
Check Point 1

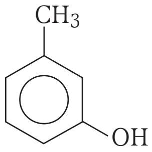
1. R–OH with less number of carbon atoms are water soluble while those with higher number of carbon atoms are not explain.
2. The relative acidity of alcohols is in the order of 3° < 2° < 1° < CH_3OH. Explain why?
3. Ethanol cannot be used as a solvent with Grignard reagent or $LiAlH_4$. Explain it.
4. Why glycerol has high viscosity and is miscible with water in all proportions?

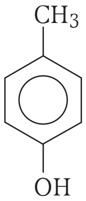
11.2 Phenols

Aromatic compounds in which hydroxyl group (— OH) is directly attached with benzene nucleus are called phenols.

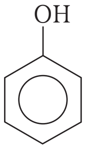

phenol (hydroxy benzene)

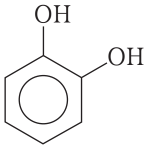

o-cresol (*o*-hydroxy toluene)

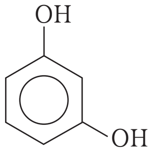

m-cresol (*m*-hydroxy toluene)

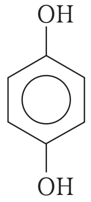

p-cresol (*p*-hydroxy toluene)

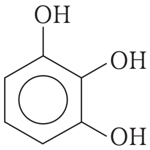
On the basis of number of —OH groups present, phenols are termed as monohydric, dihydric, trihydric phenols etc.

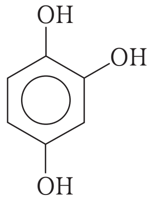

hydroxy benzene (or phenol)

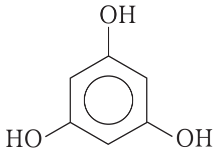

o-dihydroxy benzene (or caticol)


m-dihydroxy benzene (or resorcinol)


p-hydroxy benzene (or quinol)


1,2,3-trihydroxy benzene (or pyrogalol)

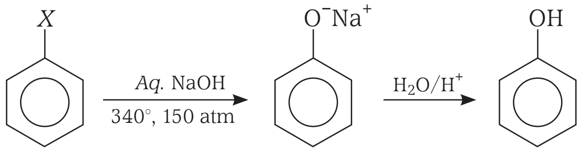

1,2,4-trihydroxy benzene (or hydroxy quinol)


1,3,5-trihydroxy benzene (or fluoroglucinol)

Preparation of Phenols

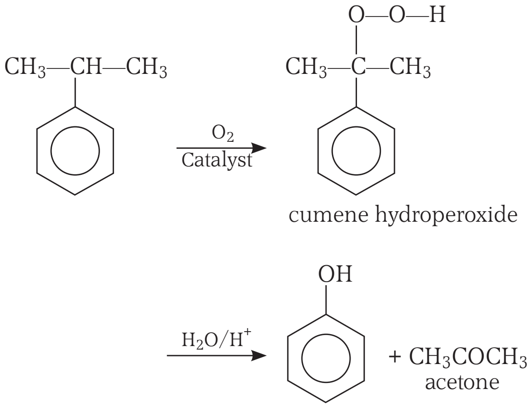
Some general and important methods of preparation of phenols are discussed below

(a) By Hydrolysis of Halobenzene



The halobenzene is prepared by Dow process or Raschig's process.

(b) Cumene Process

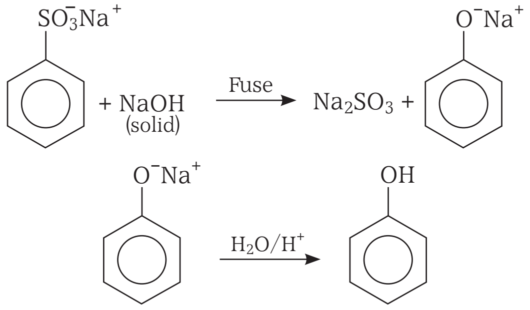


The reaction proceeds at 150°C in the presence of HBr as a catalyst. The reaction is also called **auto-oxidation.**

The advantage of this reaction is that the by product, *i.e.*, acetone is also an important reagent.

(c) From Na or K Salts of Sulphonic Acid

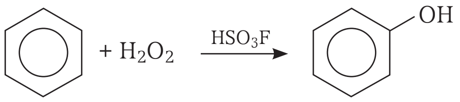
The Na or K salt of sulphonic acid when fused with NaOH, gives phenol.



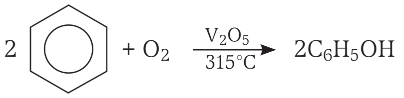
Fusion at high temperatures may leads to undesirable side products.

(d) By Hydroxylation of Benzene

Direct hydroxylation is involved,



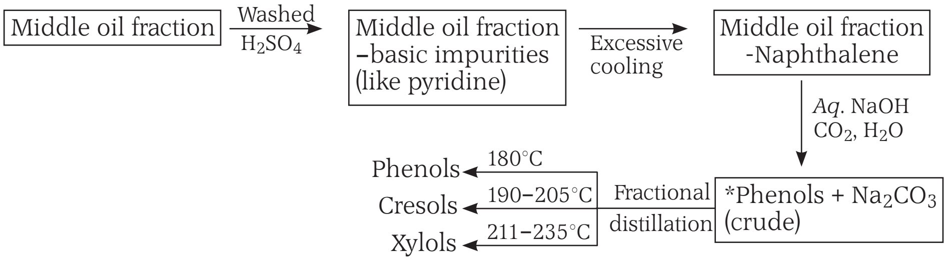
(e) By Oxidation of Benzene



It is the latest method of manufacture.

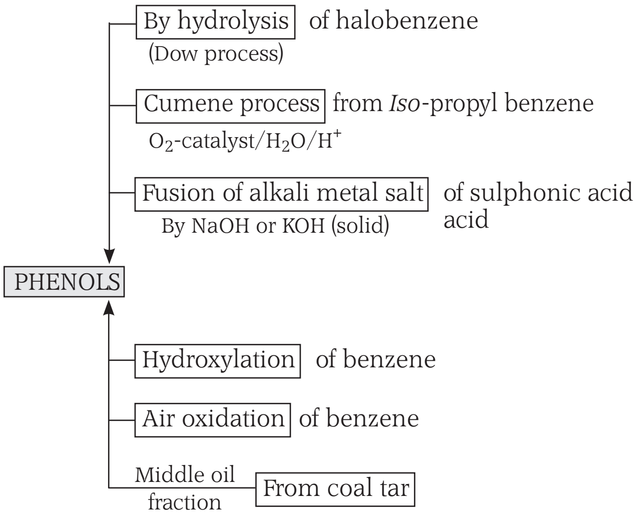
(f) By Middle Oil Fraction of Coal Tar

The middle oil fraction of coal tar distillation has naphthalene and phenolic compounds. From this fraction phenolic compounds are isolated as,



*On reaction with *aq.* NaOH, phenols are dissolved in it as phenoxides. CO_2 is then blown through this phenoxide ion solution to liberate phenols.

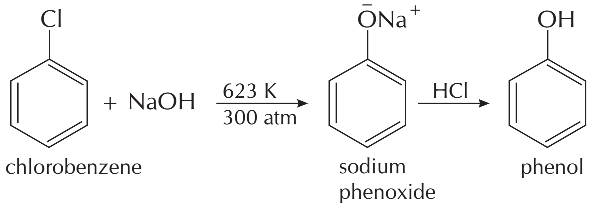
The methods of preparation of phenols in outline looks like



Sample Problem 7 *Phenol may be obtained from chlorobenzene using reagents* **[NCERT]**

(a) NaOH + HCl (b) CO_2
(c) H_2SO_4 (d) NaOH + CaO

Interpret (a)



Physical Properties of Phenols

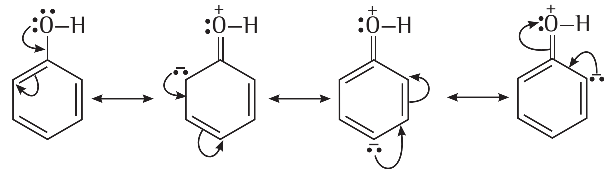
These are colourless liquids or solids with red tint and carbolic odour. They are highly toxic. Their boiling point are higher than corresponding alcohols (due to stronger intermolecular H-bonding). They are more miscible with water. They have high dipole moments and are acidic in nature. (More acidic than aliphatic alcohols.)

Hot Spot 2

ACIDIC Nature of Phenols

This is an important topic for JEE Main examination. Generally questions based on strength of phenols and their derivatives are asked. The level of question is generally easy.

Phenols are acidic in nature, even more acidic than alcohols. The more acidic character of phenols (than corresponding aliphatic alcohols) is due to conjugation between lone pair of oxygen and benzene nucleus, *i.e.*,



The (+) ve charge on oxygen signifies the weakening of O—H bond.

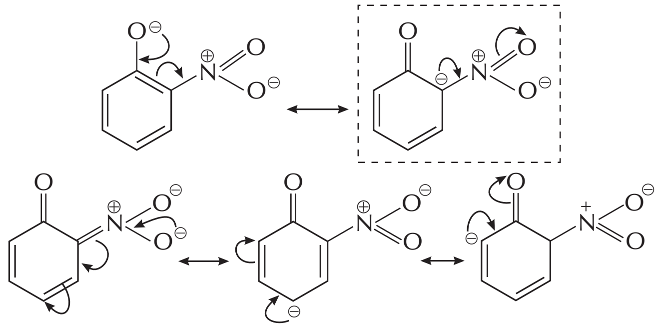
Presence of electron releasing group like —CH_3, —C_2H_5 over benzene nucleus destabilises the phenoxide ion, thus, decreases the acidity of phenol whereas presence of electron withdrawing groups like —NO_2, — CN, etc., stabilises the phenoxide ion and thus, increases the acidity of phenol.

Sample Problem 8 *Phenol is less acidic than*

(a) *ethanol* (b) *o-nitrophenol*

(c) *o-methylphenol* (d) *o-methoxyphenol*

Interpret *(b) Due to –R effect of —NO_2 group, o-nitrophenoxide ion is more stable than phenoxide ion. Consequently, nitrophenols is more acidic than phenol.*



Note Structures in boxe have negative charge on that C-atom to which electron withdrawing —NO_2 group is attached. So, this structure contributes more towards the acidic character than the others.

Sample Problem 9 *The correct increasing order of acidity of the following compounds is*

(a) *phenol < o-cresol < o-nitrophenol*

(b) *o-nitrophenol < phenol < o-cresol*

(c) *o-cresol < o-nitrophenol < phenol*

(d) *o-cresol < phenol < o-nitrophenol*

Interpret (*d*) In substituted phenols the presence of electron withdrawing groups, increases the acidic strength of phenol whereas, electron releasing groups decrease the acidic strength of phenols. Hence, correct order is *o*-cresol < phenol < *o*-nitrophenol.

Chemical Properties of Phenols

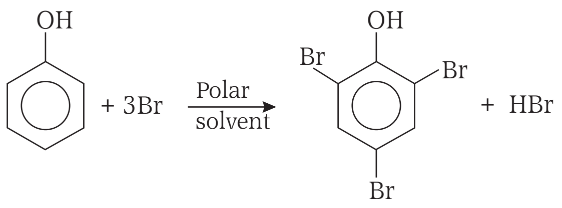
Phenols exhibit following general characteristics.

(a) Electrophilic Substitution Reactions

In phenol, the —OH group shows +*R* and –*I* effect and hence, highly activates the benzene ring towards electrophilic substitution reaction. It is *ortho* and *para* directing group.

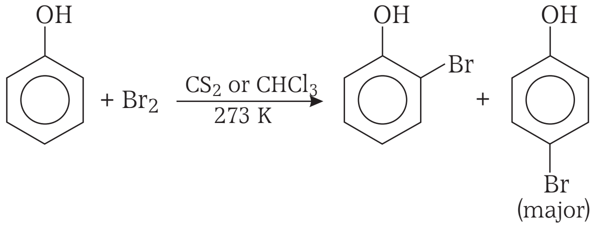
The normal electrophilic substitutions are given as

(i) **Halogenation, *i.e.,***

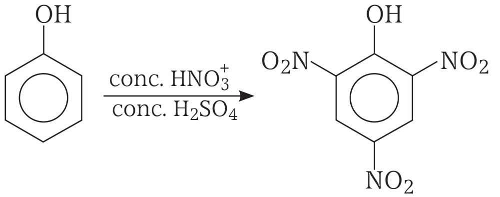


In polar solvent phenol is in equilibrium with phenoxide ion which is the actual substrate.

However, in the presence of CS_2 or $CHCl_3$, *ortho* and *para* halophenols are the main products.

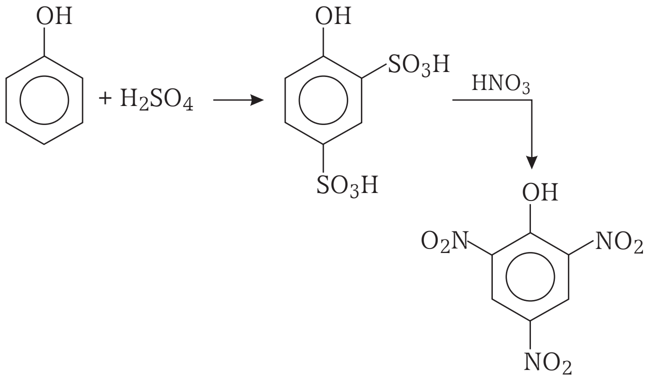


(ii) **Nitration, *i.e.,***



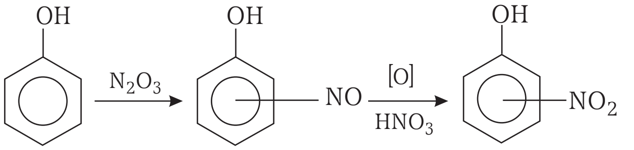
picric acid

However, nitration after deactivating the ring by sulphonation, gives picric acid in better yield.



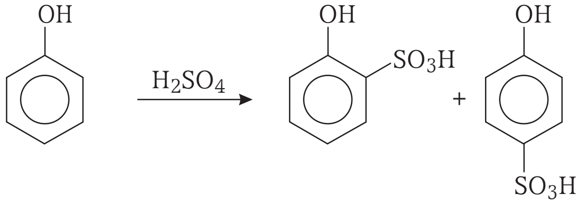
picric acid

For preparing *o*- and *p*-nitrophenols, dil. HNO_3 is used. The reaction involves initial nitrosation of phenol with N_2O_3 which is then oxidised to nitrophenol as,

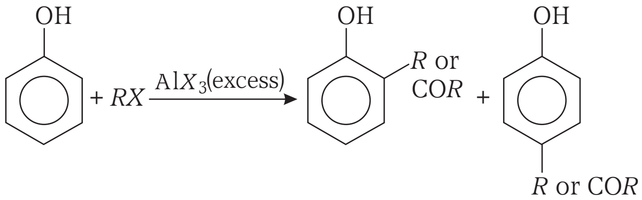


(*O*- and *p*-nitrophenol)

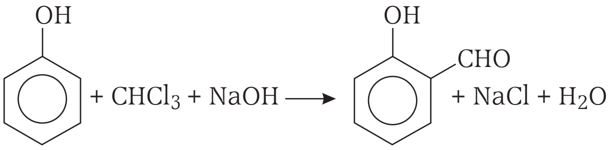
(iii) **Sulphonation *i.e.,***

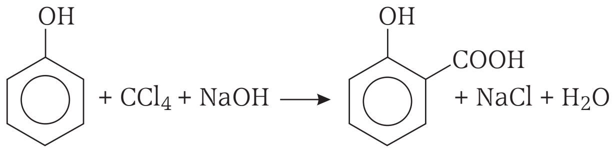


(iv) **Friedel-Craft reactions** (alkylation and acylation) These reactions occur in the excess of Lewis acid like AlX_3 as,

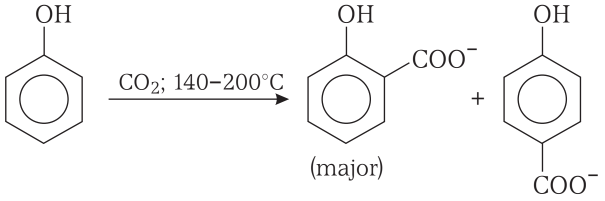


(v) **Reimer-Tiemann reaction** In this reaction, indeed the phenol reacts with trihalogen or tetrahalogen methane followed by hydrolysis with alkali. *o/p* salicylaldehyde or salicylic acid are the products of this reaction.





(vi) **Kolbe and Kolbe Schmidt Reaction** Kolbe's reaction involves electrophilic attack of very weak electrophile (CO_2) on activated *ortho* or *para* position of phenoxide ion. At lower temperatures *ortho* isomer predominates whereas *para* isomer obtained in excess at higher temperatures.



(major)

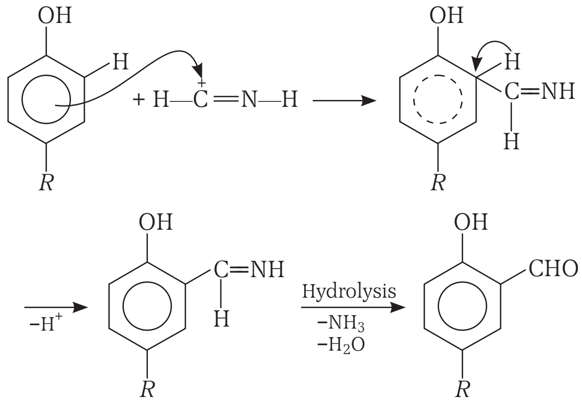
(minor)

Kolbe Schmidt reaction is infact a modification of Kolbe's reaction. Here, a pressure of 5–7 atmosphere is also applied because of which reaction occurs at comparatively lower temperatures.

(vii) **Gattermann synthesis** The reaction is an aromatic electrophilic substitution involving the attack of formaldinium ion formed by HCN and HCl with help of $AlCl_3$ giving rise to aldimine. Aldimine on hydrolysis gives phenolic aldehyde as,

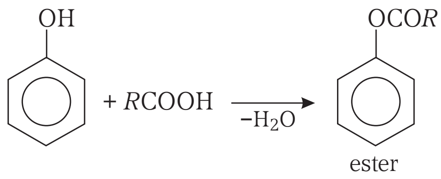
formaldinium ion

[The Cl^- of HCl is trapped by $AlCl_3$ as $Cl^- + AlCl_3 \longrightarrow AlCl_4^-$]



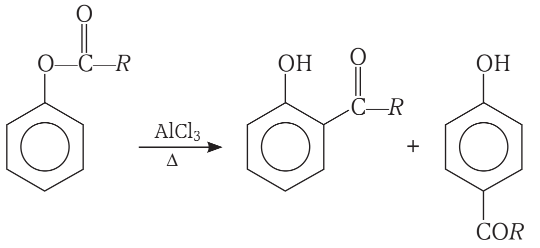
The –CHO group prefers *para*-position and attacks on *ortho*-position only if *para*-position is blocked.

(b) Esterification

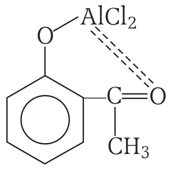


This reaction is already described completely in properties of aliphatic alcohols.

Phenolic esters on heating with $AlCl_3$ (Lewis acid) give *o*- and *p*-acyl phenols, the reaction is called **Fries migration**.*e.g.*,



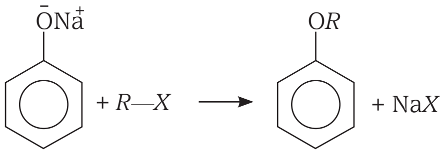
At low temperature (below 100°C) *para* isomer is major product while at high temperature *ortho* isomer is major product. This is because intermediate of *ortho* isomer is stabilised by chelation as



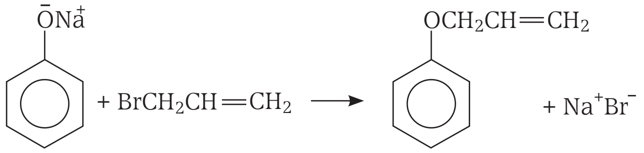
Electron withdrawing group in the substrate favours retardation of reaction.

Solvent is generally not required for the reaction. Nitrobenzene may be used which reduces the reaction temperature.

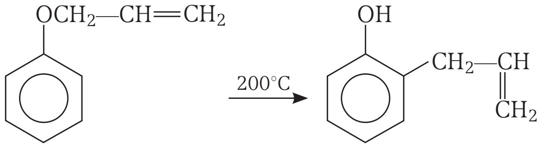
(c) Ether Formation

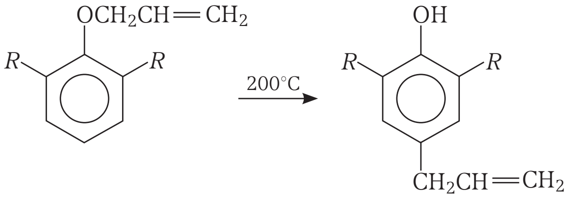


Similarly, sodium or potassium alkoxide on reaction with allyl bromide give aryl allyl ethers as,



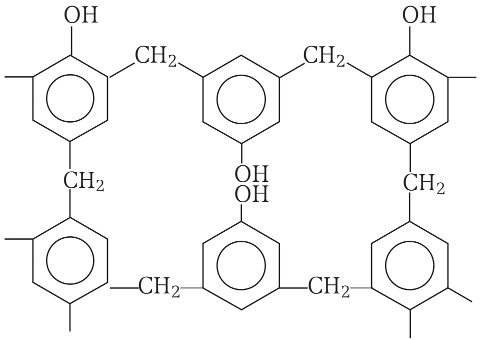
These aryl allyl ethers when heated to 200°C show **Claisen rearrangement** which involves migration of allyl group from ethereal oxygen to ring C at *ortho* position and (when both the *ortho* position are blocked) to *para* position as,





(d) Lederer-Manassae Reaction

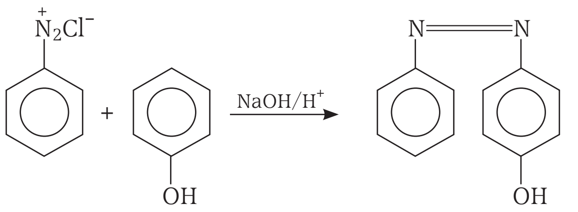
Here when phenol is refluxed with formalin (aqueous solution of HCHO) and 0.88 ammonia as catalyst then bakelite is formed with the following structure



bakelite (a portion)

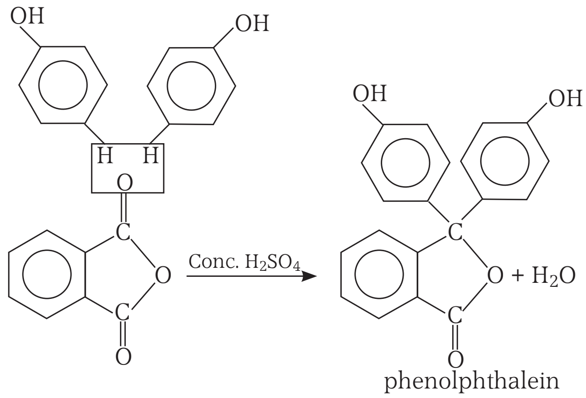
(e) Other Reactions of Phenols

(i) **Coupling reaction** Phenols couple with benzene diazonium chloride in an alkaline solution to form *p*-hydroxyazobenzene (a dye) as

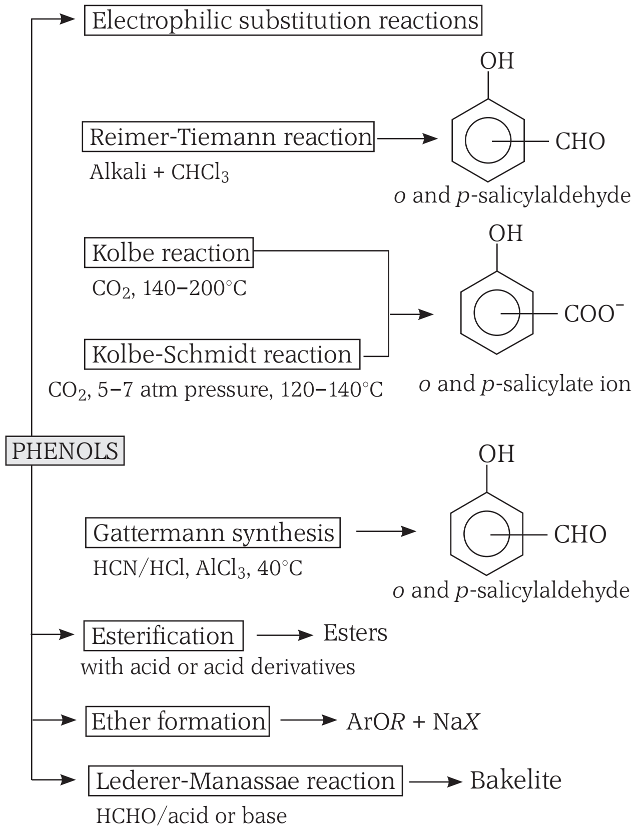


para-hydroxyazobenzene

(ii) **Condensation with phthalic anhydride** In the presence of H_2SO_4, it combines with phthalic anhydride to form phenolphthalein as



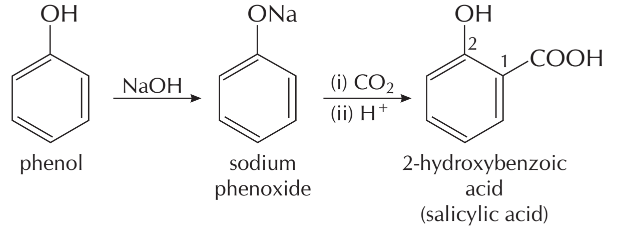
The outline of chemical properties of phenol looks like



Sample **Problem 10** *Synthesis of salicylic acid from phenol is done by* **[NCERT]**

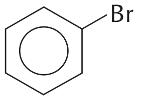
(a) *Williamson synthesis*
(b) *Reimer-Tiemann reaction*
(c) *Kolbe's reaction*
(d) *Gattermann synthesis*

Interpret (c) When phenol reacts with sodium hydroxide, reactive phenoxide ion is formed. So, electrophilic aromatic substitution takes place with CO_2 under a pressure of 4-7 atm followed by acidification and ortho hydroxybenzoic acid (salicylic acid) is formed. This is called Kolbe's reaction.

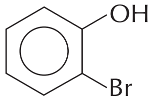


Sample **Problem 11** *The product obtained by the reaction of* HBr *with phenol is*

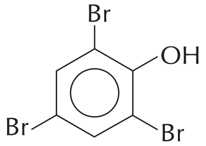
(a)



(b)



(c)



(d) *There is no reaction*

Interpret (d) Phenol reacts with PCl_5 to form chlorobenzene. Halogenation of phenol does not take place with HX.

Uses of Phenols

(i) Phenol is used in the manufacture of bakelite, soaps, lotions, etc.
(ii) It is used in the manufacture of drugs like aspirin, salol, phenacetin, etc.

Check Point 2

1. Explain, why phenol is more acidic than benzyl alcohol?
2. Phenol is an acid but does not react with $NaHCO_3$. Explain
3. During esterification of phenol, sometimes nitrobenzene is used as a solvent. Explain, why?
4. *para*-isomer is the major product of the Fries migration of phenolic esters at low temperature. Explain.

11.3 Ethers

Organic compounds having —O— functional group are called ethers. Thus, ethers may look like

$$R'—O—R''$$

In other words, esters are the derivatives of water as these are obtained when both the H-atoms of H_2O are replaced by *R* groups. The *R* groups may be same or different. When both the *R* groups (alkyl groups) are same, the ethers are called **simple** or **symmetrical ether** and when both the groups are different, the ethers are called **mixed** or **unsymmetrical ethers,** *e.g.,*

$CH_3—O—CH_3$ (simple or symmetrical ethers) $CH_3OC_2H_5$ (mixed ether)

Structure of Ethers

The ethers have following general structure

$$R\overset{\sigma}{—}\ddot{\underset{\cdot\cdot}{O}}\overset{\sigma}{—}R$$

This structure shows that O atom has two bond pairs and two lone pairs of electrons, *i.e.*, total four pairs of electrons. Hence, it is sp^3 hybridised. The two sp^3 hybridised orbitals overlap with the hybrid orbitals (one each) of two carbon atoms to form sigm bonds. The bulkier R groups result in the greater forces of repulsion and thus the $\begin{matrix}R\\R\end{matrix}\!\!>O$ bond angle is 110° (somewhat greater than the tetrahedral bond angle). Thus, ethers have a bent structure (like H_2O) and dipolar nature.

Preparation of Ethers

General methods used to synthesise ethers are as follows

(a) Williamson's Synthesis

$$R\bar{O}\,Na^+ + R'X \longrightarrow ROR' + Na^+X^-$$

Best yield of asymmetrical ethers are obtained when the alkyl halides are primary and alkoxides are tertiary. Also see the properties of alkylhalides.

(b) Reaction of *RX* with Dry Silver Oxide

It is already discussed in properties of alkylhalides.
The reaction looks as

$$2RX + Ag_2O \longrightarrow ROR + 2AgX$$

(c) By Dehydration of Alcohols

$$\underset{\text{(excess)}}{RCH_2OH} \xrightarrow[140°C]{\text{Conc. } H_2SO_4} RCH_2—O—CH_2R$$

The order of ease of dehydration of alcohols follow the sequence, tertiary < secondary < primary.

The method is generally useless for the preparation of asymmetrical ethers, since complex mixture are obtained *e.g.*,

$$ROH + R'OH \xrightarrow[140°]{\text{Conc. } H_2SO_4} ROR + ROR' + R'OR'$$

$$\underset{\text{(excess)}}{RCH_2OH} \xrightarrow[250°C]{Al_2O_3} RCH_2—O—CH_2R$$

Here, Al of Al_2O_3 works as Lewis acid.

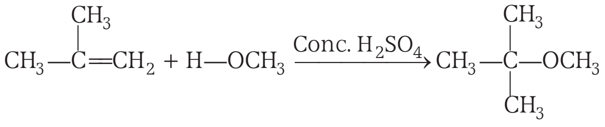
(d) By the Action of Diazomethane on Alcohols

$$ROH + CH_2N_2 \xrightarrow{HBF_4} R—O—CH_3 + N_2$$

The method is suitable for methyl ethers only and remember, tetrafluoroboric acid (HBF_4) is used as the catalyst.

(e) From Alkenes

(i) **By adding alcohols**



$$CH_3—\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH_2 + H—OCH_3 \xrightarrow{\text{Conc. } H_2SO_4} CH_3—\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}—OCH_3$$

This reaction proceeds through the formation of a carbonium ion, thus a possibility always exists that the carbonium ion may rearranges itself to form a more stable carbonium ion to affect the result.

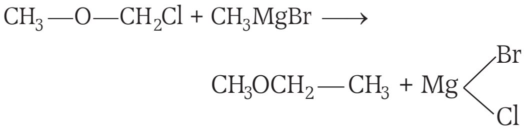
(ii) **Alkoxy mercuration-demercuration**

$$\text{Alkene} + \text{Alcohol} \xrightarrow[\text{(ii) } NaBH_4/OH^-]{\text{(i) } Hg(OOCCF_3)_2} \text{Ether}$$

This reaction does not involve carbonium ion formation thus no rearrangements are possible to affect the result of reaction.

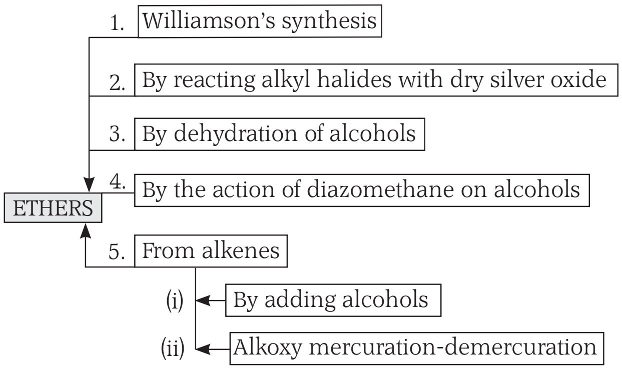
(f) Preparation of Higher Ethers

Higher ethers can be prepared by treating α-halo ethers with suitable Grignard's reagent as



$$CH_3—O—CH_2Cl + CH_3MgBr \longrightarrow CH_3OCH_2—CH_3 + Mg\begin{matrix}\diagup Br\\ \diagdown Cl\end{matrix}$$

The outlines of the methods of preparation of ethers looks like.



Here, R' and R'' may be same or different alkyl or aryl groups.

Sample **Problem 12** *Which of the following reagents will be used for the preparation of* 1*-propoxypropane?*

[NCERT]

(a) *Sodium propoxide + propane*
(b) *Sodium ethoxide +* 1*-bromopropane*
(c) *Sodium propoxide +* 1*-bromopropane*
(d) *None of the above*

Interpret (*c*) $R—X + Na—O—R' \xrightarrow[\text{synthesis}]{\text{Williamson's}} R—O—R' + NaX$

Here alkyl halide should be primary. Therefore, equation will be

$$\underset{\text{1-bromopropane}}{CH_3CH_2CH_2-Br} + \underset{\text{sodium propoxide}}{Na^+O^-CH_2CH_2CH_3} \xrightarrow{\Delta} \underset{\text{1-propoxypropane}}{CH_3CH_2CH_2—O—CH_2CH_2CH_3} + NaBr$$

Sample **Problem 13** *Which of the following reactions can be used for the preparation of tertiary butylmethyl ether?*

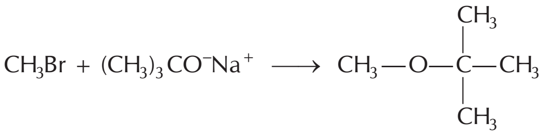
(*a*) $CH_3Br + (CH_3)_3CO^-Na^+ \longrightarrow$

(*b*) $(CH_3)_3CCl + CH_3O^-Na^+ \longrightarrow$

(*c*) $(CH_3)_3COH + CH_3Cl \longrightarrow$

(*d*) $(CH_3)_3CCl + CH_3OH \longrightarrow$

Interpret (*a*)

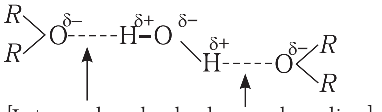


$$CH_3Br + (CH_3)_3CO^-Na^+ \longrightarrow CH_3—O—\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}—CH_3$$

tert-butylmethyl ether

Physical Properties

Dimethyl ether and ethyl methyl ether are gases at room temperature while other homologues are colourless liquids with characteristic ether smell and with a dipole moment of 1.15 to 1.3D. These have the **boiling points lower than their isomeric alcohols**. (Due to lesser hydrogen bonding than corresponding alcohols). Ethers upto 3 C-atoms are soluble in water due to the formation of intermolecular hydrogen bonds as



[Intermolecular hydrogen bonding]

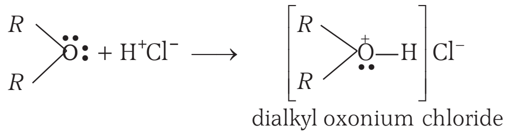
Chemical Properties

The reactions of ethers are mainly due to lone pair of ethereal O, cleavage of C—O bond and —*R* group.

(a) Reactions Due to Ethereal Oxygen

These reactions are mainly due to the lone pair of oxygen. Here ethers behave as base.

(i) **Action of concentrated acids** Oxonium salts are formed *i.e.,* such a reaction occur due to the presence of two lone pairs of electrons over oxygen.



dialkyl oxonium chloride

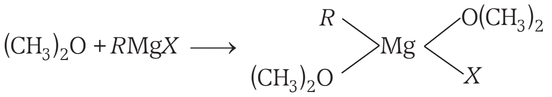
These salts are stabilised due to stabilisation by the anion of acids as

$$(CH_3)_2O + H_2SO_4 \longrightarrow \underset{\text{diethyl oxonium hydrogen sulphate}}{[(CH_3)_2OH]^+HSO_4^-}$$

(ii) **Formation of coordination complexes** Similarly, ethereal oxygen, being **Lewis base** form coordination complexes, called **etherates**, with Lewis acids such as BF_3, $AlCl_3$, $FeCl_3$, Grignard's reagent etc., as

borontrifluoride etherate

Similarly,



Grignard reagent etherate

[Due to this complex formation Grignard reagents dissolve in dry ether.]

(b) Reactions Involving Cleavage of Carbon-Oxygen Bond

(i) **With H*X***

$$R—O—R + HX \xrightarrow{100°C} R—OH + RX$$

The order of reactivity of halogen acids follow the sequence

$$HI > HBr > HCl$$

In case of asymmetrical ethers, the alkyl halide is always formed from the **smaller alkyl group** provided no tertiary (3°) alkyl group is present and if any 3° alkyl group is present, the halogen gets attached with it. *e.g.,*

$$CH_3—O—C_2H_5 + HBr \xrightarrow{100°C} CH_3Br + CH_3CH_2OH$$

In case of alkyl aryl ethers the products are **always phenol and an alkyl halide** as

$$C_6H_5—O—CH_3 + HBr \xrightarrow{100°C} C_6H_5OH + CH_3Br$$

(ii) **With sulphuric acid** With dil H_2SO_4, under pressure, ethers are hydrolysed to alcohols as

$$R—O—R + H_2O/H^+ \xrightarrow[\text{under pressure}]{\text{Dil. }H_2SO_4,\Delta} 2R—OH$$

With conc H_2SO_4, alcohols and alkyl hydrogen sulphates are formed as

$$\underset{\text{(primary ether)}}{R—O—R} + \text{conc. }H_2SO_4 \xrightarrow{\Delta} R—OH + RHSO_4$$

Secondary and tertiary ethers however, form alkenes instead of alcohols.

(iii) **With** PCl_5 The reaction looks like

$$CH_3—O—CH_3 + PCl_5 \longrightarrow 2CH_3—Cl + POCl_3$$

(iv) **With acid derivatives** Acid chlorides react with ethers in the presence of anhydrous $ZnCl_2$ or $AlCl_3$ to form alkyl halide and esters as

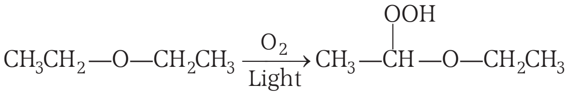
$$ROR + R'COCl \xrightarrow[\Delta]{AlCl_3 \text{ or Anhy. } ZnCl_2} RCl + R'COOR$$

Acid anhydrides form esters under similar conditions as :

$$R—O—R + (CH_3CO)_2O \xrightarrow[\text{or } ZnCl_2/\Delta]{\text{Anhy. } AlCl_3} 2CH_3COOR$$

(c) Reactions Involving Alkyl Group

(i) **Action of air and light** When exposed to air and light for a long time, ethers are oxidised to form hydroperoxides or simply peroxides as



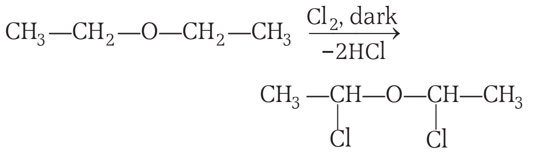
$$CH_3CH_2—O—CH_2CH_3 \xrightarrow[\text{Light}]{O_2} CH_3—\underset{}{\overset{OOH}{\overset{|}{C}H}}—O—CH_2CH_3$$

The reaction is free radical and oxidation occurs at the C-atom next to ethereal oxygen.

These peroxides are very dangerous compounds as these decompose violently at high temperatures.

(ii) **Halogenation** With halogens, ethers give substitution products. The extent of halogenation, however, depends upon the reaction conditions.

Diethyl ether reacts in dark to form only mono substituted products of alkyl group, *e.g.*,



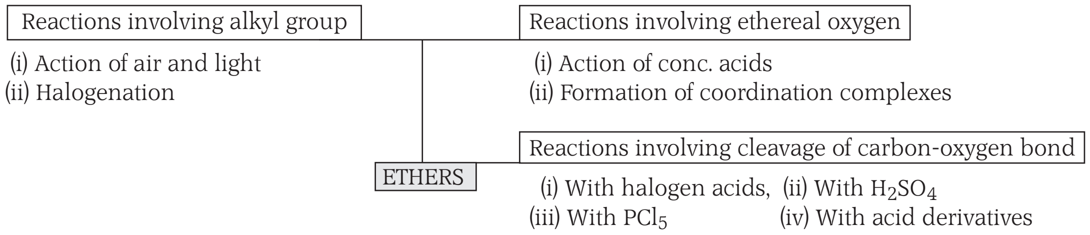
$$CH_3—CH_2—O—CH_2—CH_3 \xrightarrow[-2HCl]{Cl_2,\text{ dark}} CH_3—\underset{\underset{Cl}{|}}{CH}—O—\underset{\underset{Cl}{|}}{CH}—CH_3$$

α, α′-dichlorodiethyl ether

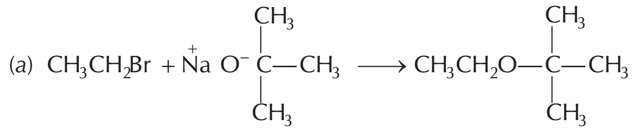
In the presence of light and excess of chlorine all hydrogen atoms are substituted as

$$CH_3—CH_2—O—CH_2—CH_3 + 10Cl_2 \xrightarrow{h\nu} C_2Cl_5—O—C_2Cl_5 + 10HCl$$

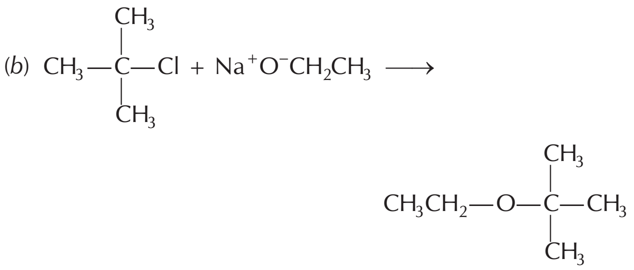
The outline of their chemical properties looks like



Sample **Problem 14** *Which of the following reactions is/are feasible?*



$$(a)\ CH_3CH_2Br + \overset{+}{Na}\,O^-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—CH_3 \longrightarrow CH_3CH_2O—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—CH_3$$



$$(b)\ CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—Cl + Na^+O^-CH_2CH_3 \longrightarrow CH_3CH_2—O—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—CH_3$$

(c) Both (a) and (b)
(*d*) None of the above

Interpret (*a*) The reactivity of primary halides is in the order, $CH_3 > CH_3CH_2 > CH_3CH_2CH_2$ and the tendency of alkyl halides to undergo elimination is $3° > 2° > 1°$. Hence, for better yield, the alkyl halide should be primary and alkoxide should be secondary or tertiary.

Uses of Ethers

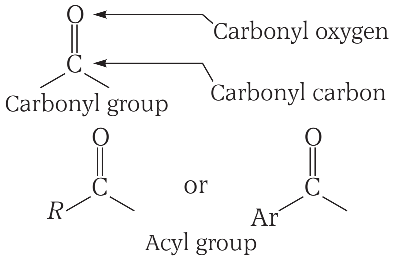
(i) Ethers are used as a solvent for oils, fats and Grignard reagent etc.
(ii) These are used as general anaesthetic.
(iii) They provide inert and moisture free medium for various reactions.

Check Point 3

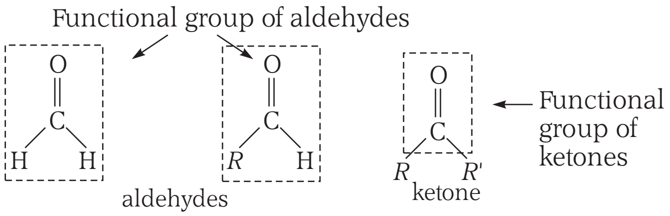
1. HI is a better reagent than HBr for cleavage of ethers. Explain, Why?
2. Account for the following
   (i) Ethers have significant dipole moments.
   (ii) Ethers are soluble in conc H_2SO_4 but separate out from the solution on adding water.
3. Why is diethylether used as a solvent for
   (i) BF_3 and (ii) RMgBr?
4. Why a non-symmetrical ether is not prepared by heating a mixture of R—OH and R' OH in acid?

11.4 Aldehydes and Ketones

The organic compounds containing carbon-oxygen double bond, *i.e.*, $>C=O$ group are called **carbonyl compounds.** These compounds are widely spread both in plants and animal kingdom and they play an important role in biological processes.



$>C=O$ group containing compounds can be divided into two classes. One class includes the carbonyl compounds in which the carbonyl group is attached to either hydrogen atoms or alkyl or aryl groups and other includes the carbonyl compounds in which $>C=O$ group gets attached to —OH, — NH_2 etc., functional groups. **Aldehydes** and **ketones** belong to the former class. The —H atom and alkyl or aryl (—*R* or —Ar) groups of aldehydes and ketones cannot be replaced by another group (*i.e.*, nucleophile).



(where, *R* and *R*′ may be similar or different alkyl or aryl group.)

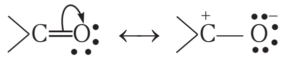
If the two *R* and *R*′ groups are different, the ketone is called a **mixed ketone** and if *R* and *R*′ represent the same group, the ketone is referred to as **simple ketone.** The functional group of aldehydes is called **the aldehydic group** (—CHO) while that of ketones is called **the ketonic group** ($>C=O$).

Nature of Carbonyl Group

In carbonyl group, π-electron cloud is displaced towards more electronegative oxygen atom thus, causing polarisation of the bond so that carbon acquires partially positive and oxygen acquires partially negative charge.

$$>\overset{+}{C}\overset{\to}{=}\overset{-}{O} \quad \text{or} \quad >\overset{\delta+}{C}-\overset{\delta-}{O}$$

In resonance terms, electron delocalisation in the carbonyl group is represented by contributions from two principal resonance forms.



Preparation of Aldehydes and Ketones

There are serveral method from which aldehydes as well as ketones can be synthesised. *These methods are as follows*

(a) Catalytic Decomposition of Acids and Calcium Salts of Acids

Catalytic decomposition of acids is done with the help of oxides of manganese and thorium.

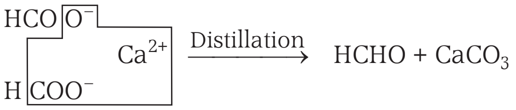
$$\underbrace{HCOOH + HCOOH}_{\text{vapour phase}} \xrightarrow[300°C]{\text{Mn or Th oxide}} HCHO + H_2O + CO_2$$

$$\underbrace{HCOOH + RCOOH}_{\text{vapour phase}} \xrightarrow[300°C]{\text{Mn or Th oxide}} RCHO + H_2O + CO_2$$

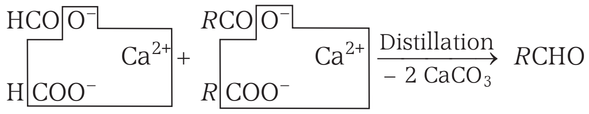
$$\underbrace{RCOOH + RCOOH}_{\text{vapour phase}} \xrightarrow[300°C]{\text{Mn or Th oxide}} RCOR + H_2O + CO_2$$

Similarly distillation of vapours of calcium salts of fatty acids produces aldehydes and ketones as

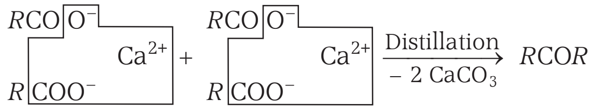
(i)



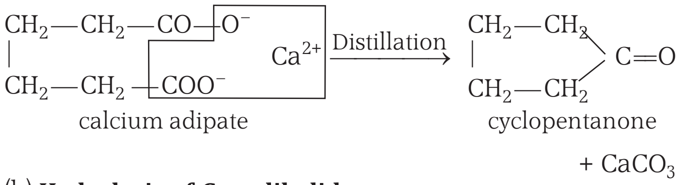
(ii)



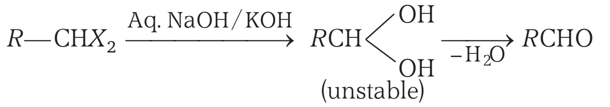
(iii)

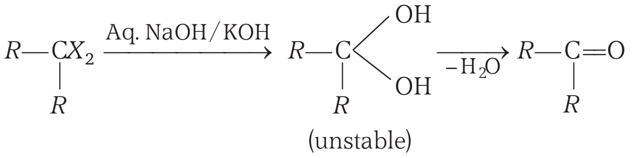


Hence, this method is not suitable for the preparation of these compounds, except formaldehyde. If instead of calcium salts of monocarboxylic acids, calcium salts of dicarboxylic acids are used, five and six-membered cyclic ketones can be prepared.



(b) Hydrolysis of *Gem*-dihalides

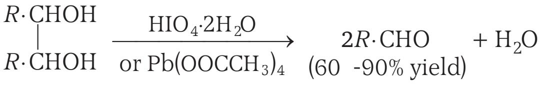




(c) Cleavage of Glycol

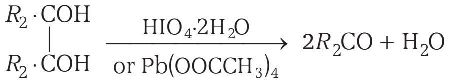
The glycol cleavage using $HIO_4\cdot 2H_2O$ (periodic acid) or $Pb(OOCCH_3)_4$ (lead tetra acetate) gives aldehydes and ketones, *e.g.*,

(i) Oxidation of secondary glycols gives aldehydes.

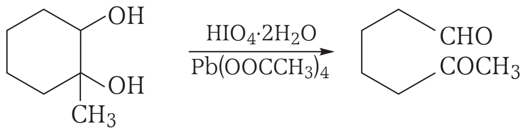


$$\begin{array}{c} R\cdot CHOH \\ | \\ R\cdot CHOH\end{array} \xrightarrow[\text{or } Pb(OOCCH_3)_4]{HIO_4\cdot 2H_2O} \underset{(60\ \text{-}90\%\ \text{yield})}{2R\cdot CHO} + H_2O$$

(ii) Tertiary glycols under similar conditions give ketones.

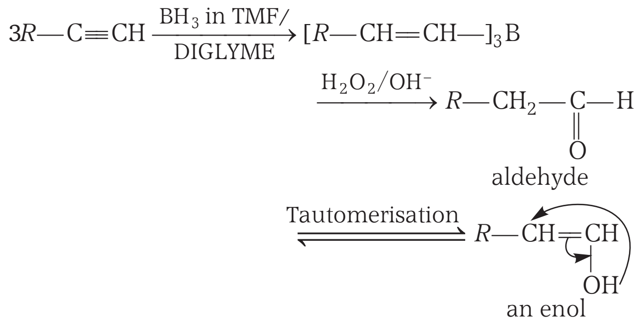


$$\begin{array}{c} R_2\cdot COH \\ | \\ R_2\cdot COH\end{array} \xrightarrow[\text{or } Pb(OOCCH_3)_4]{HIO_4\cdot 2H_2O} 2R_2CO + H_2O$$



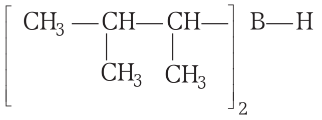
(d) Hydroboration-Oxidation of Alkynes

The reaction works as



$$3R—C\equiv CH \xrightarrow[\text{DIGLYME}]{BH_3\ \text{in TMF/}} [R—CH=CH—]_3B \xrightarrow{H_2O_2/OH^-} \underset{\text{aldehyde}}{R—CH_2—\underset{\underset{O}{\|}}{C}—H} \xrightleftharpoons{\text{Tautomerisation}} \underset{\text{an enol}}{R—CH=CH—OH}$$

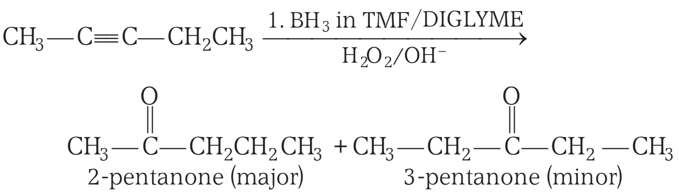
Aldehydes can be prepared from terminal alkynes. To avoid complications due to double addition of BH_3, bulky sterically hindered boranes such as *bis* (1, 2-dimethylpropyl) borane (common name-disiamyl borane) is used.



$$\left[CH_3—\underset{\underset{CH_3}{|}}{CH}—\underset{\underset{CH_3}{|}}{CH}—\right]_2 B—H$$

disiamylborane

Symmetrical non-terminal alkynes give a single ketone and unsymmetrical non-terminal alkynes gives a mixture of two ketones in which methyl ketone predominates.



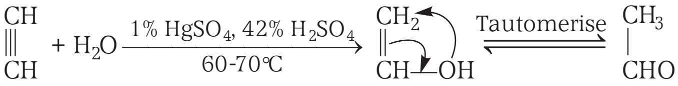
$$CH_3—C\equiv C—CH_2CH_3 \xrightarrow[H_2O_2/OH^-]{1.\ BH_3\ \text{in TMF/DIGLYME}}$$

$$\underset{\text{2-pentanone (major)}}{CH_3—\overset{\overset{O}{\|}}{C}—CH_2CH_2CH_3} + \underset{\text{3-pentanone (minor)}}{CH_3—CH_2—\overset{\overset{O}{\|}}{C}—CH_2—CH_3}$$

Formaldehyde cannot be prepared by this method.

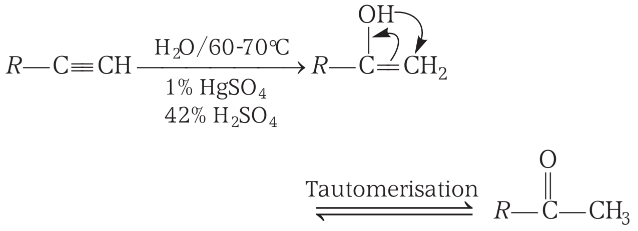
(e) Hydration of Alkynes

When acetylene is passed in 42% H_2SO_4 solution, containing 1% $HgSO_4$ at 60-70°C, acetaldehyde is formed.



$$\begin{array}{c}CH\\ ||| \\ CH\end{array} + H_2O \xrightarrow[60\text{-}70^\circ C]{1\%\ HgSO_4,\ 42\%\ H_2SO_4} \begin{array}{c}CH_2\\ \| \\ CH—OH\end{array} \xrightleftharpoons{\text{Tautomerise}} \begin{array}{c}CH_3\\ | \\ CHO\end{array}$$

Hydration of other alkynes gives ketones. The addition of water follows Markownikoff's rule.



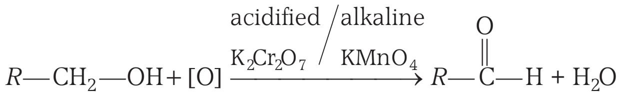
$$R—C\equiv CH \xrightarrow[\substack{1\%\ HgSO_4\\ 42\%\ H_2SO_4}]{H_2O/60\text{-}70^\circ C} R—\overset{\overset{OH}{|}}{C}=CH_2 \xrightleftharpoons{\text{Tautomerisation}} R—\overset{\overset{O}{\|}}{C}—CH_3$$

Formaldehyde cannot be prepared by this reaction.

(f) Oxidation of Alcohols

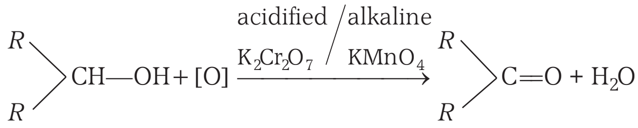
Different alcohols give different products on oxidation, *e.g.*,

(i) Primary alcohols are oxidised to give aldehydes.



$$R—CH_2—OH + [O] \xrightarrow[K_2Cr_2O_7\ /\ KMnO_4]{\text{acidified / alkaline}} R—\overset{\overset{O}{\|}}{C}—H + H_2O$$

(ii) Secondary alcohols are oxidised to give ketones.



$$\begin{matrix}R\\R\end{matrix}\!\!>CH—OH + [O] \xrightarrow[K_2Cr_2O_7\ /\ KMnO_4]{\text{acidified / alkaline}} \begin{matrix}R\\R\end{matrix}\!\!>C=O + H_2O$$

To prevent the further oxidation to acids some another reagents are also used. These are

(a) Sarett reagent – $CrO_3\cdot 2C_5H_5N$ in pyridine

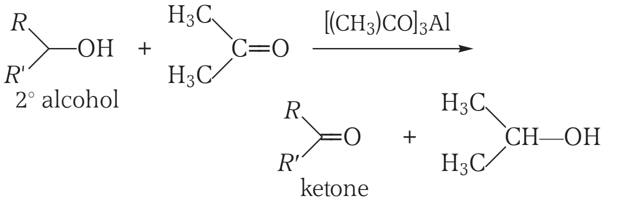
(b) Collin's reagent – $CrO_3\cdot 2C_5H_5N$ in CH_2Cl_2

(c) Corey's reagent (PCC – pyridinium chloro chromate) – $C_5H_5NH^+CrO_3Cl^-$

(d) Pyridinium dichromate (PDC) – $(C_5H_5NH^+)_2Cr_2O_7^{2-}$

As these reagents are very selective, hence used to oxidise allylic and benzylic alcohols.

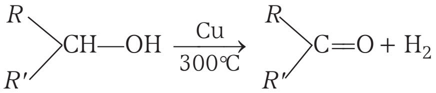
Oxidation of secondary alcohols with tertiary butoxide of aluminium in the presence of *iso*-propyl alcohol is called **Oppenauer oxidation.**



$$\underset{2^\circ\ \text{alcohol}}{\begin{matrix}R\\R'\end{matrix}\!\!>—OH} + \begin{matrix}H_3C\\H_3C\end{matrix}\!\!>C=O \xrightarrow{[(CH_3)CO]_3Al} \underset{\text{ketone}}{\begin{matrix}R\\R'\end{matrix}\!\!>=O} + \begin{matrix}H_3C\\H_3C\end{matrix}\!\!>CH—OH$$

(g) Catalytic Dehydrogenation of Alcohols

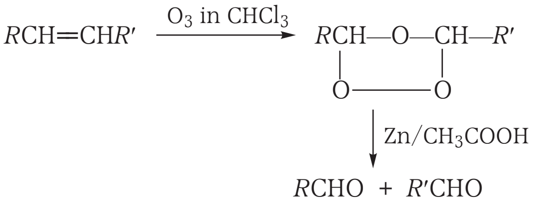
$$RCH_2OH \xrightarrow[300°C]{Cu} RCHO + H_2$$



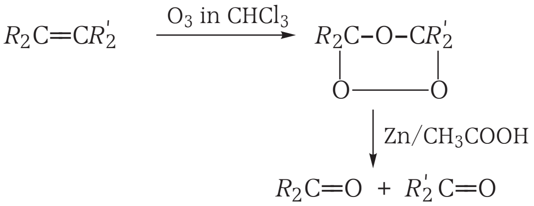
This method gives good yield.

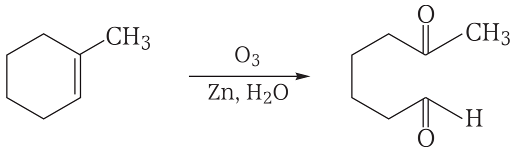
(h) Ozonolysis of Alkenes

The alkenes upon treatment with O_3 gives ozonide, which on subsequent treatment with Zn/CH_3COOH gives aldehydes and ketone depending on the structure of alkene.



With dialkyl substituted alkenes, ketones are obtained.





(i) Wacker's Process

The alkene is oxidised as

$$CH_2{=}CH_2 + \frac{1}{2} O_2 \xrightarrow[H_2O]{PdCl_2 \cdot CuCl_2} CH_3CHO$$

The oxidation is mainly done by $PdCl_2$ as

$$CH_2{=}CH_2 + PdCl_2 + H_2O \xrightarrow{CuCl_2} CH_3CHO + Pd + 2HCl$$

$$Pd + 2HCl \longrightarrow PdCl_2 + H_2$$

$CuCl_2$ is helpful in the reconversion of Pd to $PdCl_2$ as

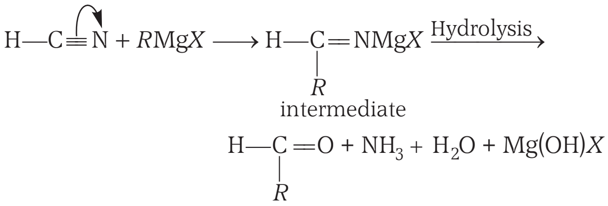
$$Pd + 2CuCl_2 \longrightarrow PdCl_2 + 2CuCl$$

$$4CuCl + 4HCl + O_2 \longrightarrow 4CuCl_2 + 2H_2O$$

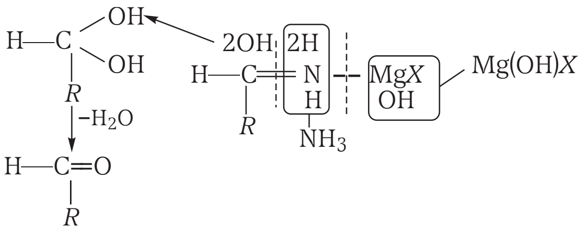
Because $PdCl_2$ is an expensive reagent, hence, cooxidant $CuCl_2$ reoxidise Pd to $PdCl_2$ and itself reoxidise by air. Hence, the atmospheric oxygen is the only oxidising agent used.

(j) From Grignard Reagent and Cyanides

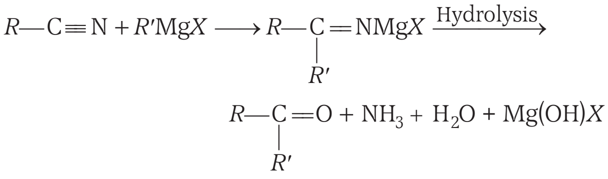
(i) Reaction of Grignard's reagent with HCN gives aldehydes other than HCHO. In fact HCHO cannot be prepared by this reaction.



The breakage of intermediate is seen as

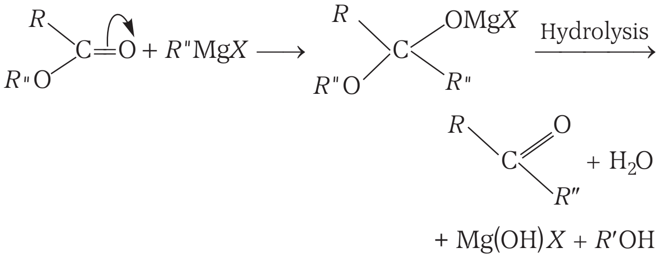


(ii) Ketones are produced by the reaction of RCN with $R'MgX$ as



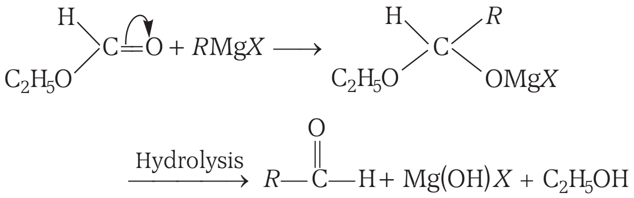
(k) From Grignard Reagent and Esters

Grignard reagents also give ketones on treatment with acid derivatives like esters as

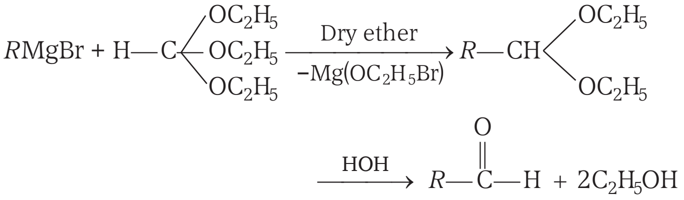


But the yield here is very less as the ketone formed further reacts with $R''MgX$.

Aldehydes are formed by reaction of ethyl formate with Grignard reagent.



Aldehydes can also be prepared by the action of Grignard reagent on orthoformic esters.



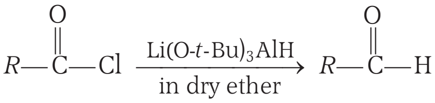
$$RMgBr + H-C(OC_2H_5)_3 \xrightarrow[-Mg(OC_2H_5Br)]{\text{Dry ether}} R-CH(OC_2H_5)_2 \xrightarrow{HOH} R-\overset{O}{\overset{\|}{C}}-H + 2C_2H_5OH$$

Methods of Preparation for Aldehydes Only

The methods given below can employed for the synthesis of aldehydes, not for the ketones.

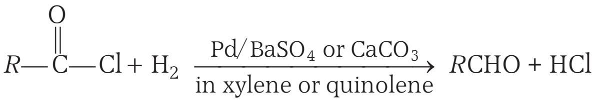
(a) Reduction of Acids and Acid Derivatives

Reduction of acids and acid derivatives under normal conditions with strong reducing agents like $LiAlH_4$ results to alcohols through carbonyl compounds. Thus, mild reducing agents like DIBAL-H (di *iso*-butyl aluminium hydride), lithium *tri*-(tertiary) butoxy aluminium hydride $[Li(O\text{-}t\text{-}C_4H_9)_3AlH]$ and *tri n*-butyl tinhydride are used for the purpose. $NaAlH_4$ also shows same results.



$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[\text{in dry ether}]{Li(O\text{-}t\text{-}Bu)_3AlH} R-\overset{O}{\overset{\|}{C}}-H$$

In particular hydrogenation of $RCOCl$ with H_2 in the presence of Lindlar's catalyst to produce aldehydes is called **Rosenmund reaction**, *i.e.*,



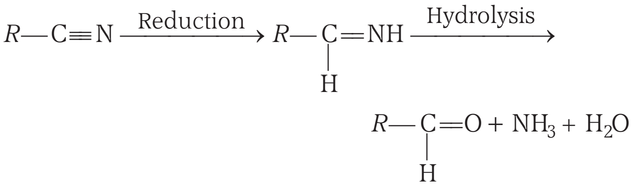
$$R-\overset{O}{\overset{\|}{C}}-Cl + H_2 \xrightarrow[\text{in xylene or quinolene}]{Pd/BaSO_4 \text{ or } CaCO_3} RCHO + HCl$$

Reduction of acids normally produces very less yield that's why acylhalides and esters are preferred over them.

Formyl chloride cannot be reduced to give formaldehyde because of being quite unstable.

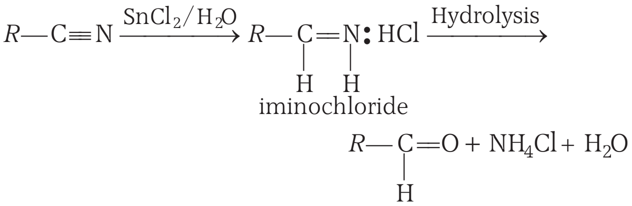
(b) Reductive Hydrolysis of Alkyl Cyanides

The generalised reaction looks like



$$R-C\equiv N \xrightarrow{\text{Reduction}} R-\underset{H}{\underset{|}{C}}=NH \xrightarrow{\text{Hydrolysis}} R-\underset{H}{\underset{|}{C}}=O + NH_3 + H_2O$$

Specifically when reduction is carried out with $SnCl_2/HCl$, it is called **Stephen's method.**

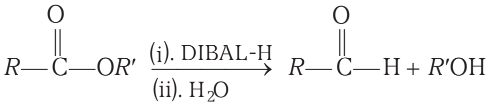


$$R-C\equiv N \xrightarrow{SnCl_2/H_2O} \underset{\text{iminochloride}}{R-\underset{H}{\underset{|}{C}}=\underset{H}{\underset{|}{N}}:HCl} \xrightarrow{\text{Hydrolysis}} R-\underset{H}{\underset{|}{C}}=O + NH_4Cl + H_2O$$

Reduction can also be seen with the help of **DIBAL-H** (di *iso*-butyl aluminium hydride). **It does not reduce double or triple bond other than nitrile group.**

(c) Reduction of Esters

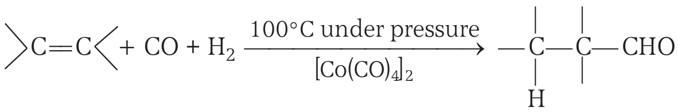
Esters are reduced to aldehydes by DIBAL-H or $NaAlH_4$.



$$R-\overset{O}{\overset{\|}{C}}-OR' \xrightarrow[\text{(ii). } H_2O]{\text{(i). DIBAL-H}} R-\overset{O}{\overset{\|}{C}}-H + R'OH$$

(d) Oxo Process

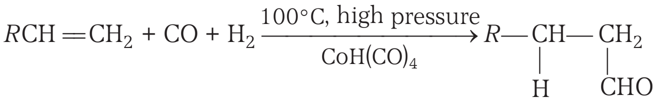
The process is also called **carboformylation** or **hydroformylation**.



$$\rangle C=C\langle + CO + H_2 \xrightarrow[[Co(CO)_4]_2]{100°C \text{ under pressure}} -\underset{H}{\underset{|}{\overset{|}{C}}}-\underset{|}{\overset{|}{C}}-CHO$$

$CoH(CO)_4$ can also be used as catalyst.

The reaction appears to be an *anti*-Markownikoff addition of formaldehyde to the alkene.



$$RCH=CH_2 + CO + H_2 \xrightarrow[CoH(CO)_4]{100°C, \text{ high pressure}} R-\underset{H}{\underset{|}{CH}}-\underset{CHO}{\underset{|}{CH_2}}$$

Methods of Preparation for Ketones Only

The methods given below are used only for the synthesis of ketones.

(a) Hydrolysis of Ethyl Acetoacetate

When ethyl acetoacetate (EAA) is hydrolysed with dil. HCl, acetoacetic acid is formed which on heating undergoes decarboxylation as

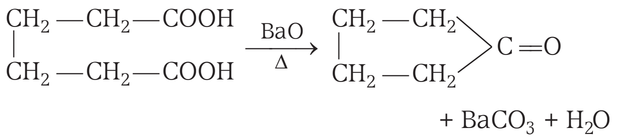
$$CH_3-COCH_2COOC_2H_5 \xrightarrow{H_2O/H^+} \underset{\text{acetoacetic acid}}{CH_3COCH_2COOH} + C_2H_5OH$$

$$CH_3COCH_2COOH \xrightarrow{\Delta} CH_3COCH_3 + CO_2 + H_2O$$

This hydrolysis is called ketonic hydrolysis of EAA. The reaction is specifically used for the preparation of acetone.

(b) From Dicarboxylic Acids

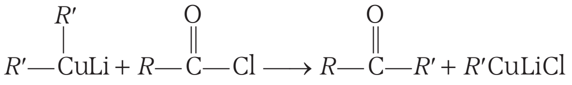
Dicarboxylic acids are heated with BaO or CaO to prepare cyclic ketones.



(c) By Organometallic Compounds

Lithium organocuprate reacts rapidly with acid chlorides to yield ketones.

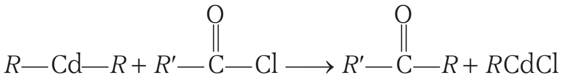
$$RX \xrightarrow{\text{Li}} R\text{Li} \xrightarrow{\text{Cu}X} \underset{\text{lithium dialkyl cuperate}}{R_2\text{CuLi}}$$



$$R'-\overset{\overset{\displaystyle R'}{|}}{\text{Cu}}\text{Li} + R-\overset{\overset{\displaystyle \text{O}}{\|}}{\text{C}}-\text{Cl} \longrightarrow R-\overset{\overset{\displaystyle \text{O}}{\|}}{\text{C}}-R' + R'\text{CuLiCl}$$

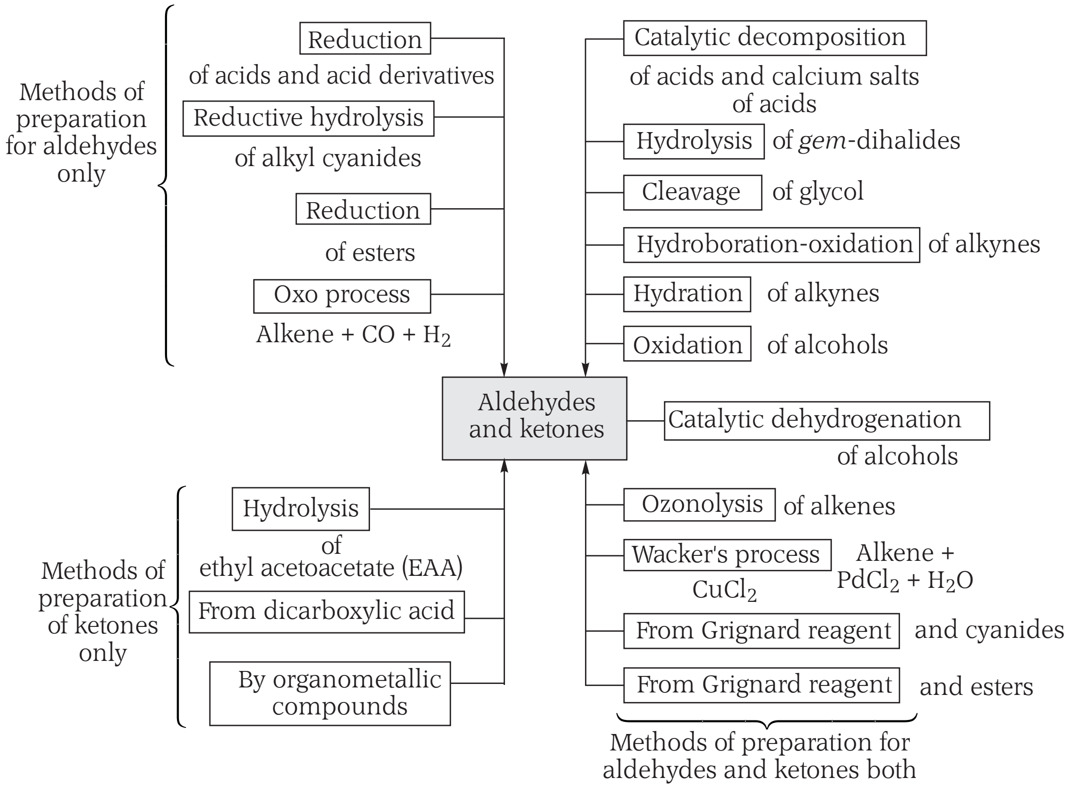
Cadmium salts may also be used.

$$2R\text{Mg}X + \text{CdCl}_2 \longrightarrow R_2\text{Cd} + \text{MgCl}_2 + \text{Mg}X_2$$



$$R-\text{Cd}-R + R'-\overset{\overset{\displaystyle \text{O}}{\|}}{\text{C}}-\text{Cl} \longrightarrow R'-\overset{\overset{\displaystyle \text{O}}{\|}}{\text{C}}-R + R\text{CdCl}$$

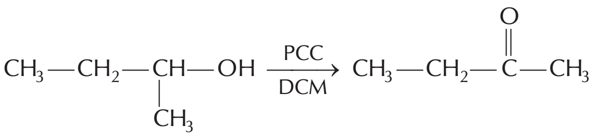
The outline of methods of preparation of these carbonyl compounds looks like



Sample **Problem 15** *Which of the following compounds is oxidised to prepare methyl ethyl ketone?* [**NCERT** Exemplar]

(a) *2-propanol* (b) *1-butanol*
(c) *2-butanol* (d) *tert-butyl alcohol*

Interpret (c) Oxidation of 2-butanol to ethyl methyl ketone can be made effective by using oxidising agent PCC/DCM (pyridinium chlorochromate in dichloro methane).



$$\text{CH}_3-\text{CH}_2-\underset{\underset{\displaystyle \text{CH}_3}{|}}{\text{CH}}-\text{OH} \xrightarrow[\text{DCM}]{\text{PCC}} \text{CH}_3-\text{CH}_2-\overset{\overset{\displaystyle \text{O}}{\|}}{\text{C}}-\text{CH}_3$$

Physical Properties

(i) **Boiling points** of aldehydes and ketones are higher than those of non-polar compounds hydrocarbons and ethers of comparable molecular masses due to dipole-dipole interactions between the opposite ends of the $>\text{C}=\text{O}$ dipoles.

(ii) **Solubility** decreases with increase in molecular mass. Lower aldehydes and ketones containing up to four carbon atoms are soluble in water.

Chemical Reactions of Aldehydes and Ketones

Aldehydes and ketones because of the presence of polar carbonyl group exhibit the following characteristics.

(a) **Nucleophilic Addition Reactions**

Carbonyl compounds show nucleophilic addition reactions. A nucleophile attacks at the electrophilic carbon atom of the polar carbonyl group.

$$\underset{sp^2,\ \text{carbonyl group}}{>C{=}O}$$

As the number of carbon atoms/number of alkyl groups increases, reactivity decreases due to steric hindrance. Hence, the order of reactivity is

$$HCHO > CH_3CHO > CH_3COCH_3 > C_2H_5COC_2H_5$$

Among the aldehydes and ketones, the size of alkyl group is inversely proportional to their reactivity. Among the ketones their less reactivity is due to $+I$ effect of alkyl group present due to which the partial (+) ve charge on carbon atom of carbonyl group decreases, thus decreasing the possibility of nucleophilic attack.

I. **Addition of hydrogen cyanide** The reaction looks like

$$>C{=}O + H^+CN^- \longrightarrow >C\begin{smallmatrix}OH\\CN\end{smallmatrix}$$

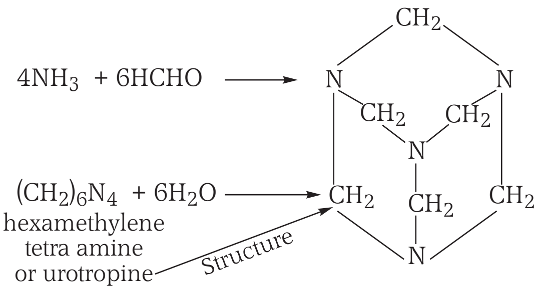
cyanohydrin

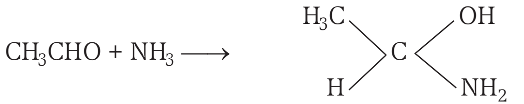
HCN is highly poisonous gas and produced by the reaction of K or Na cyanides with H_2SO_4. HCN itself is not a powerful nucleophile to attack $>C{=}O$ therefore the reaction requires base catalysis in order to convert HCN into more nucleophilic CN^-.

Ketones gives *dl* cyanohydrin only if both the alkyl groups attached to carbonyl carbon are different (*i.e.,* ketone is unsymmetrical). Cyanohydrins are useful synthetic substances since they can be readily hydrolysed to give α-hydroxy acids (Strecker synthesis).

II. **Addition of ammonia and it derivatives**

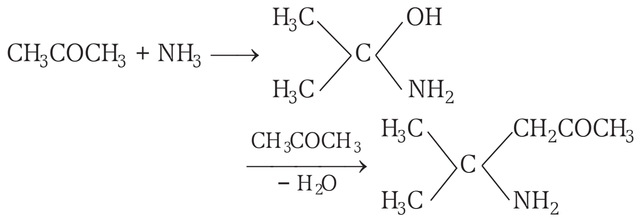
The reaction of aldehydes and ketones with ammonia and its derivatives are illustrated below





$$CH_3CHO + NH_3 \longrightarrow \begin{smallmatrix}H_3C\\H\end{smallmatrix}>C<\begin{smallmatrix}OH\\NH_2\end{smallmatrix}$$

acetaldehyde ammonia (solid)



$$CH_3COCH_3 + NH_3 \longrightarrow \begin{smallmatrix}H_3C\\H_3C\end{smallmatrix}>C<\begin{smallmatrix}OH\\NH_2\end{smallmatrix} \xrightarrow[-H_2O]{CH_3COCH_3} \begin{smallmatrix}H_3C\\H_3C\end{smallmatrix}>C<\begin{smallmatrix}CH_2COCH_3\\NH_2\end{smallmatrix}$$

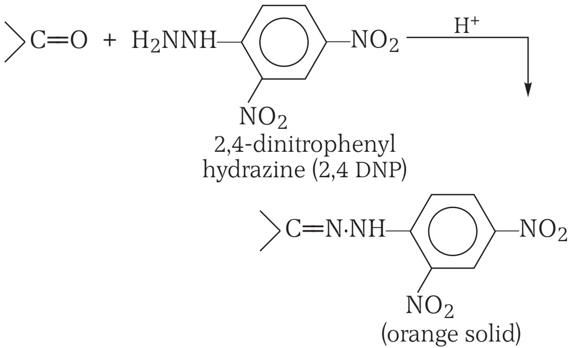
diacetone amine

$$>C{=}O + \underset{\text{hydroxyl amine}}{NH_2OH} \xrightarrow{H^+} \underset{\text{oxime}}{>C{=}NOH} + H_2O$$

$$>C{=}O + \underset{\text{hydrazine}}{NH_2{-}NH_2} \xrightarrow{H^+} \underset{\text{hydrazone}}{>C{=}NNH_2} + H_2O$$

$$>C{=}O + \underset{\text{phenyl hydrazine}}{NH_2{-}NHC_6H_5} \xrightarrow{H^+} \underset{\text{phenyl hydrazone}}{>C{=}NNHC_6H_5} + H_2O$$

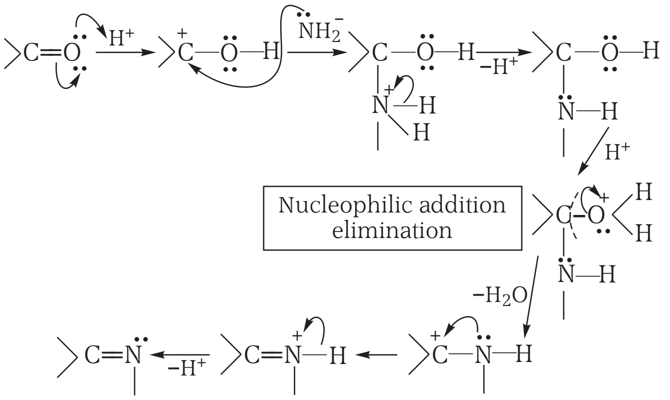
$$>C{=}O + \underset{\text{semicarbazide}}{NH_2\cdot CONH\cdot NH_2} \xrightarrow{H^+} \underset{\text{semicarbazone}}{>C{=}N\cdot NHCONH_2} + H_2O$$



2,4-dinitrophenyl hydrazine (2,4 DNP)

(orange solid) 2,4-dinitrophenyl hydrazone

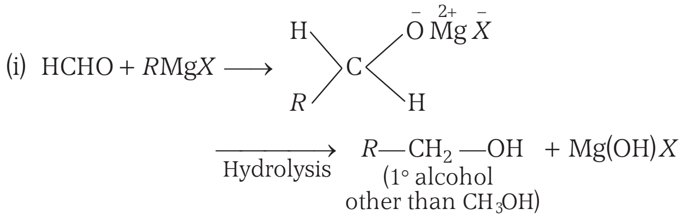
The mechanism of the reactions is summarised as

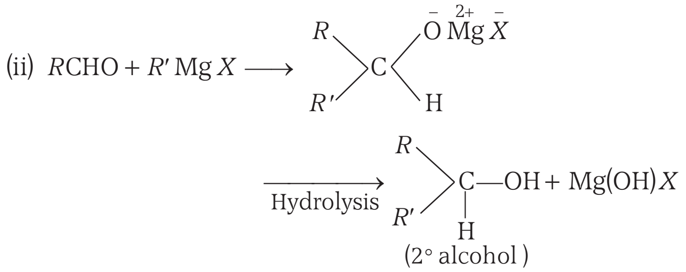


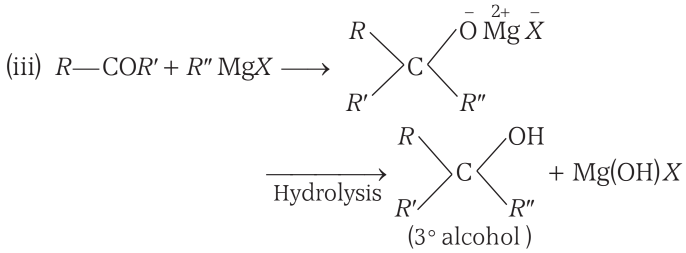
2, 4-DNP is used to distinguish carbonyl compounds from the mixture as we get solid orange precipitate of 2,4-dinitrophenyl hydrazone.

In these reactions, pH of medium must be controlled to about 3.5, *i.e.*, the medium must be weakly acidic in order to protonate the carbonyl group.

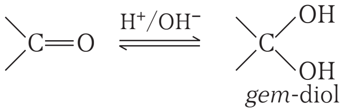
III. **Addition of Grignard reagent** The reactions are as





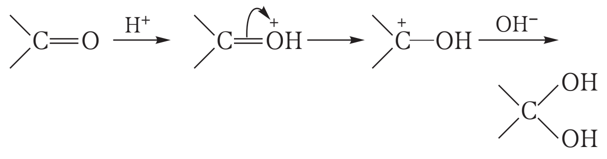


IV. **Addition of water** In aqueous solution, carbonyl compounds are in equilibrium with its hydrate– *gem*-diol, which is unstable and loses water molecule to form original compound.

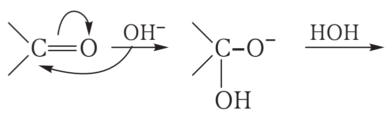


The mechanism of the reaction is summarised as,

(i) **Acid catalysed path**

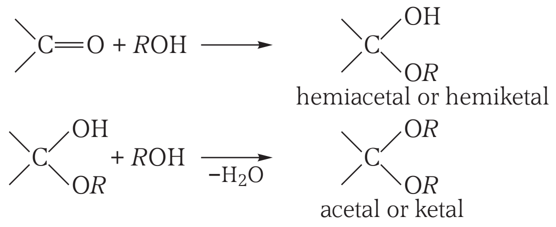


(ii) **Base catalysed path**



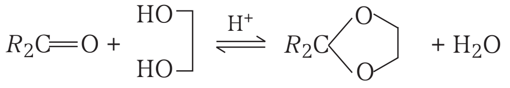
Aldehydes form more stable hydrates as compared to ketones.

V. **Addition of alcohols** Acetals (from aldehydes) and ketals (from ketones) are produced as,



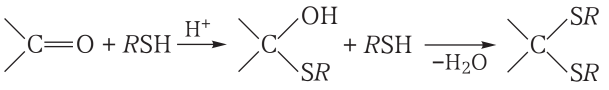
The reaction follows nucleophilic addition-elimination procedure.

Carbonyl compounds react with glycol to produce cyclic acetals or ketals.



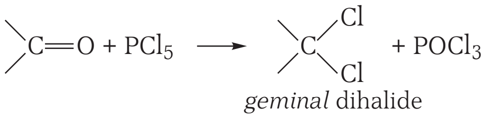
Acetals (or ketals) are stable in the presence of alkali, thus used to protect carbonyl group against alkaline oxidising agent.

VI. **Addition of thioalcohols** Mercaptals (thioacetals) and mercaptols (thioketals) are produced as,



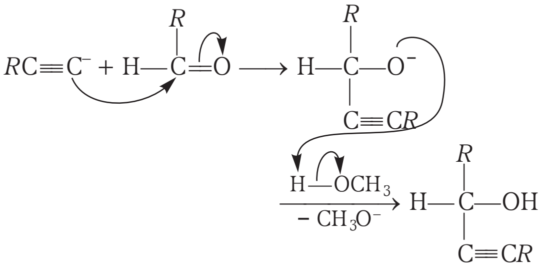
In acidic solutions, aldehyde (and ketone) groups can be protected by mercaptal and mercaptol formation respectively.

VII. **Addition of** PX_5 *Geminal* dihalides (alkylidene dihalides) are produced as,



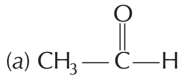
VIII. **Addition of alkynes, *i.e.*, ethinylation** Terminal alkynes ($RC{\equiv}CH$) can add on to carbonyl group in the presence of a base (RO^-) forming alkynol (alkynediol with $CH{\equiv}CH$). This reaction is called **ethinylation.**

$$RC{\equiv}CH + CH_3O^{\ominus} \longrightarrow CH_3OH + RC{\equiv}C^{\ominus}$$

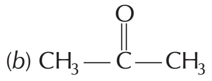


Sample **Problem 16** *Which of the following compounds is most reactive towards nucleophilic addition reactions?*

[**NCERT** Exemplar]

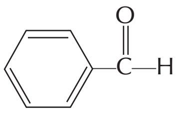


(*a*) $CH_3-\overset{\overset{O}{\|}}{C}-H$

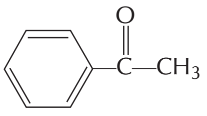


(*b*) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

(*c*)



(*d*)



Interpret (*a*) In carbonyl compounds, the size of alkyl group varies inversely with reactivity towards nucleophilic addition reactions. Therefore, $CH_3-\overset{\overset{O}{\|}}{C}-H$ is most reactive among the given carbonyl compounds.

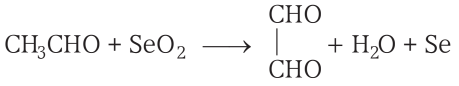
(b) Oxidation

Aldehydes (RCHO) can be easily oxidised to RCOOH by weak oxidising agents like **Tollen's reagent** (ammoniacal $AgNO_3$), **Fehling's solution** (ammoniacal Cu^{2+} solution complexes with tartarate ion), **Benedict's solution** (alkaline Cu^{2+} ion complex with citrate ion) etc.

$$R-CHO + \underset{\text{Tollen's reagent}}{2Ag(NH_3)_2^+} + 3OH^- \longrightarrow R-COO^- + 2H_2O + 4NH_3 + \underset{\text{silver mirror}}{2Ag\downarrow}$$

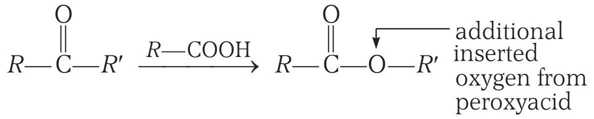
$$R-CHO + \underset{\text{Fehling's solution}}{2Cu(OH)_2} + NaOH \longrightarrow RCOONa + \underset{\text{red ppt.}}{Cu_2O\downarrow} + H_2O$$

Aldehydes and ketones with a methyl or methylene group adjacent to carbonyl group are oxidised with SeO_2 as,



$$CH_3CHO + SeO_2 \longrightarrow \begin{matrix} CHO \\ | \\ CHO \end{matrix} + H_2O + Se$$

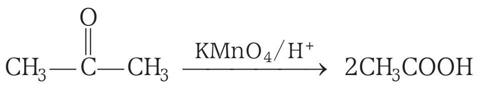
Both aldehydes and ketones are oxidised by peroxy acids to esters and the reaction is called **Baeyer-Velliger oxidation** (especially useful for ketones), *i.e.*,



$$R-\overset{\overset{O}{\|}}{C}-R' \xrightarrow{R-COOH} R-\overset{\overset{O}{\|}}{C}-O-R'$$

Aldehydes and ketones are oxidised by strong oxidising agents like $KMnO_4/H^+$, $K_2Cr_2O_7/H^+$, hot conc. HNO_3 etc.

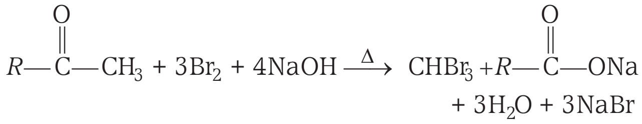
$$CH_3CHO \xrightarrow{KMnO_4/H^+} CH_3COOH$$



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{KMnO_4/H^+} 2CH_3COOH$$

(c) Haloform Reaction

Acetaldehyde and methylketones react rapidly with halogens (Cl_2, Br_2 or I_2) in the presence of alkali to form haloform and acid salt.

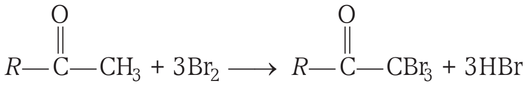


$$R-\overset{\overset{O}{\|}}{C}-CH_3 + 3Br_2 + 4NaOH \xrightarrow{\Delta} CHBr_3 + R-\overset{\overset{O}{\|}}{C}-ONa + 3H_2O + 3NaBr$$

$-CH_3$ group of $-COCH_3$ is converted into haloform as it contains acidic hydrogen atoms. Acid salt is obtained corresponding to total number of carbon atoms apart from $-CH_3$ of $RCOCH_3$.

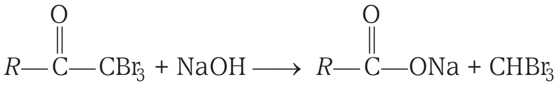
Mechanism of reaction is as follows

(i) **Halogenation**



$$R-\overset{\overset{O}{\|}}{C}-CH_3 + 3Br_2 \longrightarrow R-\overset{\overset{O}{\|}}{C}-CBr_3 + 3HBr$$

(ii) **Alkali hydrolysis of trihaloketone**

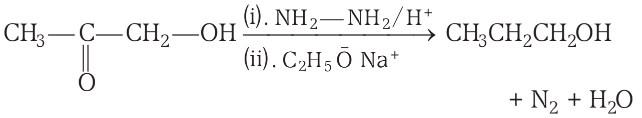


$$R-\overset{\overset{O}{\|}}{C}-CBr_3 + NaOH \longrightarrow R-\overset{\overset{O}{\|}}{C}-ONa + CHBr_3$$

This reaction is used to diagnose the presence of $CH_3-\overset{\overset{O}{\|}}{C}-$ group and also to distinguish methyl ketones from others.

(d) Reduction

Reducing agents like $LiAlH_4$ reduces $>C=O$ group to $>\underset{\underset{H}{|}}{C}-OH$ group generally. $NaBH_4$ can also show same capability but it is unable to reduce $>C=O$ group of ester and acid chlorides. Zn-Hg/HCl reduces $>C=O$ group to $>CH_2$ **(Clemmensen reduction)**. Similarly, hydrazine (NH_2-NH_2) followed by heating with strong base like alkali or alkaline glycol also reduces $>C=O$ group to $>CH_2$. Here, N_2 is also liberated and the reaction is called **Wolff-Kishner reduction. It is the specific method for the reduction of $>C=O$ group.**

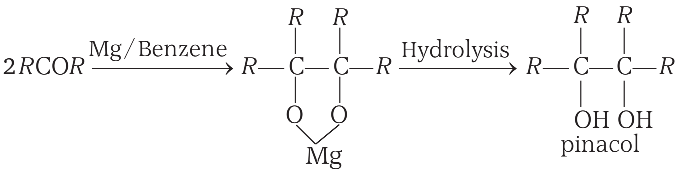


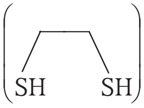
$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-OH \xrightarrow[\text{(ii). } C_2H_5\bar{O}\,Na^+]{\text{(i). } NH_2-NH_2/H^+} CH_3CH_2CH_2OH + N_2 + H_2O$$

Aluminium *iso*propoxide ($Al[OCH(Me)_2]_3$) in the presence of excess of *iso*propyl alcohol reduces $>C=O$ group to $>\underset{\underset{H}{|}}{C}-OH$ group and the reaction is called **Meerwein-Ponndrof-Verley's** (MPV) **reduction.**

$$R_2CO + [(Me)_2CHO]_3Al \rightleftharpoons R_2CHOAl[OHCMe_2]_2 + MeCOMe \xrightarrow{\text{Dil. } H_2SO_4} R_2CHOH$$

Mg in the presence of benzene reduces carbonyl compounds to pinacols as,



Reduction with Raney Ni (Ni : Al = 1 : 1) along with dimercaptal  produces hydrocarbon with same number of carbon atoms. HI/Red P can be also used effectively at high temperature to reduce $>C{=}O$ to $>CH_2$.

(e) Halogenation

In aliphatic aldehydes and ketones, one or more α-hydrogen atoms are replaced by the halogen atoms in the presence of acid or base.

$$CH_3CHO + Cl_2 \xrightarrow{H^+/OH^-} CH_2ClCHO + HCl$$

α-chloroacetaldehyde

$$CH_3COCH_3 + Br_2 \xrightarrow{H^+/OH^-} CH_2BrCOCH_3 + HBr$$

α-bromoacetone

Hot Spot 3

ALDOL Condensation

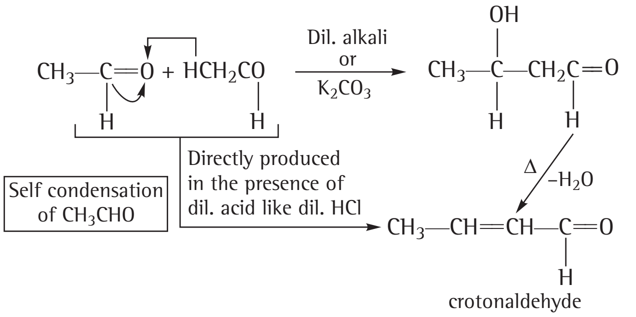
It is an important topic for JEE Main examination. Questions based upon this topic may vary from simple to moderate.

It is a very important reaction of aldehydes and ketones from synthetic point of view. **Enolisation property** (ability to convert into enol form on tautomerisation) **is responsible for the reaction.** As tautomerisation (keto-enol) is possible with acid or base both that's why this reaction can occur in the presence of dil acid as well as dil base.

The reaction can occur between

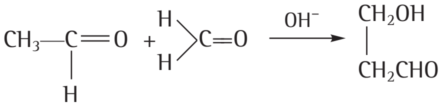
(i) two identical or different aldehydes,
(ii) two identical or different ketones,
(iii) one aldehyde and one ketone.

Presence of α-hydrogen in atleast one type of molecules is necessity of the reaction. The products formed here are called **aldols** as these contain atleast one **aldehyde** (carbonyl) and at least one **alcoholic** groups. However, the ultimate product of the reaction are α,β – unsaturated carbonyl compounds.



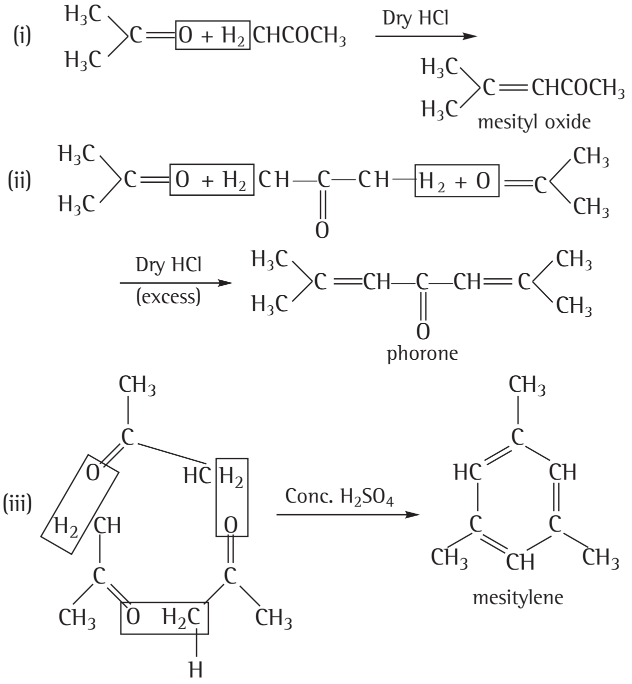
crotonaldehyde
α, β-unsaturated aldehyde.

When the condensation is between two different carbonyl compounds, it is called **'cross aldol condensation'.** In brief, the products (self as well as different) of HCHO, CH_3CHO and CH_3COCH_3 are,

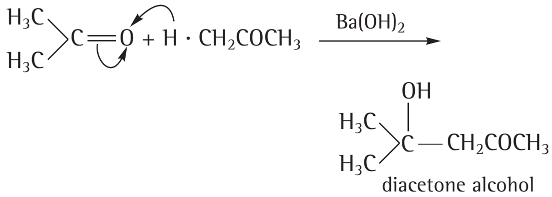


Cross aldol condensation

The different condensation products formed by acetone in different conditions are,

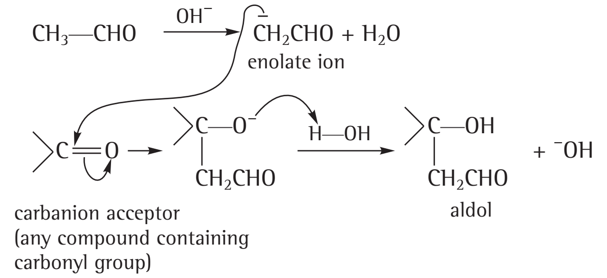


(iv)

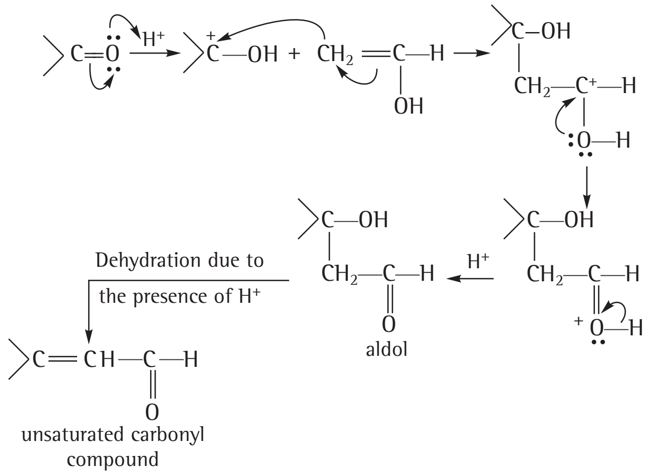


The mechanism of reaction is summarised as

(i) **In the presence of base**



(ii) **In the presence of acid**



Sample **Problem 17** *Which of the following compounds will not undergo aldol condensation?* **[NCERT]**

(*a*) *Methanol*

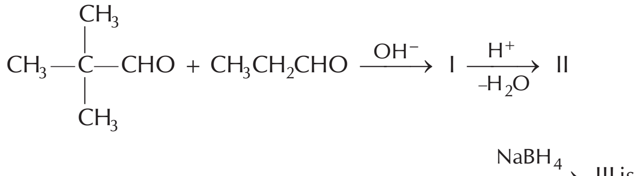
(*b*) *2-methyl pentanal*

(*c*) *Cyclohexanone*

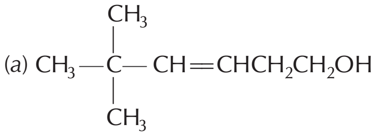
(*d*) *1-phenyl prepanone*

Interpret (*a*) Aldehydes or ketones having at least one α-H-atom undergo aldol condensation. Among the given, methanol is not a carbonyl compound. That's why it does not give aldol condensation reaction.

Sample **Problem 18** *The final product* (III) *obtained in the reaction*

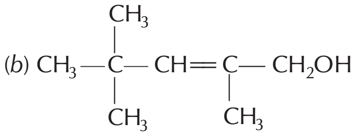


(*a*)



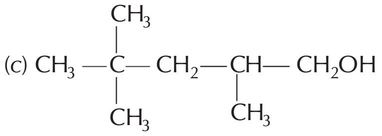
$CH_3-C(CH_3)_2-CH=CHCH_2CH_2OH$

(*b*)



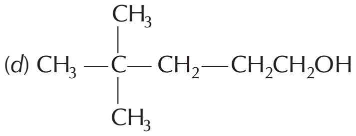
$CH_3-C(CH_3)_2-CH=C(CH_3)-CH_2OH$

(*c*)



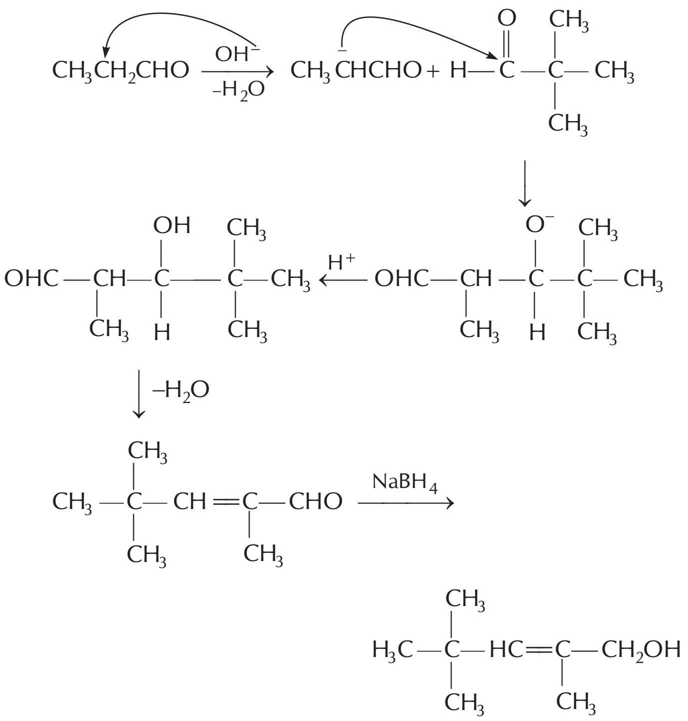
$CH_3-C(CH_3)_2-CH_2-CH(CH_3)-CH_2OH$

(*d*)



$CH_3-C(CH_3)_2-CH_2-CH_2CH_2OH$

Interpret (*b*) Aldol condensation takes place as,



Chemical Properties of Aldehydes

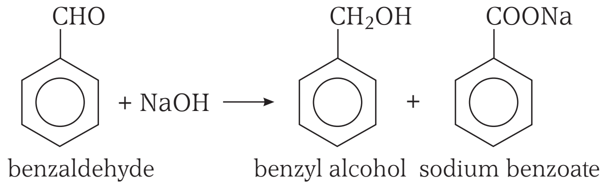
There are several reactions that are shown by aldehydes but not by ketones so these are helpful in differentiating the aldehydes from ketones.

(a) Cannizzaro Reaction

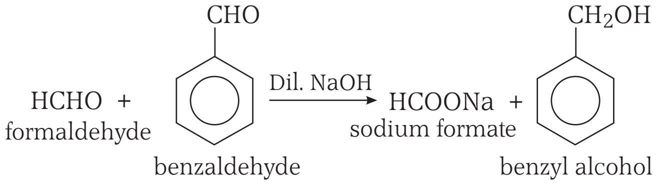
This reaction is given by aldehydes which do not have α-hydrogen atom. It is disproportionation

(self oxidation-reduction) reaction in which half of the molecules of aldehyde are oxidised and other half are reduced.

$$\underset{\text{formaldehyde}}{2HCHO} + NaOH \longrightarrow \underset{\text{methanol}}{CH_3OH} + \underset{\text{sodium formate}}{HCOONa}$$



In cross Cannizzaro reaction two different aldehydes which don't have alpha hydrogen atoms undergo Cannizzaro reaction.



HCHO being smaller molecule having lesser steric hindrance is easily oxidised and other aldehyde is reduced.

Caution Point *2-methylpropanal although has α-hydrogen atom but undergoes both aldol condensation and Cannizzaro reaction.*

(b) Tischenko Reaction

The reaction is similar to reaction (a) with certain differences, which are

(i) A weak base, *i.e.*, aluminium ethoxide is used here instead of alkali.

(ii) The reaction can be shown by any aldehyde (with or without α-hydrogen).

(iii) The final product of reaction is an **ester** instead of a carboxylic acid salt and an alcohol.

The reaction looks like

$$2CH_3CHO \xrightarrow{Al(OEt)_3} \underbrace{CH_3COOH + CH_3CH_2OH}_{\text{Combine to give}}$$

$$\downarrow$$

$$\text{Final products} \longrightarrow CH_3COOC_2H_5 + H_2O$$

(c) Action of Schiff's Reagent

Aldehydes restore the pink colour of Schiff's reagent (megenta or rosaniline hydrochloride dissolved in water and its red or pink colour decolourises by passing SO_2). while ketones do not respond to this test.

$$\text{Aldehyde} + \underset{\text{(colourless)}}{\text{Schiff's reagent}} \longrightarrow \text{pink colour}$$

(d) Polymerisation

HCHO polymerises as,

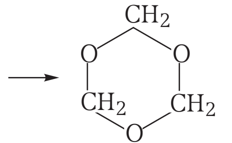
(i) Formalin evaporated to dryness

$$\longrightarrow \underset{\text{paraformaldehyde } (n = 5-60)}{HOCH_2(CH_2O)_nCH_2OH}$$

(ii) HCHO on treatment with conc. H_2SO_4

$$\longrightarrow \underset{\text{polyoxymethylene } (n > 100)}{(CH_2O)_n 2H_2O}$$

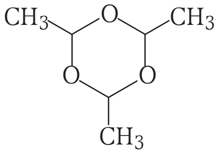
(iii) HCHO gas at room temperature slowly polymerises to



trioxane or metaformaldehyde

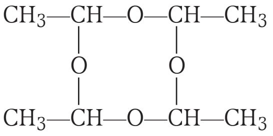
CH_3CHO polymerises as

(i) CH_3CHO + small amount of conc. $H_2SO_4 \xrightarrow[\text{temperature}]{\text{Room}}$



paraldehyde

(ii) CH_3CHO + conc. H_2SO_4 (small amount) $\xrightarrow{0°C}$



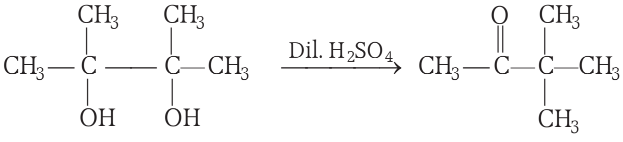
metaldehyde

Chemical Properties of Ketones

Ketones exhibit following reactions that are not shown by aldehydes.

(a) Pinacol-Pinacolone Rearrangement

This is the most common rearrangement involving the carbonyl compounds. The conversion of pinacol into pinacolone is an example of 1, 2-shift and is known as Pinacol-pinacolone rearrang ement.

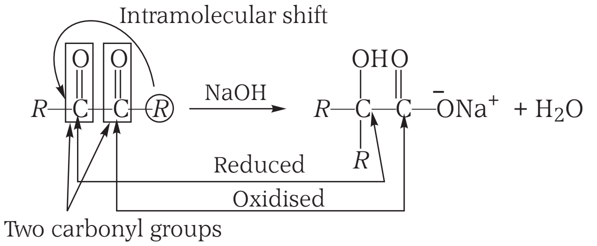


$$CH_3-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3 \xrightarrow{\text{Dil. } H_2SO_4} CH_3-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

The pinacol-pinacolone rearrangement is general for 1, 2-glycols under acid conditions, the migratory group may be alkyl or aryl.

(b) Benzilic Acid Rearrangement

The intramolecular Cannizzaro reaction type procedure when seen in the case of diketones, the reaction is called **benzilic acid rearrangement.** The reaction looks like

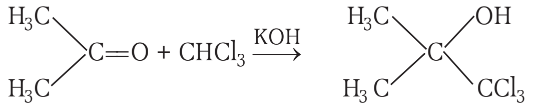


Here, the oxidation and reduction of carbonyl groups is associated with an intramolecular alkyl shift from the carbonyl group to be oxidised to the carbonyl group to be reduced as seen above.

It is seen that barium and thallous hydroxides are more effective than NaOH or KOH.

(c) Addition of Chloroform

Chloroform reacts with ketones in the presence of KOH to form chlorohydroxy condensation compounds.

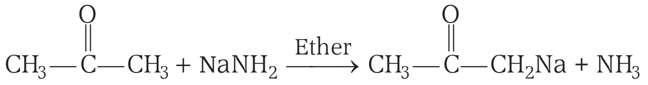


chloretone
(1,1,1-trichloro-2-methyl
propanol-2)

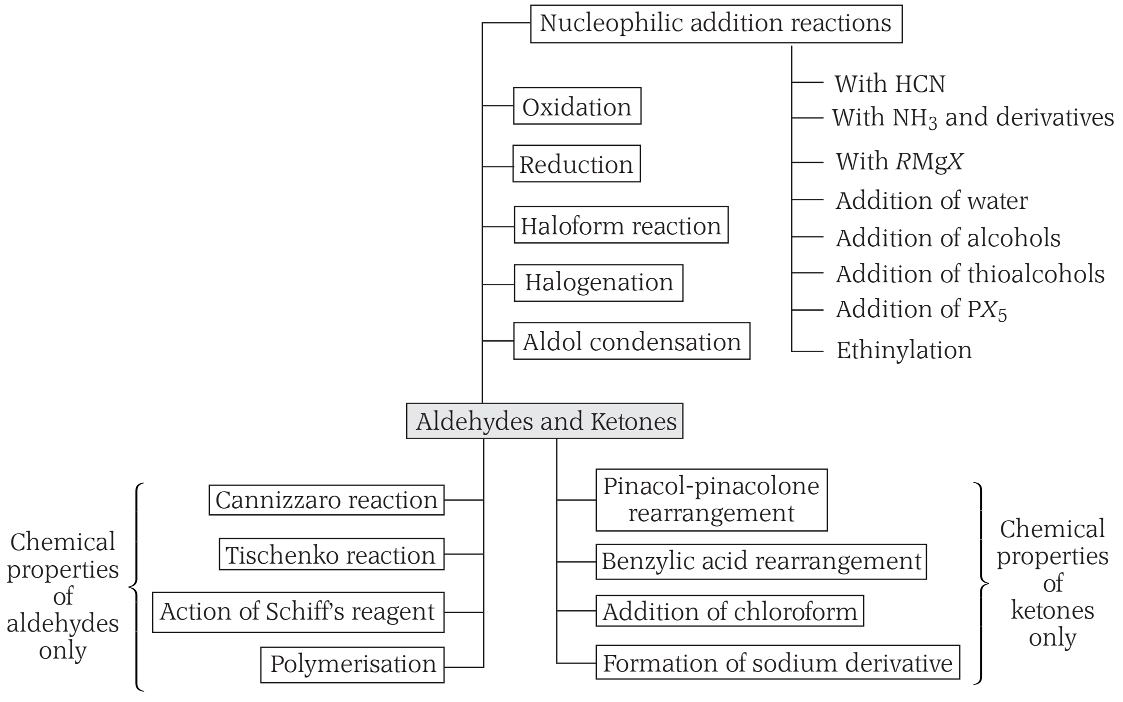
It is an hypnotic chemical.

(d) Formation of Sodium Derivative

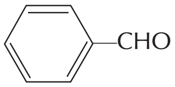
Ketones when treated with sodamide in ethereal solution, give sodium derivative of ketones.

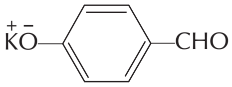


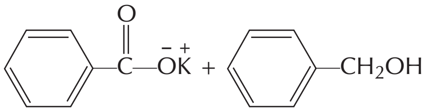
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + NaNH_2 \xrightarrow{\text{Ether}} CH_3-\overset{\overset{O}{\|}}{C}-CH_2Na + NH_3$$

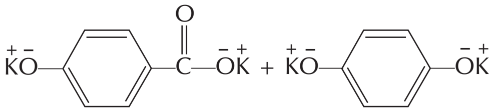


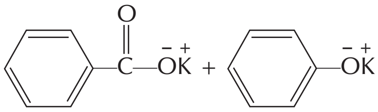
Flow chart showing reactions of aldehydes and ketones

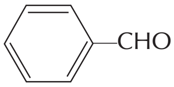
Sample **Problem 19** *Which product is formed when the compound*  *is treated with concentrated aqueous* KOH *solution?* [**NCERT** Exemplar]

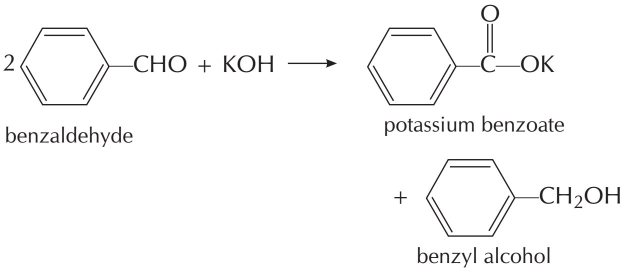
(*a*) 

(*b*) 

(*c*) 

(*d*) 

Interpret (*b*) Since,  does not contain α-H atom, so it will perform Cannizzaro reaction with aqueous KOH solution.



Sample **Problem 20** *Three of the following four reactions are due to one similar feature of carbonyl compounds, while the fourth one is different. Which one is fourth?*

(*a*) *Aldol condensation*

(*b*) *Knoevenagel reaction*

(*c*) *Wittig reaction*

(*d*) *Haloform reaction*

Interpret (*c*) Aldol condensation, haloform reaction and Knovenagel reaction involve the formation of a resonance stabilised anion, while the Wittig reaction involves the addition of a nucleophile on the carbonyl carbon. The driving force for the Wittig reaction is the formation of a very strong P—O bond.

Chemical Test to Distinguish Between Aldehydes and Ketones

Aldehydes and ketones can be distinguished by several tests which are tabulated below

Distinguision between Aldehydes and Ketones

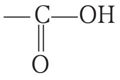
Name of test	Reagent	Aldehydes	Ketones
Tollen's test	Ammoniacal silver nitrate	Silver mirror (deposition of Ag on surface of test tube) formed	No change
Fehling's test	Alkaline solution of $CuSO_4$ containing Rochelle salt (sodium potassium tartarate.)	Red precipitate of Cu_2O. (only aliphatic aldehydes give this test)	No change
Benendict test	Alkaline solution of copper acetate and sodium citrate	Red precipitate of Cu_2O. (only aliphatic aldehydes give this test)	No change
Schiff's test	*p*-rosaniline hydrochloride	Pink colour	No change

Caution Point *Aromatic aldehydes do not reduce Fehling solution and Benedict solution because they are weak reagents.*

Check Point 4

1. Ketones are less reactive than aldehydes. Why?
2. How many type of products are formed when calcium formate is distilled with calcium acetate?
3. Justify the significance of pH on the nucleophilic addition of ammonia derivatives to carbonyl compounds.
4. What reagent the doctors used to detect diabetes disease by testing the presence of glucose in urine?
5. The presence of acid or base activates the carbonyl compounds for reaction. Explain.

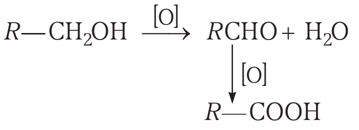
11.5 Carboxylic Acids

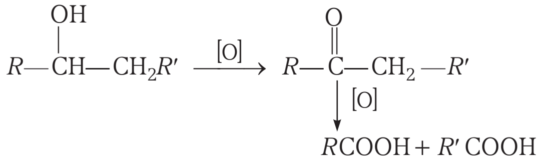
Organic compounds which contain carboxyl group (—COOH) are called **carboxylic acids.** The name carboxyl is derived from carbonyl and hydroxyl as  $—\underset{\underset{O}{\|}}{C}—OH$ contain both the group in it.

In other words, these are the carbonyl compounds in which acyl group is attached to an atom or group that can be easily replaced by another group. Acid derivatives also belongs to this class.

Preparation of Carboxylic Acids

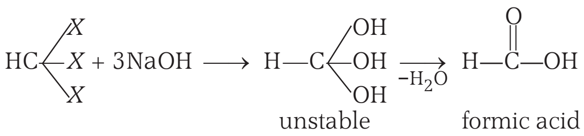
(i) Oxidation of alcohols, aldehydes and ketones yields carboxylic acids.



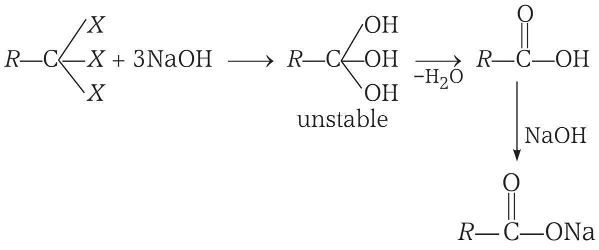


The oxidising agents are acidified $K_2Cr_2O_7$, alkaline $KMnO_4$, Tollen's reagent, Fehling's solution, Benedict's solution (the last 3- for aldehydes only).

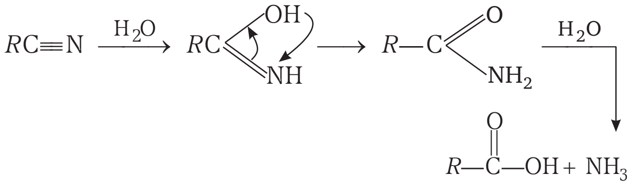
(ii) Haloform on aqueous alkali hydrolysis gives formic acid.



Trihaloderivatives of alkanes give, other carboxylic acids on aqueous alkali hydrolysis.

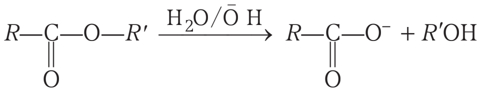


(iii) A very good synthetic method is the hydrolysis of cyanides with acid or alkali.



(iv) Hydrolysis of acid derivative

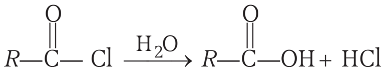
1. **Hydrolysis of ester**



$$R{-}\underset{\underset{O}{\|}}{C}{-}O{-}R' \xrightarrow{H_2O/\bar{O}H} R{-}\underset{\underset{O}{\|}}{C}{-}O^- + R'OH$$

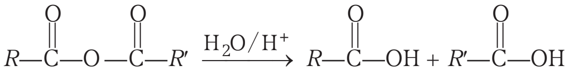
The alkaline hydrolysis is preferred for good yield as in the case of acidic hydrolysis the reaction is reversible.

2. **Hydrolysis of acid chloride**



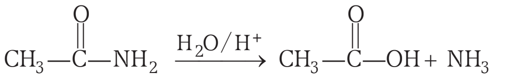
$$R{-}\overset{\overset{O}{\|}}{C}{-}Cl \xrightarrow{H_2O} R{-}\overset{\overset{O}{\|}}{C}{-}OH + HCl$$

3. **Hydrolysis of anhydride**



$$R{-}\overset{\overset{O}{\|}}{C}{-}O{-}\overset{\overset{O}{\|}}{C}{-}R' \xrightarrow{H_2O/H^+} R{-}\overset{\overset{O}{\|}}{C}{-}OH + R'{-}\overset{\overset{O}{\|}}{C}{-}OH$$

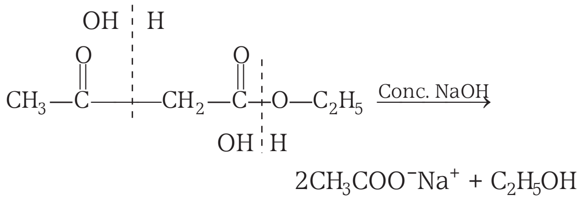
4. **Hydrolysis of amide**



$$CH_3{-}\overset{\overset{O}{\|}}{C}{-}NH_2 \xrightarrow{H_2O/H^+} CH_3{-}\overset{\overset{O}{\|}}{C}{-}OH + NH_3$$

Relative reactivity of acyl compounds towards hydrolysis is,

$$RCOCl > RCO{-}O{-}COR > RCOOR' > RCONH_2$$

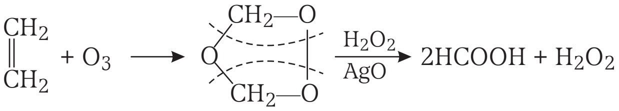
(v) 

$$CH_3{-}\overset{\overset{O}{\|}}{C}{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}O{-}C_2H_5 \xrightarrow{\text{Conc. NaOH}} 2CH_3COO^-Na^+ + C_2H_5OH$$

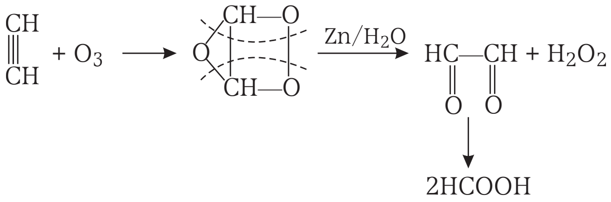
As reaction gives acid as its product that's why it is called acidic hydrolysis.

(vi) From alkenes

1. **Ozonolysis of alkenes**



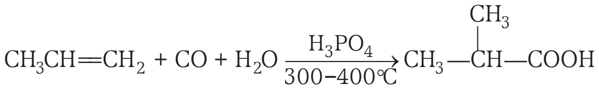
2. **Ozonolysis of alkynes**



3. The recent industrial method of making carboxylic acids looks like

$$CH_2{=}CH_2 + CO + H_2O \xrightarrow[300\text{–}400°C]{H_3PO_4} CH_3CH_2COOH$$

This reaction involves the electrophilic addition of H^+ ion on the alkene to produce more stable carbocation followed by the attack of CO as nucleophile.



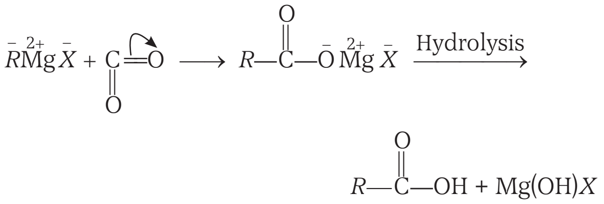
$$CH_3CH{=}CH_2 + CO + H_2O \xrightarrow[300\text{–}400°C]{H_3PO_4} CH_3{-}\overset{\overset{CH_3}{|}}{C}H{-}COOH$$

Formic acid cannot be prepared by this reaction.

(vii) From phenoxide

$$R\bar{O}\,Na^+ + CO \xrightarrow[\text{under pressure}]{\Delta} RCOO^-Na^+ \xrightarrow{H_2O/H^+} RCOOH$$

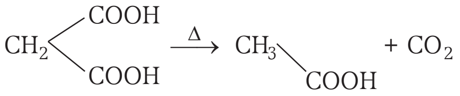
(viii) From Grignard's reagent



$$\bar{R}\overset{2+}{Mg}\bar{X} + \overset{O}{\overset{\|}{C}}{=}O \longrightarrow R-\overset{O}{\overset{\|}{C}}-\bar{O}\,\overset{2+}{Mg}\,\bar{X} \xrightarrow{\text{Hydrolysis}} R-\overset{O}{\overset{\|}{C}}-OH + Mg(OH)X$$

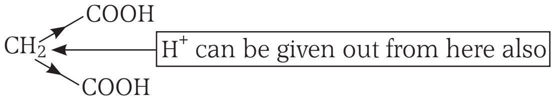
(ix) **From dicarboxylic acid** Malonic acid is β-acid and very useful in the preparation of different carboxylic acids due to its 2 main properties

1. It is decarboxylated very easily on heating as,



$$CH_2(COOH)_2 \xrightarrow{\Delta} CH_3COOH + CO_2$$

2. Due to $-I$ effect of —COOH group, H^+ can also be eliminated from —CH_2 group *i.e.,*



(x) Oxidative cleavage of alkenes and alkynes also gives carboxylic acid.

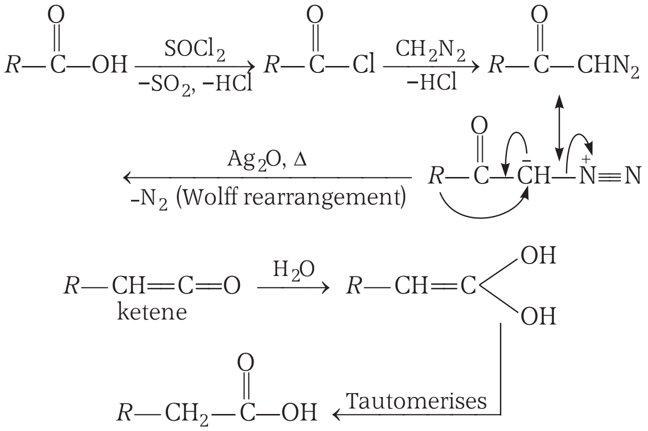
$$R-CH=CH-R' \xrightarrow[\text{(hot, conc)}]{KMnO_4} RCOOH + R'COOH$$

$$CH_3-C\equiv CH \xrightarrow[\text{(hot, conc)}]{KMnO_4} CH_3COOH + HCOOH$$

(xi) Long chain hydrocarbons are oxidised by air at 120°C in the presence of manganous sterate (catalyst).

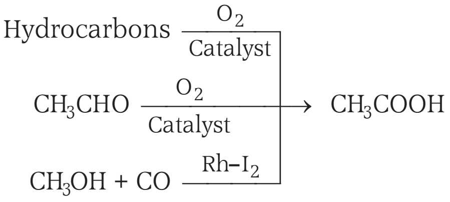
$$\underset{\text{higher alkanes}}{2RCH_3} + 3O_2 \longrightarrow \underset{\text{fatty acid}}{2\ RCOOH} + 2H_2O$$

(xii) The conversion of an acid (RCOOH) into its next higher homologue (RCH$_2$COOH) is called homologation of an acid and carried out by Arndt Eistert synthesis.



$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[-SO_2,\ -HCl]{SOCl_2} R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[-HCl]{CH_2N_2} R-\overset{O}{\overset{\|}{C}}-CHN_2 \longleftrightarrow R-\overset{O}{\overset{\|}{C}}-\overset{-}{C}H-\overset{+}{N}\equiv N \xrightarrow[-N_2\ \text{(Wolff rearrangement)}]{Ag_2O,\ \Delta} \underset{\text{ketene}}{R-CH=C=O} \xrightarrow{H_2O} R-CH=C(OH)_2 \xrightarrow{\text{Tautomerises}} R-CH_2-\overset{O}{\overset{\|}{C}}-OH$$

(xiii) Acetic acid is the most important carboxylic acid, prepared by the following methods



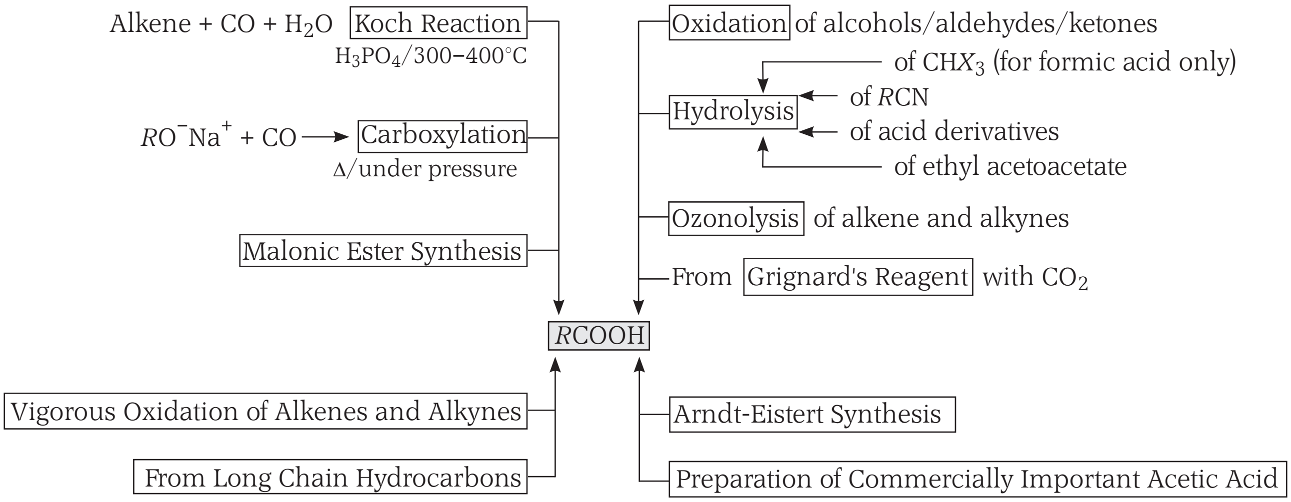
$$\text{Hydrocarbons} \xrightarrow[\text{Catalyst}]{O_2} CH_3COOH$$

$$CH_3CHO \xrightarrow[\text{Catalyst}]{O_2} CH_3COOH$$

$$CH_3OH + CO \xrightarrow{Rh-I_2} CH_3COOH$$

Large amount of acetic acid is produced from oxidation of ethyl alcohol in the presence of aceto-bacter bacteria. This dilute aqueous solution is known as **vinegar**.

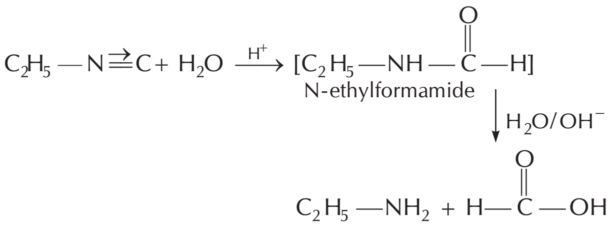
The outline of their methods of preparation looks like



Sample **Problem 21** *Ethyl isocyanide on acidic hydrolysis generates*

(*a*) *ethylamine salt and methanoic acid*
(*b*) *propanoic acid and ammonium salt*
(*c*) *ethanoic acid and ammonium salt*
(*d*) *methyl amine salt and ethanoic acid*

Interpret (*a*)



$$C_2H_5{-}N\overset{\rightarrow}{=}C + H_2O \xrightarrow{H^+} [C_2H_5{-}NH{-}\overset{O}{\overset{\|}{C}}{-}H] \xrightarrow{H_2O/OH^-} C_2H_5{-}NH_2 + H{-}\overset{O}{\overset{\|}{C}}{-}OH$$

N-ethylformamide

Sample **Problem 22** *With the help of following Grignard synthesis which carboxylic acid is formed?*

$$CH_2{=}CHCH_2Br \xrightarrow{Mg/ether} \xrightarrow[(ii)\ H_3O^+]{(i)\ CO_2}$$

(*a*) $CH_2{=}CHCH_2COOH$ (*b*) $CH_3CH_2CH_2COOH$
(*c*) $CH_2{=}CHCOOH$ (*d*) $CH_3CH{=}CH{-}COOH$

Interpret (*a*)

$$CH_2{=}CHCH_2Br \xrightarrow{Mg\ /\ ether} CH_2{=}CHCH_2MgBr \xrightarrow{(i)\ CO_2} CH_2{=}CHCH_2COOMgBr \xrightarrow[-Mg\,(OH)\,Br]{H_3O^+} CH_2{=}CHCH_2COOH$$

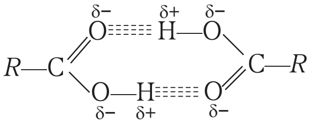
Physical Properties

(i) First three members of this series are colourless, pungent smelling liquids. C_4—C_9 are oily liquids.

(ii) Carboxylic acids exist in the form of dimer due to hydrogen bonding.

(iii) **Solubility** of carboxylic acids in water decreases due to increase in size of hydrophobic hydrocarbon part. Lower carboxylic acids having upto four carbon atoms are miscible in water due to the formation of hydrogen bonds with water.

(iv) **Boiling point** of carboxylic acids is higher than those of hydrocarbons, aldehydes, ketones and alcohols of comparable molecular masses due to intermolecular H-bonding as shown in the figure.



(v) **Melting points** of carboxylic acids increase with increase in their molecular mass. The melting point of an acid with even number of carbon atom is higher than the next lower and next higher homologue containing odd number of carbon atoms.

Hot Spot 4

ACIDIC Strength of Carboxylic Acids

It is an important topic for JEE Main examination. From this topic, questions based upon strength of different acids are asked.

Carboxylic acids are acidic in nature but they are weaker acids than mineral acids but stronger acids than phenols (because the carboxylate ion is more stabilised as compared to phenoxide ion).

The carboxylic acids liberate hydrogen on reaction with electropositive metals like sodium. They form salts with alkalies.

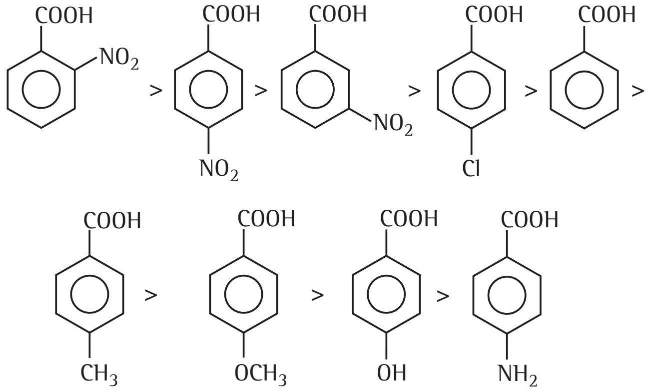
Strength of acid is indicated by pK_a value. Higher the value of K_a or lower the value of pK_a, stronger is the acid.

Aromatic acids are more acidic than aliphatic acids.

Effect of substituent on acidity of aromatic carboxylic acids. Electron donating groups decrease the acidity and electron withdrawing groups increase the acidity of carboxylic acids.

$HCOOH > CH_3COOH > (CH_3)_2CHCOOH > (CH_3)_3COOH$
$Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH > CH_3COOH$
$CH_3CH_2CHClCOOH > CH_3CHClCH_2COOH > ClCH_2CH_2CH_2COOH$
$CF_3COOH > CCl_3COOH > CHCl_2COOH > NO_2CH_2COOH$
$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > HCOOH$

Among substituted aromatic acids the strength decreases as follows



***Ortho* effect** The effect of a group is maximum at *ortho* position due to nearness. It is called *ortho* effect.

Sample **Problem 23** *Choose the correct order of strength of following acids* [**NCERT**]

(*I*) $CH_3CH_2CH_2COOH$ (*II*) $CH_3CH_2CH(Br)COOH$

(*III*) $CH_3CH(Br)CH_2COOH$ (*IV*) $(CH_3)_2CHCOOH$

(a) $I < II < III < IV$ (b) $IV < I < III < II$

(c) $IV < III < I < II$ (d) $II < I < III < IV$

Interpret (*b*) Alkyl group with +*I* effect decreases the acidic strength whereas with –*I* effect increases the acidic strength. –*I* effect decreases with distance.

∴**Increasing order of acidic strength is**

$$(CH_3)_2CHCOOH < CH_3CH_2CH_2COOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$$

Sample **Problem 24** *Which of the following represents the correct order of the activity in the given compounds?*

(a) $CH_3COOH > BrCH_2COOH > ClCH_2COOH > FCH_2COOH$

(*b*) $FCH_2COOH > CH_3COOH > BrCH_2COOH > ClCH_2COOH$

(c) $BrCH_2COOH > ClCH_3COOH > FCH_2COOH > CH_3COOH$

(*d*) $FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH$

Interpret (*d*) The acidity of halogenated acid increases almost proportionately with the increase in electronegativity of the halogen present. Therefore, the correct order is

$$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH$$

Chemical Properties

Carboxylic acids exhibit following characteristic properties.

Reactions of Carboxyl Group

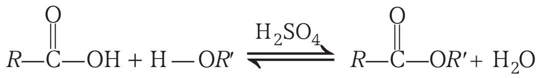
(i) **With alkalies and carbonates** Carboxylic acids react with bases to form ionic salts with pronounced ionic characters and are soluble in water.

$$2RC^{14}OOH + NaHCO_3 \longrightarrow RC^{14}OONa + CO_2 + H_2O$$
$$2RC^{14}OOH + Na_2CO_3 \longrightarrow 2RC^{14}OONa + CO_2 + H_2O$$
$$RCOOH + NaOH \longrightarrow RCOONa + H_2O$$
$$2RCOOH + CaO \longrightarrow (RCOO)_2Ca + H_2O$$
$$RCOOH + AgOH \longrightarrow RCOOAg + H_2O$$

(ii) **With metals** The reaction looks like,

$$2RCOOH + 2Na \longrightarrow 2RCOONa + H_2\uparrow$$
$$2RCOOH + Zn \longrightarrow (RCOO)_2Zn + H_2\uparrow$$

(iii) **Esterification** Carboxylic acids react with alcohols in the presence of conc H_2SO_4 to form ester.

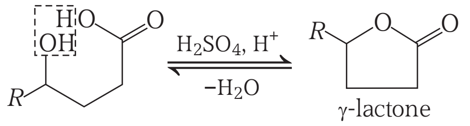


$$R—\overset{O}{\overset{\|}{C}}—OH + H—OR' \xrightleftharpoons{H_2SO_4} R—\overset{O}{\overset{\|}{C}}—OR' + H_2O$$

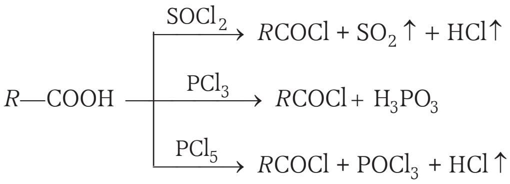
The order of reactivity follows the sequence,

$$HCOOH > CH_3COOH > (CH_3)_2COOH > (CH_3)_3CCOOH$$
$$CH_3OH > CH_3CH_2OH > (CH_3)_2CHOH > (CH_3)_3COH$$

γ or δ hydroxy carboxylic acids undergo an intramolecular esterification to give cyclic ester-lactones.



(iv) **With $SOCl_2$, PCl_3 and PCl_5** Acyl halides are formed.



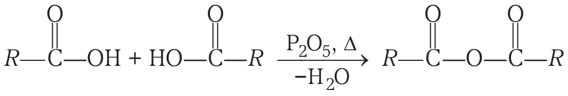
$$R—COOH \xrightarrow{SOCl_2} RCOCl + SO_2\uparrow + HCl\uparrow$$
$$R—COOH \xrightarrow{PCl_3} RCOCl + H_3PO_3$$
$$R—COOH \xrightarrow{PCl_5} RCOCl + POCl_3 + HCl\uparrow$$

$SOCl_2$ is preferred over other two reagents, because SO_2 and HCl escape the reaction mixture (as these are gases) and make the purification of product easier.

(v) **With NH_3** The reaction looks like,

$$RCOOH + NH_3 \longrightarrow RCOO^-NH_4^+ \xrightarrow{Heat} RCONH_2 + H_2O$$

(vi) **Dehydration** The reaction proceeds as,



$$R—\overset{O}{\overset{\|}{C}}—OH + HO—\overset{O}{\overset{\|}{C}}—R \xrightarrow[-H_2O]{P_2O_5,\ \Delta} R—\overset{O}{\overset{\|}{C}}—O—\overset{O}{\overset{\|}{C}}—R$$

(vii) **Decarboxylation** Salts of carboxylic acid on heating with sodalime (NaOH and CaO) undergo decarboxylation to produce alkanes.

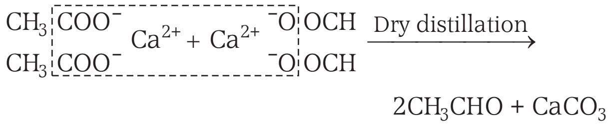
$$RCOONa + NaOH \longrightarrow R—H + Na_2CO_3$$

(viii) **Kolbe's electrolysis** The aqueous solution of sodium or potassium salts of carboxylic acids on electrolysis gives alkanes.

$$2RCOONa + H_2O \xrightarrow{Electrolysis} \underbrace{R—R + 2CO_2}_{anode} + \underbrace{2NaOH + H_2}_{cathode}$$

(ix) The Ca salts of carboxylic acids gives carbonyl compounds on dry distillation.

$$\boxed{\begin{matrix} CH_3CO\boxed{O^-} \\ CH_3\boxed{COO^-} \end{matrix} Ca^{2+}} \xrightarrow{\text{Dry distillation}} CH_3—\overset{O}{\overset{\|}{C}}—CH_3 + CaCO_3$$



$$\begin{array}{l} CH_3\,COO^- \quad Ca^{2+} + Ca^{2+} \quad {}^-O\,OCH \\ CH_3\,COO^- \qquad\qquad\qquad\quad {}^-O\,OCH \end{array} \xrightarrow{\text{Dry distillation}} 2CH_3CHO + CaCO_3$$

(x) **Borodine-Hunsdiecker reaction** The silver salts of carboxylic acids upon treatment with Br_2/CCl_4 give alkyl bromide.

$$RCOOAg + Br_2 \xrightarrow{CCl_4} RBr + CO_2\uparrow + AgBr\downarrow$$

The silver salts of carboxylic acids on treatment with I_2/ether form esters. (Birnbaum-Simonini reaction).

$$2RCOOAg + I_2 \xrightarrow{\text{Ether}} RCOOR + CO_2\uparrow + 2AgI\downarrow$$

(xi) 1. **Reduction to alkanes**

$$RCOOH + 6HI \xrightarrow[\Delta]{\text{Red P}} R{-}CH_3 + 2H_2O + 3I_2$$

2. **Reduction to alcohols**

$$RCOOH \xrightarrow[\text{(ii) } H_3O^+,\ H^+]{\text{(i) } LiAlH_4/\text{ether}} RCH_2OH$$

3. **Reduction to aldehydes and ketones**

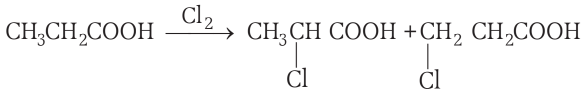
$$\underbrace{HCO\boxed{OH + HCOO}H}_{\text{vapour phase}} \xrightarrow[\Delta]{MnO} HCHO + CO_2 + H_2O$$

$$\underbrace{CH_3CO\boxed{OH + HOOC}CH_3}_{\text{vapour phase}} \xrightarrow[\Delta]{MnO} CH_3COCH_3 + CO_2 + H_2O$$

(xii) **Schmidt reaction** Reaction proceeds as,

$$RCOOH + N_3H \xrightarrow[\Delta]{H_2SO_4} RNH_2 + N_2\uparrow + CO_2\uparrow$$

(xiii) **Halogenation** In monocarboxylic acid bromination takes place only at the α-position, but chlorination may also takes place further in the chain.

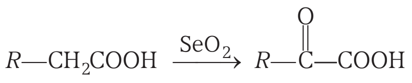


$$CH_3CH_2COOH \xrightarrow{Cl_2} CH_3\underset{\displaystyle Cl}{\underset{|}{CH}}\ COOH + \underset{\displaystyle Cl}{\underset{|}{CH_2}}\ CH_2COOH$$

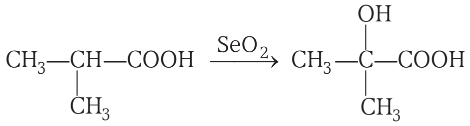
(xiv) **Oxidation**

1. All acids, except formic acid are resistance to oxidation. On prolonged heating, with powerful oxidising agent ($KMnO_4$) they results in CO_2 and H_2O.

$$HCOOH \xrightarrow{SeO_2} CO_2 + H_2O$$

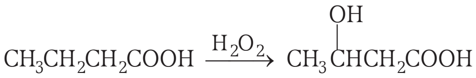


$$R{-}CH_2COOH \xrightarrow{SeO_2} R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}COOH$$



$$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}COOH \xrightarrow{SeO_2} CH_3{-}\overset{\displaystyle OH}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}COOH$$

2. With mild oxidising agent such as H_2O_2, they are oxidised to β-hydroxy acids.

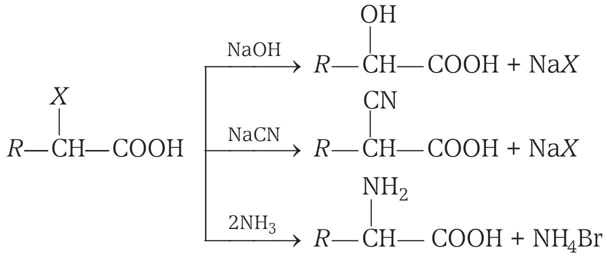


$$CH_3CH_2CH_2COOH \xrightarrow{H_2O_2} CH_3\overset{\displaystyle OH}{\overset{|}{C}}HCH_2COOH$$

(xv) **Hell-Volhard Zelinsky Reaction** α-hydrogen of a carboxylic acid can be replaced by halogen using red phosphorus.

$$R{-}CH_2COOH + X_2 \xrightarrow{\text{Red P}} R{-}\overset{\displaystyle X}{\overset{|}{C}}H{-}COOH$$

α-halogenated acids are infact good starting material for preparing other α-substituted acids as



$$R{-}\overset{\displaystyle X}{\overset{|}{C}}H{-}COOH \xrightarrow{NaOH} R{-}\overset{\displaystyle OH}{\overset{|}{C}}H{-}COOH + NaX$$

$$R{-}\overset{\displaystyle X}{\overset{|}{C}}H{-}COOH \xrightarrow{NaCN} R{-}\overset{\displaystyle CN}{\overset{|}{C}}H{-}COOH + NaX$$

$$R{-}\overset{\displaystyle X}{\overset{|}{C}}H{-}COOH \xrightarrow{2NH_3} R{-}\overset{\displaystyle NH_2}{\overset{|}{C}}H{-}COOH + NH_4Br$$

Caution Points *The first member of series, i.e.,* HCOOH *is unique and different from rest in many aspects, i.e.,*

(*i*) *It decolourises* $KMnO_4$,

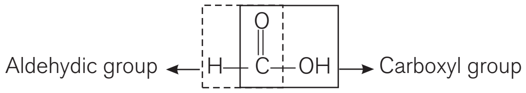
(*ii*) *Gives positive tests with Tollen's reagent (silver mirror) and Fehling's solution,*

(*iii*) *Reduces mercuric chloride to mercurous chloride which is further converted to grey precipitate of mercury.*

$$HCOOH + 2HgCl_2 \longrightarrow CO_2 + Hg_2Cl_2\downarrow + 2HCl$$

$$HCOOH + Hg_2Cl_2 \longrightarrow CO_2 + 2Hg\downarrow + 2HCl$$

Thus, it is the only monocarboxylic acid which can oxidise easily. The abnormal behaviour of formic acid is due to the presence of aldehydic group.



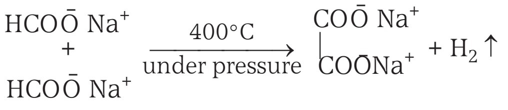
Its boiling point is 373.5 K (H_2O – 373K).

Action of heat

$$HCOOH \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} H_2O + CO_2\uparrow$$

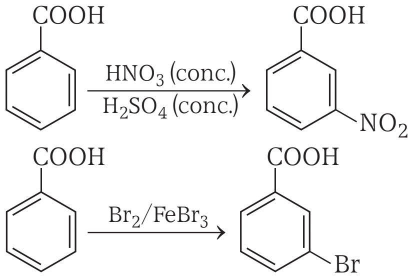
$$HCOOH \longrightarrow CO_2\uparrow + H_2\uparrow$$

Its Na or K salt on heating under pressure at about 400°C produces sodium or potassium salt of oxalic acid. H_2 is liberated in the process as



$$\begin{array}{c} HCO\bar{O}\ Na^+ \\ + \\ HCO\bar{O}\ Na^+ \end{array} \xrightarrow[\text{under pressure}]{400^\circ C} \begin{array}{l} CO\bar{O}\ Na^+ \\ | \\ CO\bar{O}Na^+ \end{array} + H_2\uparrow$$

(xvi) **Electrophilic substitution reaction** Aromatic carboxylic acids undergo electrophilic substitution reaction —COOH group shows –*R* effect, therefore acts as a deactivating and *meta*-directing group. Carboxylic acids do not undergo Friedel-Crafts reaction because the carboxylic group is deactivating and the catalyst $AlCl_3$ (anhyd) gets bonded to the carboxylic group.



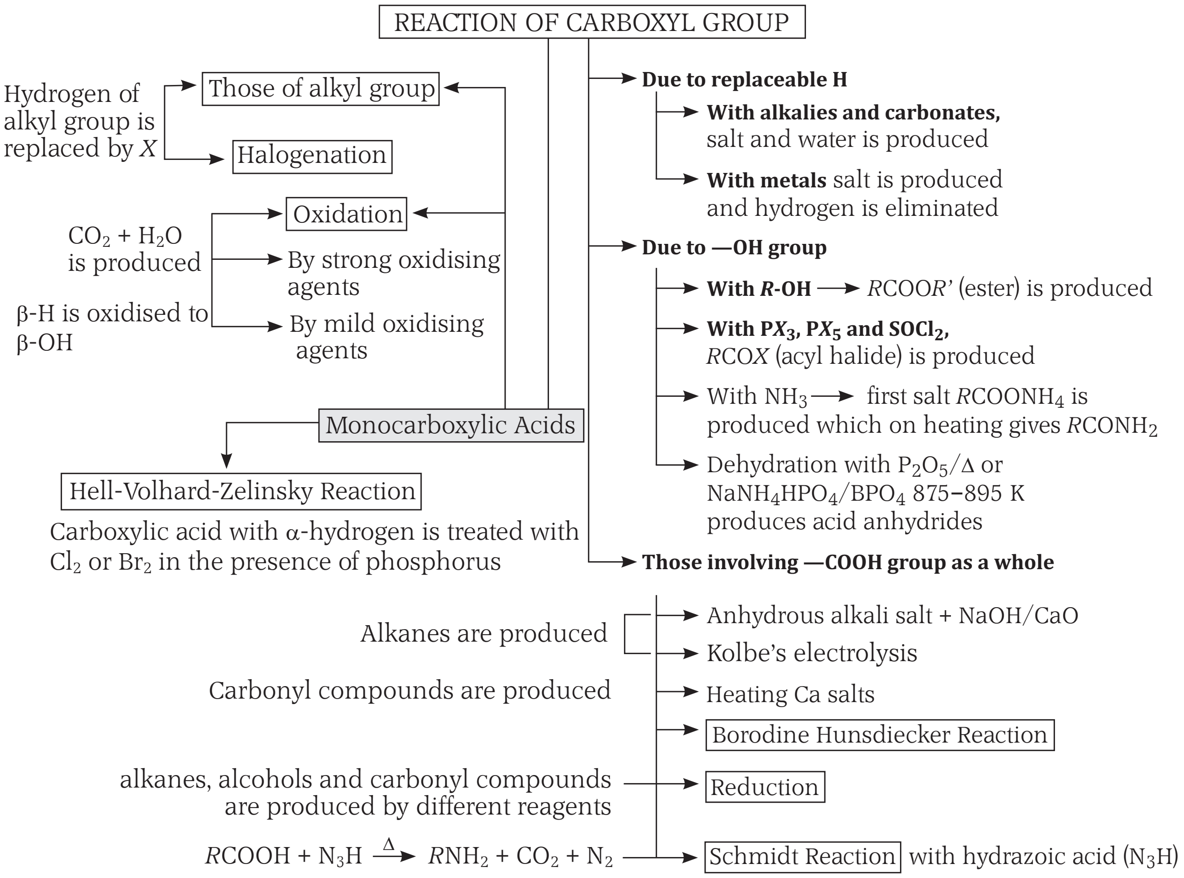
Uses of Carboxylic acids

(i) Formic acid is used in leather tanning, textile dyeing and finishing.

(ii) Acetic acid is used in the manufacture of rayon and in plastics, rubber and silk industries and in cooking.

(iii) Benzoic acid and its salts are used as urinary antiseptics.

The outline of the chemical properties of carboxylic acids looks like



WORKED **OUT**

Examples

Example 1 *An alcohol on oxidation is found to give* CH_3COOH *and* CH_3CH_2COOH. *The structure of the alcohol is*

(*a*) $CH_3CH_2CH_2OH$ (*b*) $CH_3(CH_2)_3CH_2OH$

(*c*) $CH_3CHOHCH_2CH_3$ (*d*) $(CH_3)_2C(OH)CH_2CH_3$

Solution (*c*) $CH_3CHOHCH_2CH_3 \xrightarrow{[O]} CH_3COCH_2CH_3 \xrightarrow{[O]} CH_3COOH + CH_3CH_2COOH$

Example 2 *Which of the following can't be made by using Williamson's synthesis?*

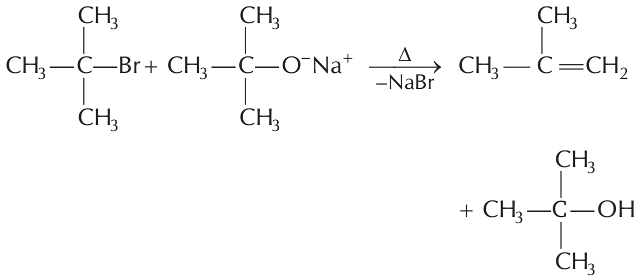
(*a*) *Di-tert-butyl ether*

(*b*) *Methoxybenzene*

(*c*) *Benzyl p-nitrophenyl ether*

(*d*) *Methyl tertiary butyl ether*

Solution (*a*) Di-*tert*-butyl ether can't be made by Williamson's synthesis, since *tert*-alkyl halides prefer to undergo elimination rather than substitution, *i.e.*,



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O^-Na^+ \xrightarrow[-NaBr]{\Delta} CH_3-\overset{CH_3}{C}=CH_2 + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH$$

Example 3 *Phenol on reaction with* Br_2 *in non-polar aprotic solvent furnishes*

(*a*) *p-bromophenol* (*b*) *m-bromophenol*

(*c*) *o/p-bromophenol* (*d*) *2,4,6-tribromophenol*

Solution (*c*) In the presence of non-polar aprotic solvents such as $CHCl_3$, CCl_4 etc., Br_2 reacts with phenol to give a mixture of *o*-and *p*-bromophenol.

Example 4 *An organic compound* (*X*) *with* Na *gives* (*Y*) *and with* PCl_5 *gives* (*Z*). (*Y*) *and* (*Z*) *react together to form diethyl ether. The compounds* (*X*), (*Y*) *and* (*Z*) *respectively are*

(*a*) C_2H_5Cl, C_2H_6 *and* C_2H_5OH

(*b*) C_2H_5OH, C_2H_5ONa *and* C_2H_5Cl

(*c*) C_2H_5OH, C_2H_5Cl *and* C_2H_5ONa

(*d*) C_2H_5OH, C_2H_6 *and* C_2H_5Cl

Solution (*b*)

$$\begin{tikzcd} \underset{(X)}{C_2H_5OH} \arrow[r, "PCl_5"'] \arrow[d, "Na"] & \underset{(Z)}{C_2H_5Cl} + POCl_3 + HCl \\ \underset{(Y)}{C_2H_5ONa} & \end{tikzcd}$$

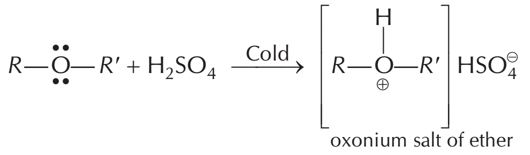
$$\underset{(Y)}{C_2H_5ONa} + \underset{(Z)}{ClC_2H_5} \longrightarrow C_2H_5-O-C_2H_5 + NaCl$$

Example 5 *An ether reacts with cold* H_2SO_4 *to give*

(*a*) *a Zwitter ion* (*b*) *an oxonium ion*

(*c*) *an oxy anion* (*d*) *an alkyl free radical*

Solution (*b*)



$$R-\ddot{\underset{\cdot\cdot}{O}}-R' + H_2SO_4 \xrightarrow{\text{Cold}} \underset{\text{oxonium salt of ether}}{\left[R-\underset{\oplus}{\overset{H}{O}}-R'\right]HSO_4^{\ominus}}$$

Example 6 *Which of the following will not be formed when calcium acetate is distilled with calcium formate?*

(a) *Acetone* (b) *Propanal*

(c) *Ethanal* (d) *Methanal*

Solution (*b*) Propanal will not be formed while all the other three will be formed as shown below

$$\underset{\text{calcium formate}}{(HCOO)_2Ca} \xrightarrow[-CaCO_3]{\Delta} \underset{\text{methanal}}{HCHO}$$

$$(CH_3COO)_2Ca \xrightarrow[-CaCO_3]{\Delta} \underset{\text{acetone}}{CH_3COCH_3}$$

$$(CH_3COO)_2Ca + (HCOO)_2Ca \xrightarrow[-2CaCO_3]{} \underset{\text{ethanal}}{2CH_3CHO}$$

Example 7 *Reagent used for the oxidation of allyl alcohol to acrolein is*

(a) $KMnO_4$ (*b*) H_2O_2

(c) *active* MnO_2 (*d*) OsO_4

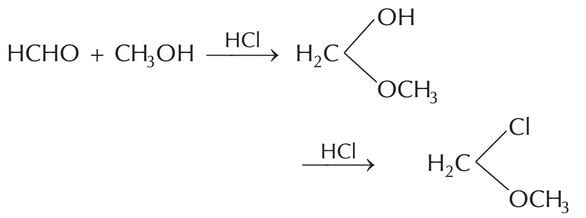
Solution (c) Active MnO_2 is a mild oxidising agent and is used for oxidation of allylic alcohol to the corresponding aldehydes.

$$\underset{\text{allyl alcohol}}{CH_2=CH-CH_2OH} \xrightarrow[MnO_2]{\text{Active}} \underset{\text{acrolein}}{CH_2=CH-CHO}$$

Example 8 *When methanol reacts with formaldehyde in the presence of excess of* HCl*, the product is*

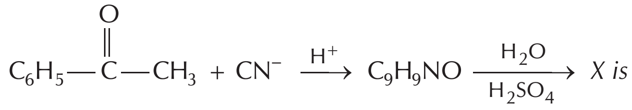
(*a*) $CH_2(OCH_3)_2$ (*b*) CH_2Cl_2
(*c*) CH_3OCH_2OH (*d*) CH_3OCH_2Cl

Solution (*d*) With the excess of methanol, acetal is formed but with excess of HCl, α-chloroethers are formed,



methoxy methyl chloride

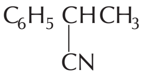
Example 9 *The product X in the reaction*



$$C_6H_5-\overset{O}{\overset{\|}{C}}-CH_3 + CN^- \xrightarrow{H^+} C_9H_9NO \xrightarrow[H_2SO_4]{H_2O} X \text{ is}$$

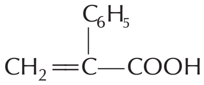
(*a*) $C_6H_5CH_2COOCH_3$

(*b*)



$C_6H_5\underset{CN}{\underset{|}{C}H}CH_3$

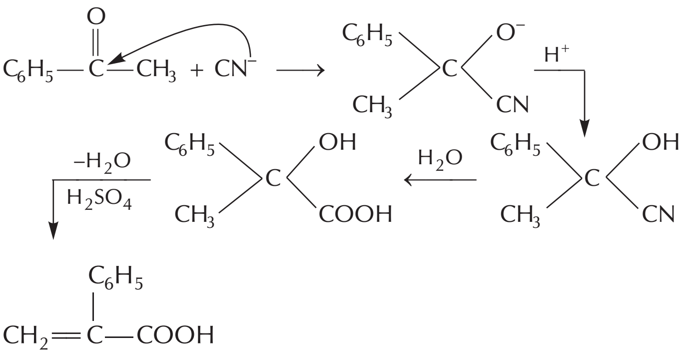
(*c*)



$CH_2=\overset{C_6H_5}{\overset{|}{C}}-COOH$

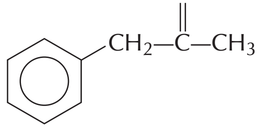
(*d*) $C_6H_5CH=CHCOOH$

Solution (*c*) The reaction proceeds as,

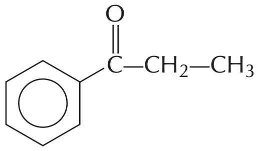


Example 10 *An organic compound (A) with molecular formula* $C_9H_{10}O$ *forms an orange-red precipitate with 2,4-DNP reagent and gives yellow precipitate on heating with iodine and* NaOH. *It does not reduce Tollen's reagent or Fehling's solution nor it decolourises bromine water as Baeyer's reagent. On drastic oxidation with chromic acid, it gives a carboxylic acid having molecular formula* $C_7H_6O_2$. *Identify the compound (A).*

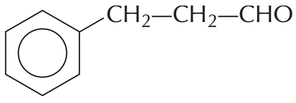
(*a*)



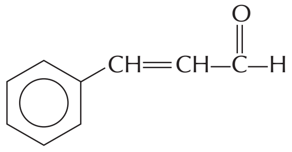
(*b*)



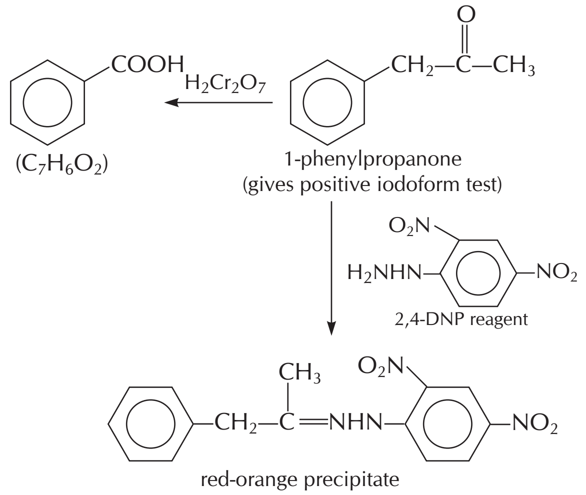
(*c*)



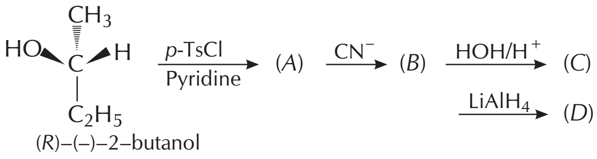
(*d*)



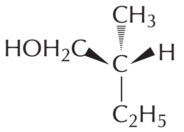
Solution (*a*)



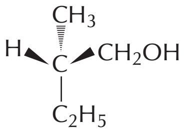
Example 11 *Give stereochemical formula for compound (D)*



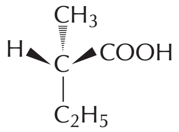
(a)



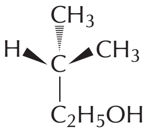
(*b*)



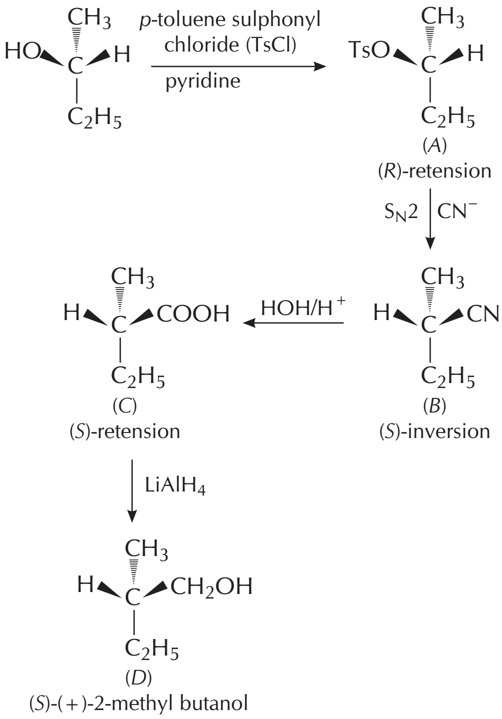
(*c*)



(*d*)



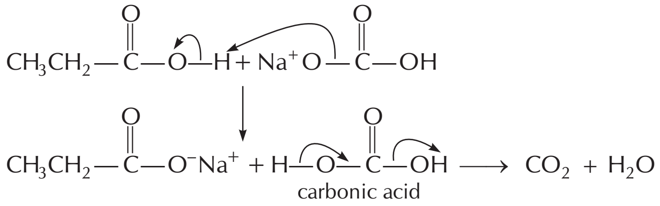
Solution (*b*)



Example 12 *When propionic acid is treated with aqueous sodium bicarbonate, CO_2 is liberated. The C from CO_2 comes from*

(*a*) methyl group
(*b*) carboxylic acid group
(*c*) methylene group
(*d*) bicarbonate

Solution (*d*) Carboxylic acids reacts with weaker bases such as bicarbonates producing CO_2. The CO_2 evolved comes from $NaHCO_3$, not from carboxylic group as shown below

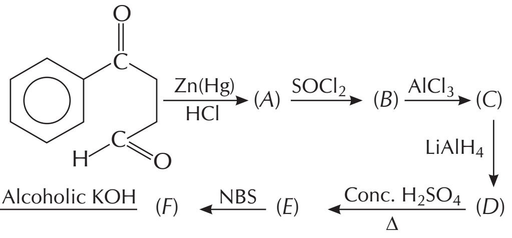


$$CH_3CH_2-\overset{O}{\overset{\|}{C}}-O-H + Na^+\,O-\overset{O}{\overset{\|}{C}}-OH$$

$$CH_3CH_2-\overset{O}{\overset{\|}{C}}-O^-Na^+ + H-O-\overset{O}{\overset{\|}{C}}-OH \longrightarrow CO_2 + H_2O$$

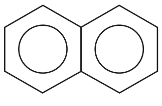
carbonic acid

Example 13

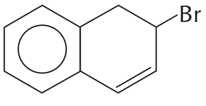


Show the final product of the reaction.

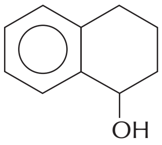
(*a*)



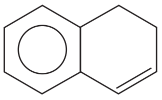
(*b*)



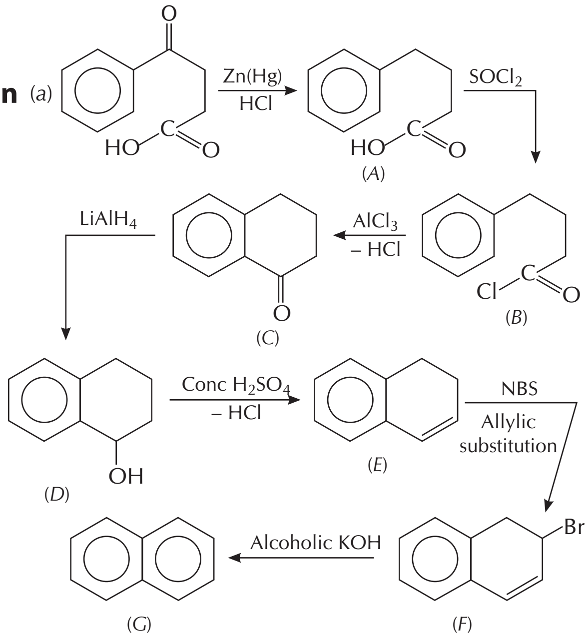
(*c*)



(*d*)



Solution (*a*)

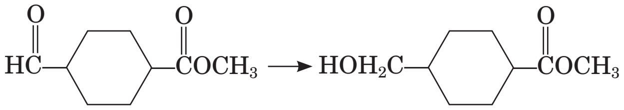


Start Practice for JEE Main

Round I (Topically Divided Problems)

Alcohols

1. The reduction,



can be achieved by using

(a) $NaBH_4$ (b) $LiAlH_4$

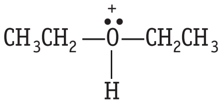
(c) $CuO \cdot CuCN_2O_4$ (d) None of these

2. The reaction,

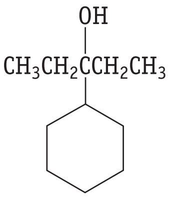
$$2CH_3CH_2OH \xrightarrow[413\ K]{H^+} CH_3CH_2OCH_2CH_3$$

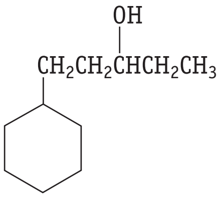
is believed to occur through the formation of

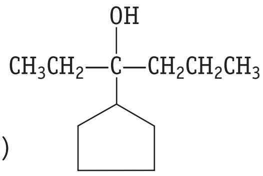
(a) $CH_3CH_2\overset{+}{O}H_2$ (b) $CH_3\overset{+}{C}H_2$

(c)  $CH_3CH_2-\underset{H}{\overset{+}{\ddot{O}}}-CH_2CH_3$ (d) Both (b) and (c)

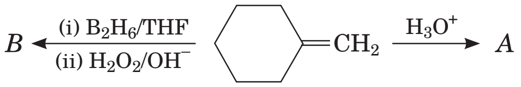
3. Which of the following structure is represented by 3-cyclohexylpentan-3-ol? [NCERT]

(a) 

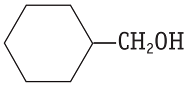
(b) 

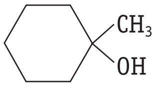
(c) 

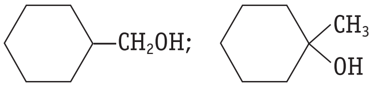
(d) None of these

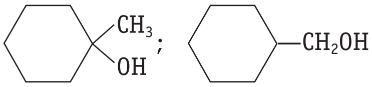
4. 

A and *B* respectively are

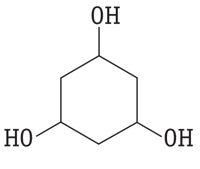
(a) Both 

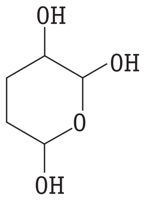
(b) Both 

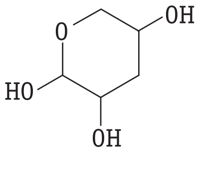
(c) 

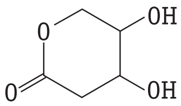
(d) 

5. In which molecule, cleavage by HIO_4 is not observed?

(a) 

(b) 

(c) 

(d) 

6. The acidic character of $1°, 2°, 3°$ alcohols, H_2O and $RC\equiv CH$ is of the order

(a) $H_2O > 1° > 2° > 3° > RC\equiv CH$

(b) $RC\equiv CH > 3° > 2° > 1° > H_2O$

(c) $1° > 2° > 3° > H_2O > RC\equiv CH$

(d) $3° > 2° > 1° > H_2O > RC\equiv CH$

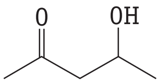
7. Choose the incorrect statement.

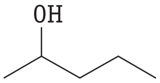
(a) Ordinary ethyl alcohol is known as rectified spirit
(b) The alcohol sold in the market for polishing etc., is known as methylated spirit
(c) Absolute alcohol is 100% ethanol
(d) Power alcohol is 100% ethanol

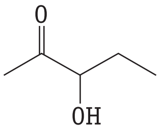
8. Reaction of tertiary butyl alcohol with hot Cu at 350°C produces

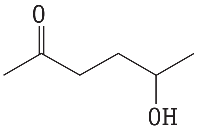
(a) butanol
(b) butanal
(c) 2-butene
(d) 2-methylpropene

9. Which one of the following will most readily be dehydrated in acidic condition?

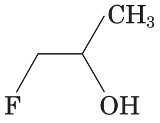
(a)


(b)


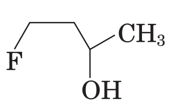
(c)


(d)


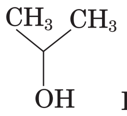
10. The order of reactivity of the following alcohols is



(I)



(II)



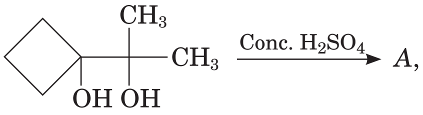
(III)

(IV)

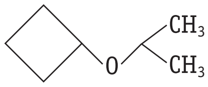
(a) I > II > III > IV
(b) I > III > II > IV
(c) IV > III > II > I
(d) IV > III > I > II

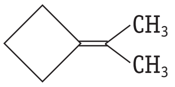
11. In the following reaction, identify X. Methyl magnesium bromide $+ X \longrightarrow$ 2-methyl propan-2-ol **[NCERT]**

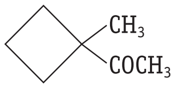
(a) propanol
(b) ethanone
(c) propanone
(d) butane

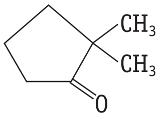
12.


The product A is

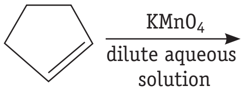
(a)


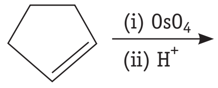
(b)


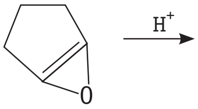
(c)


(d)


13. By which of the following reactions can *trans*-cyclopentane-1,2- diol be obtained?

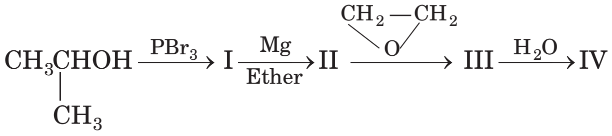
(a)


(b)


(c)


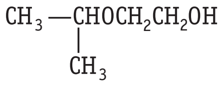
(d) None of these

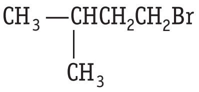
14. The final product (IV) in the sequence of reactions

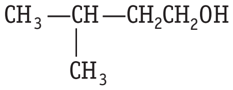


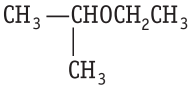
$$\mathrm{CH_3\underset{\substack{|\\CH_3}}{C}HOH \xrightarrow{PBr_3} I \xrightarrow[Ether]{Mg} II \xrightarrow{\overset{CH_2-CH_2}{\diagdown O \diagup}} III \xrightarrow{H_2O} IV}$$

is

(a)

$\mathrm{CH_3-\underset{\substack{|\\CH_3}}{C}HOCH_2CH_2OH}$

(b)

$\mathrm{CH_3-\underset{\substack{|\\CH_3}}{C}HCH_2CH_2Br}$

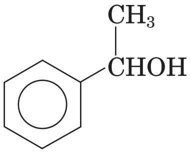
(c)

$\mathrm{CH_3-\underset{\substack{|\\CH_3}}{CH}-CH_2CH_2OH}$

(d)

$\mathrm{CH_3-\underset{\substack{|\\CH_3}}{C}HOCH_2CH_3}$

15. Arrange the following compounds in increasing order of boiling point. Propan-1-ol, butan-1-ol, butan-2-ol, pentan-1-ol. **[NCERT Exemplar]**

(a) Propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol
(b) Propan-1-ol, butan-1-ol, butan-2-ol, pentan-1-ol
(c) Pentan-1-ol, butan-2-ol, butan-1-ol, propan-1-ol
(d) Pentan-1-ol, butan-1-ol, butan-2-ol, propan-1-ol

16. Correct order of dehydration of

I.


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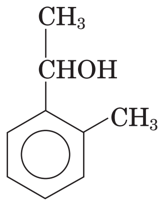
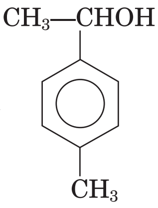
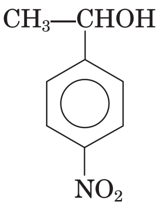


III.


IV.


is

(a) I > II > III > IV
(b) II > III > I > IV
(c) IV > I > III > II
(d) IV > I > II > III

Phenols

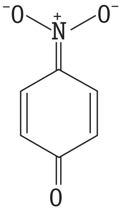
17. IUPAC name of *m*-cresol is **[NCERT** Exemplar]

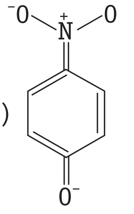
(a) 3-methylphenol
(b) 3-chlorophenol
(c) 3-methoxyphenol
(d) benzene-1,3-diol

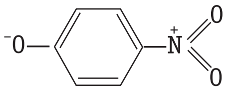
18. On Friedel-Crafts acetylation, anisole yields **[NCERT]**

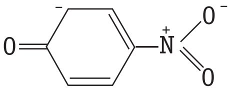
(a) 2-methoxyacetophenone
(b) 4-methoxyacetophenone
(c) Both (a) and (b)
(d) None of the above

19. The most unlikely representation of resonance structures of *p*-nitrophenoxide ion is

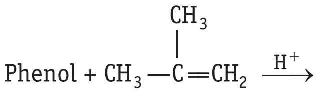
(a)


(b)


(c)


(d)


20. Which of the following reactions will not yield *p-tert* butylphenol?

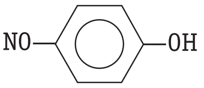
(a) 
$\text{Phenol} + CH_3{-}\overset{\overset{\large CH_3}{|}}{C}{=}CH_2 \xrightarrow{H^+}$

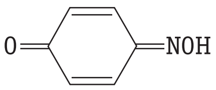
(b) Phenol + $(CH_3)_3COH \xrightarrow{H^+}$

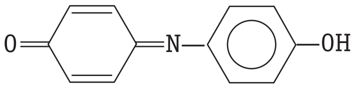
(c) Phenol + $(CH_3)_3C \cdot Cl \xrightarrow{AlCl_3}$

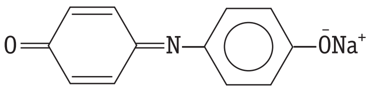
(d) Phenol + $CHCl_3 \xrightarrow{NaOH}$

21. In the Liebermann test for phenols, the blue or green colour produced is due to the formation of

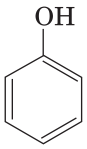
(a)


(b)


(c)


(d)


22. Mark the correct order of decreasing acid strength of the following compounds.

I.


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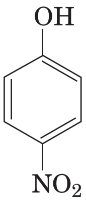
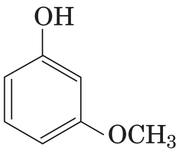
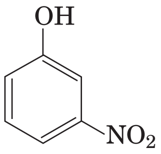
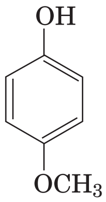


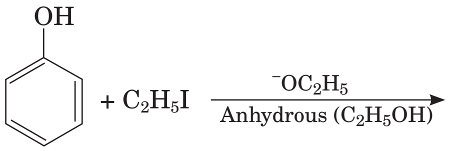
III.


IV.


V.


[NCERT Exemplar]

(a) V > IV > II > I > III (b) II > IV > I > III > V
(c) IV > V > III > II > I (d) V > IV > III > II > I

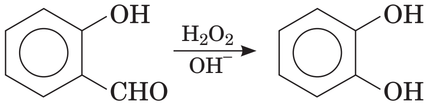
23.


(a) $C_6H_5OC_2H_5$ (b) $C_2H_5OC_2H_5$
(c) $C_6H_5OC_6H_5$ (d) C_6H_5I

24. Phenol $\xrightarrow[\text{(ii) } CO_2/140^\circ C]{\text{(i) NaOH}} A \xrightarrow{H^+/H_2O} B \xrightarrow{Ac_2O} C$

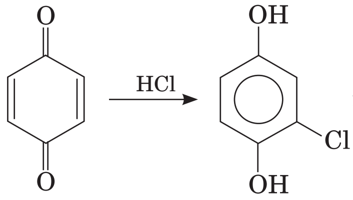
In this reaction, the end product C is **[NCERT]**

(a) salicylaldehyde (b) salicylic acid
(c) phenyl acetate (d) aspirin

25.


This reaction is called

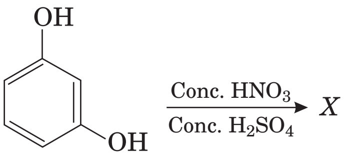
(a) Reimer-Tiemann reaction
(b) Liebermann's nitroso reaction
(c) Dakin reaction
(d) Lederer-Manasse reaction

26.


is an example of

(a) 1,2-addition of HCl followed by tautomerism
(b) 1,2-addition followed by reduction
(c) 1,4-addition followed by tautomerism
(d) 1,4-addition followed by oxidation

27. Consider the following reaction,



Product X is

(a) picric acid (b) styphnic acid
(c) salicylic acid (d) benzoic acid

Ethers

28. Which of the following is the best method for making *iso*-propylmethyl ether?

(a) $CH_3I + (CH_3)_2CHOH \longrightarrow$
(b) $CH_3I + (CH_3)_2CHO^- \longrightarrow$
(c) $(CH_3)_2CHI + CH_3O^- \longrightarrow$
(d) $(CH_3)_2CHCl + CH_3OH \longrightarrow$

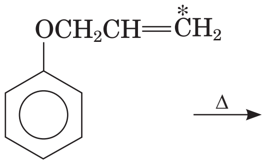
29. Some time explosion occurs while distilling ethers. It is due to the presence of

(a) oxide (b) ketones (c) aldehyde (d) peroxides

30. An ether is more volatile than an alcohol having the same molecular formula. This is due to

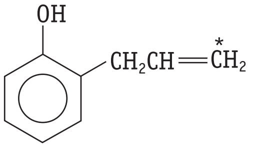
(a) intermolecular hydrogen bonding in alcohols
(b) dipolar character of ethers
(c) alcohols having resonance structures
(d) intermolecular hydrogen bonding in ether

31.

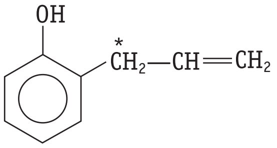


? Product is

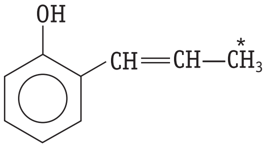
(a)



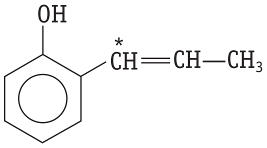
(b)



(c)



(d)



32. C—O—C angle would be maximum in

(a) $CH_3{-}O{-}CH_3$
(b) $CH_3{-}O{-}C_2H_5$
(c) $C_2H_5{-}O{-}C_2H_5$
(d) $(CH_3)_2CH{-}O{-}CH(CH_3)_2$

33. To prepare an ether by Williamson's synthesis, the reactants needed are

(a) ethyl alcohol and *tert* butyl alcohol
(b) sodium ethoxide and *tert* butyl bromide
(c) sodium *tert* butoxide and ethyl bromide
(d) sodium ethoxide and sodium *tert* butoxide

34. Ether in contact with air for a long time form peroxides. The presence of peroxide in ether can be tested by adding Fe^{2+} ion and then adding

(a) KCN (b) $SnCl_2$
(c) $HgCl_2$ (d) KCNS

35. On boiling with concentrated hydrobromic acid, phenyl ethyl ether yields

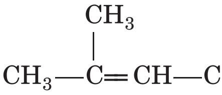
(a) phenol and ethane
(b) phenol and ethyl bromide
(c) bromobenzene and ethanol
(d) bromobenzene and ethane

36. Which of the following reactions does not yield an ether?

(a) Sodium methoxide reacts with dimethyl sulphate
(b) Sodium ethoxide reacts with ethyl bromide
(c) Sodium ethoxide reacts with bromocyclopropane
(d) Ethanol reacts with CH_2N_2 in presence of HBF_4

Aldehydes and Ketones

37. The compound



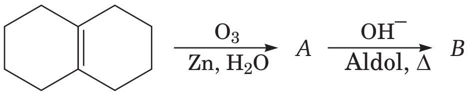
$CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH{-}CH_3$ on reaction with $NaIO_4$ in the presence of $KMnO_4$ gives

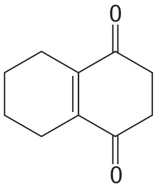
(a) CH_3COCH_3
(b) $CH_3COCH_3 + CH_3COOH$
(c) $CH_3COCH_3 + CH_3CHO$
(d) $CH_3CHO + CO_2$

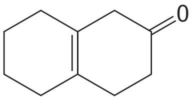
38. Arrange the following compounds in increasing order of their boiling points. CH_3CHO, CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$ **[NCERT]**

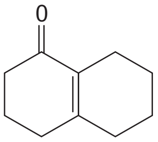
(a) $CH_3CH_2CH_3 < CH_3CH_2OH < CH_3OCH_3 < CH_3CHO$
(b) $CH_3OCH_3 < CH_3CH_2CH_3 < CH_3CH_2OH < CH_3CHO$
(c) $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$
(d) $CH_3CH_2OH < CH_3CHO < CH_3OCH_3 < CH_3CH_2OH$

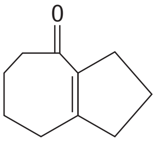
39. Identify the final product of the reaction.



(a) 

(b) 

(c) 

(d) 

40. Collin's reagent is used to convert

(a) $>C{=}O \longrightarrow >CHOH$

(b) $—CH_2OH \longrightarrow —CHO$

(c) $—CHO \longrightarrow —COOH$

(d) $—CHO \longrightarrow —CH_2OH$

41. Etard's reaction involves the preparation of benzaldehyde from

(a) toluene (b) ethyl benzene

(c) benzoyl chloride (d) sodium benzoate

42. Which of the following compounds will give butanone on oxidation with alkaline $KMnO_4$ solution? **[NCERT** Exemplar]

(a) Butan-1-ol (b) Butan-2-ol

(c) Both (a)and (b) (d) None of these

43. Compounds A and C in the following reaction are **[NCERT** Exemplar]

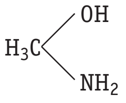
$$CH_3CHO \xrightarrow[\text{(ii) } H_2O]{\text{(i) } CH_3MgBr} (A) \xrightarrow{H_2SO_4,\ \Delta} (B) \xrightarrow{\text{Hydroboration oxidation}} (C)$$

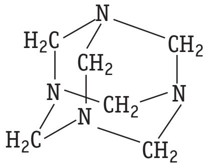
(a) identical (b) positional isomers

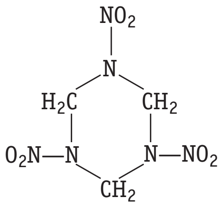
(c) functional isomers (d) optical isomers

44. The final product obtained in the reaction

$$CH_2O + NH_3 \longrightarrow [\quad] \xrightarrow[Ac_2O]{HNO_3} \text{ is}$$

(a) 

(b) 

(c) 

(d) None of these

45. $2DCDO \xrightarrow{OH^-} [X]$ and $[Y]$ are

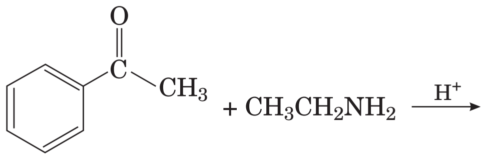
(a) $DCOO^-$, D_2CHOH

(b) $HCOO^-$, CH_3OH

(c) $HCOO^-$, CD_3OH

(d) $DCOO^-$, CD_3OH

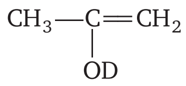
46. Predict the product of the following reaction. **[NCERT]**



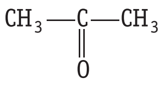
(a) Schiff's base (b) Tollen's reagent

(c) Bendict solution (d) Molisch's reagent

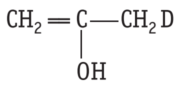
47. The enol form of acetone, after treatment with D_2O gives

(a) 

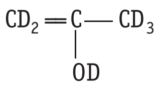
$CH_3—\underset{OD}{\underset{|}{C}}{=}CH_2$

(b) 

$CH_3—\underset{O}{\underset{\|}{C}}—CH_3$

(c) 

$CH_2{=}\underset{OH}{\underset{|}{C}}—CH_2D$

(d) 

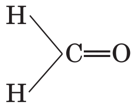
$CD_2{=}\underset{OD}{\underset{|}{C}}—CD_3$

48. Which of the following has the most acidic hydrogen?

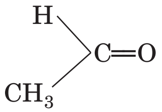
(a) 3-hexanone (b) 2,4-hexanedione

(c) 2,5-hexanedione (d) 2,3-hexanedione

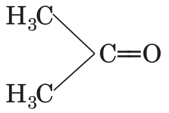
49. What will be the order of reactivity of the following carbonyl compounds with Grignard's reagent?



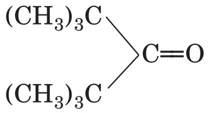
I



II



III



IV

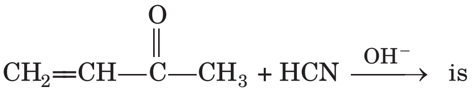
(a) I > II > III > IV

(b) IV > III > II > I

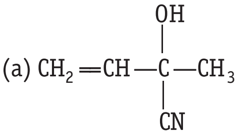
(c) II > I > IV > III

(d) III > II > I > IV

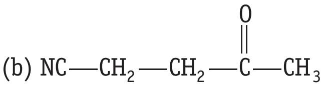
50. The major product obtained in the reaction,

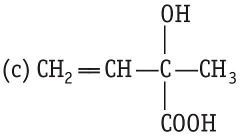


$$CH_2{=}CH—\overset{O}{\overset{\|}{C}}—CH_3 + HCN \xrightarrow{OH^-} \text{ is}$$

(a) 

$CH_2{=}CH—\underset{CN}{\underset{|}{\overset{OH}{\overset{|}{C}}}}—CH_3$

(b) 
$NC-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

(c) 
$CH_2=CH-\underset{COOH}{\overset{OH}{C}}-CH_3$

(d) None of the above

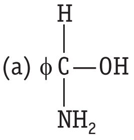
51. Which of the following steps will be required for the conversion of ethanal into butane-1,3-diol? **[NCERT]**

(a) Acylation, reduction
(b) Cross aldol condensation, dehydration
(c) Aldol condensation, oxidation
(d) Aldol condensation, reduction

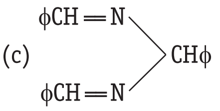
52. Which of the following does not undergo benzoin condensation?

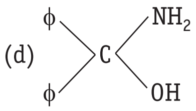
(a) Benzene carbaldehyde
(b) *p*-toluene carbaldehyde
(c) Phenylethanal
(d) 4-methoxybenzaldehyde

53. $\phi CHO + NH_3 \longrightarrow$? Product is

(a) 
$\phi\underset{NH_2}{\overset{H}{C}}-OH$

(b) $\phi CH=NH$

(c) 

(d) 

54. A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives

(a) benzyl alcohol and sodium formate
(b) sodium benzoate and methyl alcohol
(c) sodium benzoate and sodium formate
(d) benzyl alcohol and methyl alcohol

55. Match the following.

I. $\phi COCH_3 \longrightarrow \phi CH_2CH_3$	(A) $SnCl_2$
II. $\phi COCH_3 \longrightarrow \phi CH(OH)CH_3$	(B) Zn-Hg/HCl
III. $\phi NO_2 \longrightarrow \phi NHOH$	(C) $NaBH_4$
IV. $\phi CH_2-OTs \rightarrow \phi CH_3$	(D) Zn/NH_4Cl

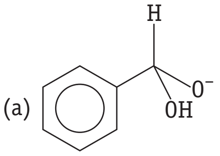
Codes

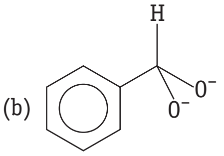
(a) (I)-B, (II)-C, (III)-D, (IV)-A
(b) (I)-B, (II)-A, (III)-D, (IV)-C
(c) (I)-B, (II)-A, (III)-C, (IV)-D
(d) (I)-A, (II)-B, (III)-D, (IV)-C

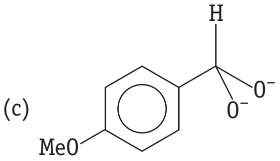
56. φCHO undergoes Claisen condensation with another aldehyde to give cinnamaldehyde. The aldehyde is

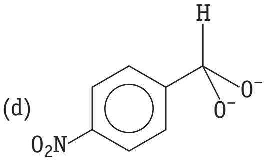
(a) formaldehyde (b) acetaldehyde
(c) crotonaldehyde (d) propanaldehyde

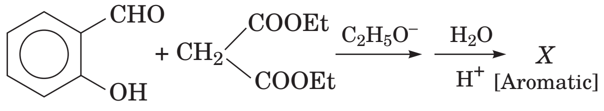
57. In a Cannizzaro reaction, the intermediate that will be best hydride donor is

(a) 

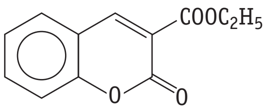
(b) 

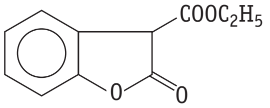
(c) 

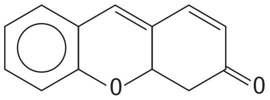
(d) 

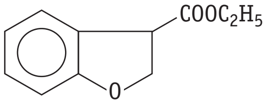
58. 

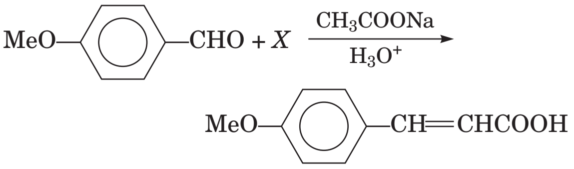
Identify the final product *X*.

(a) 

(b) 

(c) 

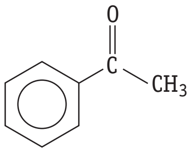
(d) 

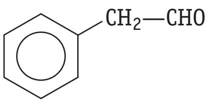
59. 

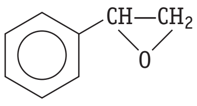
The compound *X* is

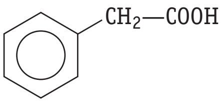
(a) CH_3-COOH (b) $BrCH_2-COOH$
(c) $(CH_3CO)_2O$ (d) $CHO-COOH$

60. A compound (*A*) (molecular formula—C_8H_8O) on treatment with $NH_2OH \cdot HCl$ gives *B* and *C*. *B* and *C* rearrange to give *D* and *E* respectively on treatment with acid. *B, C, D* and *E* are all isomers of molecular formula (C_8H_9NO). When *D* is boiled with the alcoholic KOH, an oil *F* (C_6H_7N) separates out. *F* reacts rapidly with CH_3COCl to give back *D*. On the other hand, *E* on boiling with alkali followed by acidification gives a white solid *G* ($C_7H_6O_2$). Identify *A*.

(a) 

(b) 

(c) 

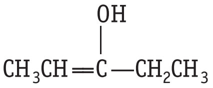
(d) 

61. Which of the following statements is correct about a carbonyl group?

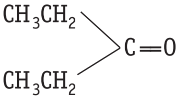
(a) The carbonyl carbon is *sp*-hybridised
(b) The carbonyl carbon is sp^3-hybridised
(c) The three groups attached to the carbonyl carbon lie in the same plane
(d) The three groups attached to the carbonyl carbon lie in different planes

62. An organic compound contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollen's reagent but forms an addition compound with sodium hydrogen sulphite and give positive iodoform test. On vigorous oxidation it gives ethanoic and propanoic acid. Write the possible structure of the compound. **[NCERT]**

(a) $CH_3COCH_2CH_2CH_3$

(b) 
$CH_3CH{=}C(OH){-}CH_2CH_3$

(c) $CH_3CH_2COCH_2CH_3$

(d) 

Carboxylic Acids

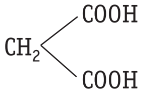
63. Tamarind contains

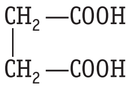
(a) (+) tartaric acid
(b) (–) tartaric acid
(c) ± tartaric acid
(d) None of these

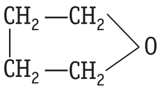
64. $CH{\equiv}CH \xrightarrow{CH_3MgBr} A \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CO_2} B \xrightarrow{HgSO_4/H_2SO_4}$

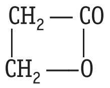
$D \xleftarrow[\text{(ii) } H^+]{\text{(i)} [Ag(NH_3)_2]^+,\ OH^-} C$

In the given reaction, product *D* is,

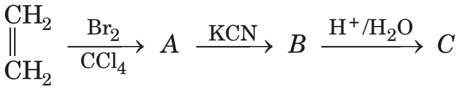
(a) 

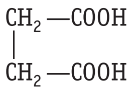
(b) 
$CH_2{-}COOH$ / $CH_2{-}COOH$

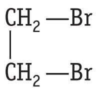
(c) 

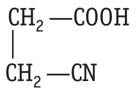
(d) 

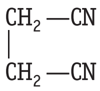
65. The final product of the following sequence of reaction is


$CH_2{=}CH_2 \xrightarrow[CCl_4]{Br_2} A \xrightarrow{KCN} B \xrightarrow{H^+/H_2O} C$

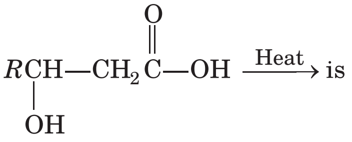
(a) 
$CH_2{-}COOH$ / $CH_2{-}COOH$

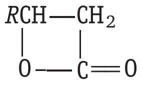
(b) 
$CH_2{-}Br$ / $CH_2{-}Br$

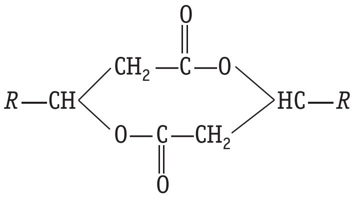
(c) 
$CH_2{-}COOH$ / $CH_2{-}CN$

(d) 
$CH_2{-}CN$ / $CH_2{-}CN$

66. The product obtained in the reaction,


$RCH(OH){-}CH_2C(=O){-}OH \xrightarrow{Heat}$ is

(a) 

(b) 

(c) $RCH{=}CHCOOH$

(d) None of the above

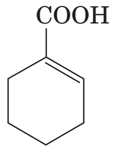
67. Which can reduce $RCOOH \longrightarrow RCH_2OH$?

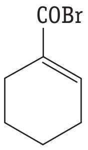
(a) $NaBH_4$
(b) Na/C_2H_5OH
(c) $BH_3/THF/H_3O^+$
(d) H_2/catalyst

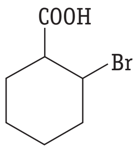
68. 
$\underset{[X]}{R{-}\overset{O}{\overset{\|}{C}}{-}OH_2^+} \xleftarrow{H_2SO_4} RCOOH \xrightarrow{H_2SO_4} \underset{[Y]}{R{-}\overset{^+OH}{\overset{\|}{C}}{-}OH}$

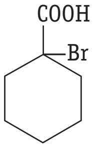
Which is more stable ?

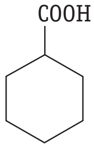
(a) *X*
(b) *Y*
(c) Both are equally stable
(d) Can't be predicted

69.  $\xrightarrow{HBr}$? Product is

(a) 

(b) 

(c) 

(d) 

70.

	Column I		**Column II**
I.		(A)	Schmidt
II.	$RCOOH \rightarrow RCH_2COOH$	(B)	Baeyer Villiger
III.	$RCOOH \xrightarrow[H_2O]{N_3H} RNH_2$	(C)	Arndt Eistert

Codes

(a) I–A, II–B, III–C (b) I–C, II–B, III–A

(c) I–B, II–C, III–A (d) None of these

71. Which of the following order represent acidic strength of (I) benzoic acid, (II) 4-nitrobenzoic acids, (III) 3,4-dinitro benzoic acid and (IV) 4-methoxy benzoic acid? **[NCERT]**

(a) $I < II < III < IV$

(b) $IV < I < II < III$

(c) $II < III < I < IV$

(d) $IV < II < III < I$

72. Which statement is correct ?

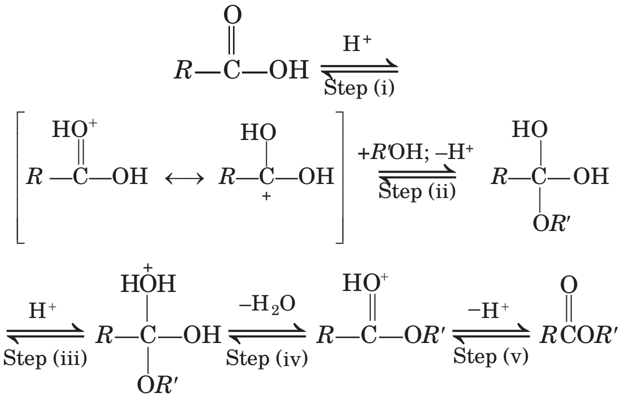
(a) $RCOOOH$ is stronger acid than $RCOOH$

(b) Maleic acid is stronger than fumaric acid

(c) Both (a) and (b)

(d) None of the above

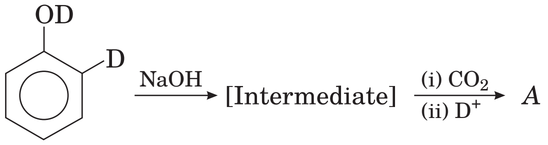
73. The mechanism of ester formation in acidic medium is as follows



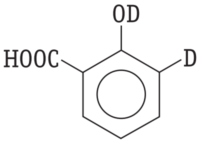
The slowest step in the above mechanism is

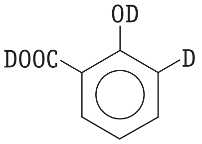
(a) step (i) (b) step (ii)

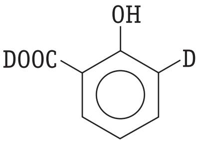
(c) step (iii) (d) step (iv)

74. 

Here, A is

(a) 

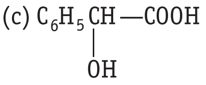
(b) 

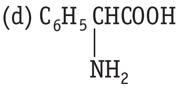
(c) 

(d) reaction not possible

75. Which of the following carboxylic acids undergoes decarboxylation easily ?

(a) $C_6H_5COCH_2COOH$ (b) $C_6H_5COCOOH$

(c)  $C_6H_5CH(OH)COOH$

(d)  $C_6H_5CH(NH_2)COOH$

76. Phthalic acid

$$\text{Phthalic acid} \xrightarrow{\Delta} A \xrightarrow{NH_3} B \xrightarrow[H_2O]{NaOH} C \xrightarrow{Br_2/KOH} D \xrightarrow{HCl} E$$

In this reaction, the product E is

(a) o-nitrobenzoic acid (b) salicylic acid

(c) anthranilic acid (d) crotonic acid

77. Match the following.

I. Claisen condensation	(A) Free radical
II. Allylic bromination	(B) Carbon anion
III. Fries rearrangement	(C) Alkyl migration
IV. Wolff rearrangement	(D) Acyl migration

Codes

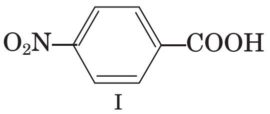
(a) I–B, II–A, III–C, IV–D

(b) I–B, II–A, III–D, IV–C

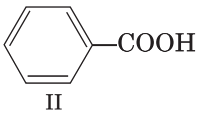
(c) I–A, II–B, III–C, IV–D

(d) I–A, II–B, III–D, IV–C

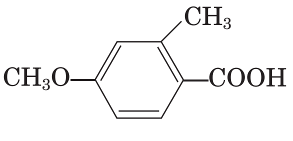
78. Give the order of ease of the esterification of the following acids



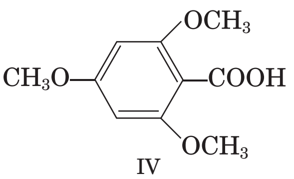
I



II



III



IV

Codes

(a) $I > II > III > IV$ (b) $IV > III > II > I$

(c) $II > I > IV > III$ (d) $I > III > II > IV$

79. In the reaction,

$$C_6H_5COOH + CH_3\overset{*}{O}H \xrightarrow{H^+} \text{Ester + water}$$

(a) isotopically labelled oxygen (O^{18}) is present in water

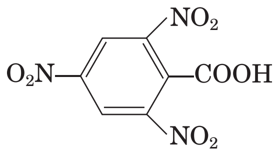
(b) O^{18} is present with ester

(c) O^{18} shifts from acid to alcohol

(d) no reaction takes place

80. Give the order of ease of decarboxylation of the following acids.

$$\underset{I}{CH_3COOH};\quad \underset{II}{CH_2{=}CH{-}CH_2COOH};\quad \underset{III}{CH_2(COOH)_2}$$



IV

(a) I > II > III > IV

(b) III > IV > II > I

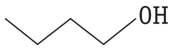
(c) IV > III > II > I

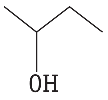
(d) I > III > II > IV

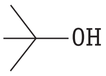
Round II (Mixed Bag)

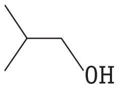
1. $C_4H_{10}O$ gives white precipitate within 5 min with concentrated hydrochloric acid in the presence of anhydrous zinc chloride.

Alcohol can be

(a) 

(b) 

(c) 

(d) 

2. Monochlorination of toluene in sunlight followed by hydrolysis with aqueous NaOH yields. **[NCERT Exemplar]**

(a) *o*-cresol (b) *m*-cresol

(c) 2,4-dihydroxytoluene (d) benzyl alcohol

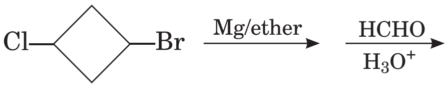
3. What is the correct order of reactivity of alcohols in the following reaction?

$$R{-}OH + HCl \xrightarrow{ZnCl_2} R{-}Cl + H_2O$$

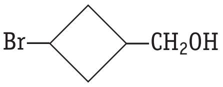
[NCERT Exemplar]

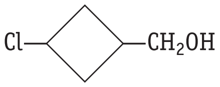
(a) 1° > 2° > 3° (b) 1° < 2° > 3°

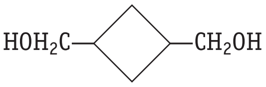
(c) 3° > 2° > 1° (d) 3° > 1° > 2°

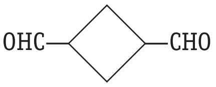
4. 

A, *A* is

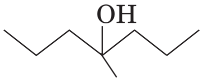
(a) 

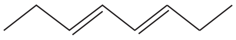
(b) 

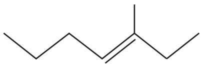
(c) 

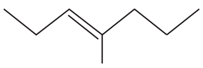
(d) 

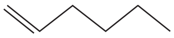
5. Which of the following alkene will give the following alcohol? **[NCERT]**



(a) 

(b) 

(c) 

(d) 

6. 2-methoxy butane is obtained by reacting diazomethane with

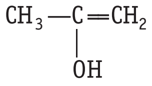
(a) 2-butanol (b) 1-butanol

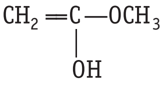
(c) 2-butanone (d) butanal

7. 

$$CH_3OH \xrightarrow{CH_2{=}C{=}O} A \xrightarrow{\text{Rearrangement}} CH_3{-}\underset{\underset{O}{\|}}{C}{-}OCH_3$$

In the above reaction, *A* is

(a) 
$CH_3{-}\underset{OH}{\underset{|}{C}}{=}CH_2$

(b) 
$CH_2{=}\underset{OH}{\underset{|}{C}}{-}OCH_3$

(c) $CH_2{=}CHOH$ (d) None of these

8. The end product of which of the following reaction is isomer of alcohols?

(a) $C_2H_4 \xrightarrow{B_2H_6} A \xrightarrow[NaOH]{H_2O_2} B$

(b) $CHI_3 \xrightarrow[\Delta]{Ag} A \xrightarrow[Hg^{2+}]{\text{Dil. } H_2SO_4} B \xrightarrow{\text{Reduction}} C$

(c) $C_2H_4 \xrightarrow{HI} A \xrightarrow{\text{Aqueous KOH}} B \xrightarrow[140°C]{\text{Conc. } H_2SO_4} C$

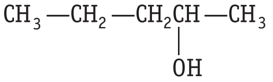
(d) $CH_3MgBr \xrightarrow{CH_2O} A \xrightarrow{H_2O} C$

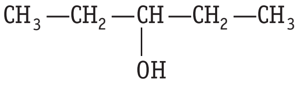
9. An organic compound C_3H_6O neither gives precipitate with semicarbazide nor reacts with sodium. It could be

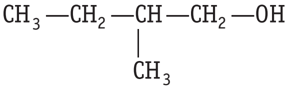
(a) CH_3CH_2CHO (b) CH_3COCH_3
(c) $CH_2{=}CHCH_2OH$ (d) $CH_2{=}CHOCH_3$

10. A compound 'A' having the molecular formula $C_5H_{12}O$, on oxidation gives a compound 'B' with molecular formula $C_5H_{10}O$. Compound 'B' gave a 2,4-dinitrophenylhydrazine derivative but did not answer haloform test or silver mirror test. The structure of compound 'A' is

(a) $CH_3CH_2CH_2CH_2CH_2OH$

(b) 
$CH_3-CH_2-CH_2\underset{\underset{OH}{|}}{CH}-CH_3$

(c) 
$CH_3-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3$

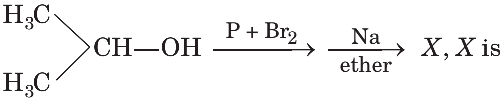
(d) 
$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-OH$

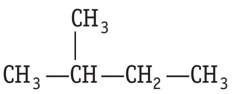
11. An organic compound 'X' with molecular formula, C_7H_8O is insoluble in aqueous $NaHCO_3$ but dissolves in NaOH. When treated with bromine water, 'X' rapidly gives 'Y', $C_7H_5OBr_3$. The compounds 'X' and 'Y' respectively, are

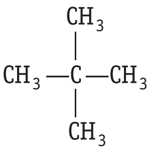
(a) benzyl alcohol and 2,4,6-tribromo-3-methoxybenzene
(b) benzyl alcohol and 2,4,6-tribromo-3-methylphenol
(c) *o*-cresol and 3,4,5-tribromo-2-methylphenol
(d) *m*-cresol and 2,4,6-tribromo-3-methylphenol

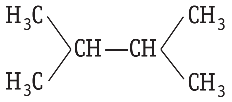
12. The products obtained when benzyl phenyl ether is heated with HI in the mole ratio 1 : 1 are

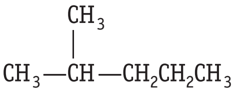
I. phenol II. benzyl alcohol
III. benzyl iodide IV. iodobenzene
(a) I and III only (b) III and IV only
(c) I and IV only (d) II and IV only

13. 
$(H_3C)_2CH-OH \xrightarrow{P + Br_2} \xrightarrow[ether]{Na} X$, X is

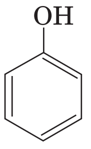
(a) 
$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_3$

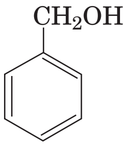
(b) 
$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

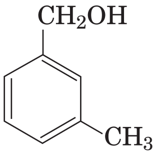
(c) 
$(H_3C)_2CH-CH(CH_3)_2$

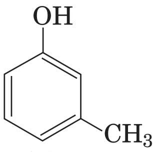
(d) 
$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2CH_2CH_3$

14. Which of the following compounds is aromatic alcohol?


(A)


(B)


(C)


(D)

[NCERT Exemplar]

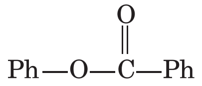
(a) *A, B, C, D*
(b) *A, D*
(c) *B, C*
(d) *A*

15. In the Rosenmund's reaction

$$RCOCl + H_2 \xrightarrow{Pd/BaSO_4} RCHO + HCl$$

$BaSO_4$ here

(a) promotes catalytic activity of Pd
(b) removes the HCl formed in the reaction
(c) deactivates palladium
(d) activates palladium

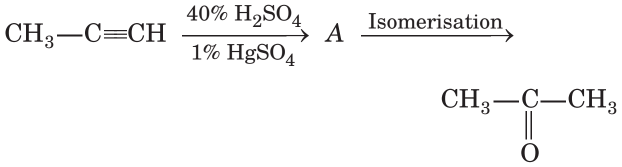


16. Compound $Ph-O-\overset{\overset{O}{\|}}{C}-Ph$ can be prepared by the reaction of [NCERT Exemplar]

(a) Phenol and benzoic acid in the presence of NaOH
(b) Phenol and benzoyl chloride in the presence of pyridine
(c) phenol and benzoyl chloride in the presence of $ZnCl_2$
(d) phenol and benzaldehyde in the presence of palladium

17. The reagent which does not react with both, acetone and benzaldehyde is [NCERT Exemplar]

(a) sodium hydrogensulphite
(b) phenyl hydrazine
(c) Fehling's solution
(d) Grignard reagent

18. 
$CH_3-C{\equiv}CH \xrightarrow[1\%\ HgSO_4]{40\%\ H_2SO_4} A \xrightarrow{Isomerisation} CH_3-\underset{\underset{O}{\|}}{C}-CH_3$

Structure of 'A' and type of isomerism in the above reaction are respectively. [NCERT Exemplar]

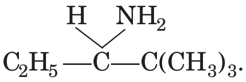
(a) Prop-1-en-2-ol, metamerism
(b) Pro-1-en-1-ol, tautomerism
(c) Prop-2-en-2-ol, geometrical isomerism
(d) Prop-1-en-2-ol, tautomerism

19. Compound *A* when treated with ethyl magnesium iodide in dry ether forms an addition compound which on hydrolysis forms compound *B*. The compound *B* on oxidation form 3-pentanone. Hence, the compound *A* and *B* are

(a) propanal, 3-pentanol (b) pentanol, 3-pentanol

(c) ethanal, pentanal (d) acetone, 3-pentanol

20. A product obtained by the reaction of *X* with hydroxylamine and on further reduction gives



$C_2H_5—\overset{H\ \ NH_2}{C}—C(CH_3)_3$. Hence, the compound *X* can be

(a) 2,2-dimethyl-3-pentanone

(b) 3,3-dimethyl-3-butanone

(c) 1-methyl-3-pentanone

(d) diethyl ketone

21. Hydride ion transfer takes place in

(a) Frankland method

(b) Wurtz reaction

(c) Cannizzaro's reaction

(d) Wolff-Kishner reduction

22. An aromatic compound '*X*' with molecular formula $C_9H_{10}O$ gives the following chemical tests. It

I. forms 2, 4-DNP derivative

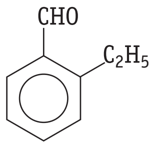
II. reduces Tollen's reagent

III. undergoes Cannizzaro reaction and

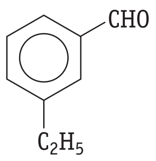
IV. on vigorous oxidation 1,2-benzenedicarboxylic acid is obtained.

X is **[NCERT]**

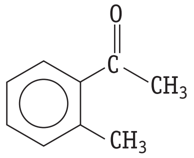
(a)



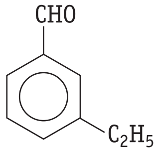
(b)



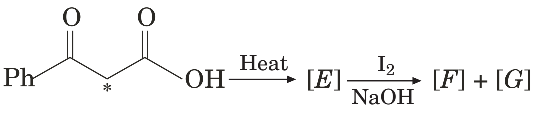
(c)



(d)

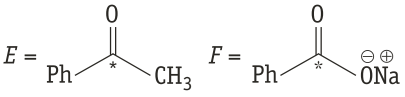


23. In the following reaction sequence, the correct structures of *E, F* and *G* are



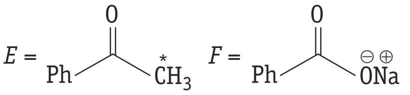
(* implies ^{13}C labelled carbon)

(a)



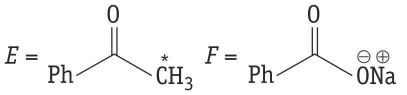
$G = CHI_3$

(b)



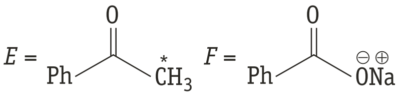
$G = CHI_3$

(c)



$G = \overset{*}{C}HI_3$

(d)

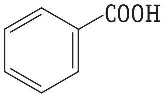


$G = \overset{*}{C}H_3I$

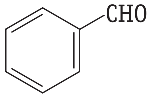
24. The reactant (*X*) in the reaction

$$(X) \xrightarrow[(CH_3CO)_2O]{CH_3COONa} \text{Cinnamic acid, is}$$

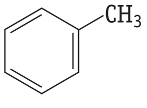
(a)



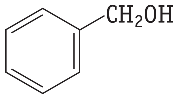
(b)



(c)



(d)



25. Acetyl nitrate is formed when acetic anhydride reacts with

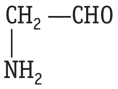
(a) nitrogen pentoxide (b) nitric acid

(c) nitrous acid (d) potassium nitrate

26. $CH_3COOH \xrightarrow{NH_3} \xrightarrow{\Delta}$?

The product of the reaction is isomeric with

(a)



$\underset{NH_2}{CH_2}—CHO$

(b) $CH_3CH{=}NOH$

(c) $HCONH—CH_3$ (d) All of these

27. Match Column I with Column II and choose the correct answer from the codes

Column I	Column II
(A) CH_3CONH_2 and PCl_5	(I) Acid strengthening
(B) $—NO_2$ group	(II) Optically active
(C) Lactic acid	(III) Hydrogen is liberated
(D) CH_3COOH and Na	(IV) Acetonitrile

Codes

	A	B	C	D		A	B	C	D
(a)	I	II	III	IV	(b)	IV	I	II	III
(c)	IV	I	III	II	(d)	III	I	II	IV

28. $CH_3CH_2OH \xrightarrow[I]{Cu,\ 573\ K} X \xrightarrow[II]{[O]} Y \xrightarrow[III]{Br_2,\ P} BrCH_2COOH$

Reactions I, II and III respectively are

(a) reduction, oxidation and substitution

(b) dehydration, oxidation and substitution

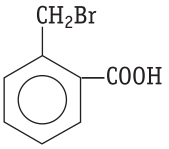
(c) dehydrogenation, oxidation and substitution

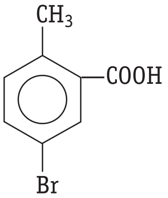
(d) dehydration, oxidation and elimination

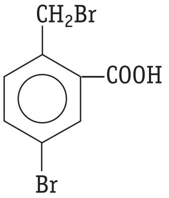
29. A colourless water soluble organic liquid decomposes sodium carbonate and liberates CO_2. It produces black precipitate with Tollen's reagent. The liquid is

(a) acetaldehyde (b) acetamide
(c) formic acid (d) acetone

30. *o*-toluic acid on reaction with Br_2 + Fe gives

(a)


(b)


(c)


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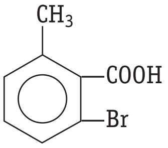


31. On mixing ethyl acetate with aqueous sodium chloride, the composition of the resultant solution is

(a) $CH_3COOC_2H_5$ + NaCl
(b) $C_3COONa + C_2H_5OH$
(c) $CH_3COCl + C_2H_5OH + NaOH$
(d) $CH_3Cl + C_2H_5COONa$

32. Formic acid and acetic acid are distinguished by

(a) $NaHCO_3$ (b) $FeCl_3$
(c) Victor Meyer test (d) Tollen's reagent

33. Acetyl bromide reacts with excess of CH_3MgI followed by treatment with a saturated solution of NH_4Cl to give

(a) acetone
(b) acetamide
(c) 2-methyl-2-propanol
(d) acetyl iodide

34. $C_8H_6O_4 \xrightarrow{\Delta} X \xrightarrow{NH_3} Y$

The compound *X* is

(a) *o*-xylene (b) phthalic acid
(c) phthalic anhydride (d) salicylic acid

35. The reaction involved in the oil of winter green test is salicylic acid $\xrightarrow[\text{Conc } H_2SO_4]{\Delta}$ product. The product is treated with Na_2CO_3 solution. The missing reagent in the above reaction is

(a) phenol (b) NaOH
(c) ethanol (d) methanol

36. An ester (*A*) with molecular formula $C_9H_{10}O_2$ was treated with excess of CH_3MgBr and the complex so formed was treated with H_2SO_4 to give an olefin (*B*). Ozonolysis of (*B*) gave a ketone with molecular formula C_8H_8O which shows positive iodoform test. The structure of (*A*) is

(a) $C_6H_5COOC_2H_5$
(b) $C_6H_5COOC_6H_5$
(c) $C_6H_5COOCH_3$
(d) *p*-$H_3CO—C_6H_4COCH_3$

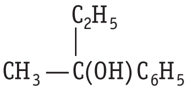
37. In a set of the given reactions, acetic acid yielded a product *C*.

$$CH_3COOH + PCl_5 \longrightarrow A$$

$$A \xrightarrow[\text{anhy. } AlCl_3]{C_6H_6} B \xrightarrow[\text{ether}]{C_6H_5MgBr} C$$

Product *C* would be

(a) $CH_3CH(OH)C_6H_5$

(b)

$CH_3—\overset{\overset{\large C_2H_5}{|}}{C}(OH)C_6H_5$

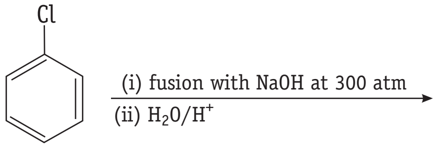
(c) $CH_3CH(OH)C_2H_5$ (d) $CH_3COC_6H_5$

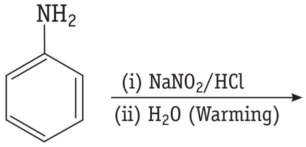
More than One Correct Option

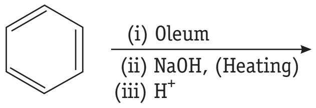
38. Which of the following ae used to convert *R*CHO into RCH_2OH? **[NCERT Exemplar]**

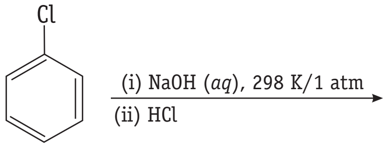
(a) H_2/Pd
(b) $LiAlH_4$
(c) $NaBH_4$
(d) Reaction with *R*Mg*X* followed by hydrolysis

39. Which of the following reactions will yield phenol?

(a)


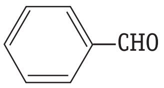
(b)


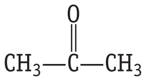
(c)


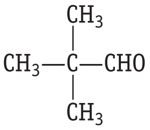
(d)


40. Which of the following compounds do not undergo aldol condensation? **[NCERT Exemplar]**

(a) $CH_3—CHO$

(b) 

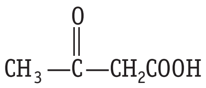
(c) 
$CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—CH_3$

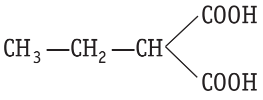
(d) 
$CH_3—\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}—CHO$

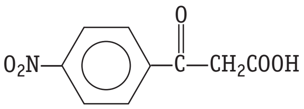
41. Which of the following conversions can be carried out by Clemmensen reduction? **[NCERT Exemplar]**

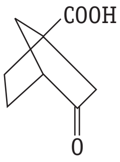
(a) Benzaldehyde into benzyl alcohol
(b) Cyclohexanone into cyclohexane
(c) Benzoyl chloride into benzaldehyde
(d) Benzophenone into diphenyl methane

42. On gently warming, which of the following acids undergo decarboxylation?

(a) 
$CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—CH_2COOH$

(b) 
$CH_3—CH_2—CH\begin{cases} COOH \\ COOH \end{cases}$

(c) 

(d) 

Assertion and Reason

Directions (Q. No. 43 to 47) *Each of these questions contains two statements : Statement* I (*Assertion*) *and Statement* II (*Reason*). *Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes* (*a*), (*b*), (*c*), (*d*) *given below*

(a) Statement I is true; Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true; Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

43. Statement I Dehydration of $CH_3CH_2CH(OH)CH_3$ gives $CH_3\,CH_2CH{=}CH_2$ as the minor product and $CH_3\,CH{=}CHCH_3$ as the major product.

Statement II $CH_2{=}CH(OH)CH—CH_3$ can be dehydrated more readily than $CH_3CH_2CH(OH)CH_3$.

44. Statement I Friedel-Crafts reaction between benzene and acetic anhydride in the presence of anhydrous $AlCl_3$ yields acetophenone and not polysubstituted products.

Statement II Acetophenone formed poisons catalyst preventing further reaction.

45. Statement I Pure acetic acid is converted into ice like solid, called glacial acetic acid.

Statement II Acetic acid is stronger than HCOOH.

46. Statement I In sodium formate, both the C—O bonds have same value 1.27 Å.

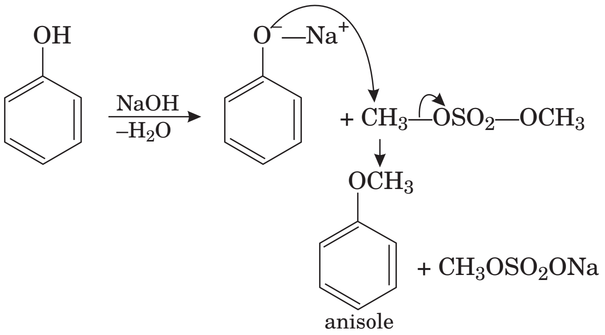
Statement II Same bond length is due to the phenomenon of resonance.

47. Statement I Bond angle in ethers is slightly less than the tetrahedral angle.

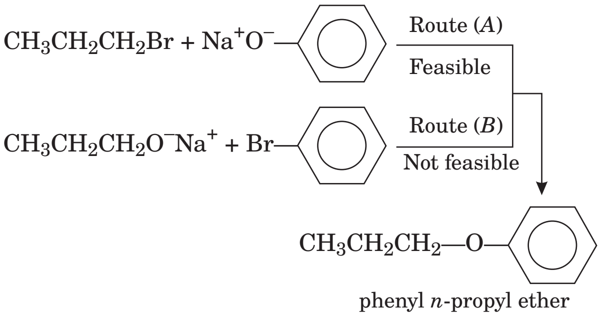
Statement II There is a repulsion between the two bulky (—*R*) groups. **[NCERT Exemplar]**

Comprehension Based Questions

Directions (Q. Nos. 48 to 50) Phenols are converted into alkyl aryl ethers by reaction in alkaline solution with alkyl halides. For the preparation of aryl methyl ethers, dimethy sulphate is frequently used instead of more expensive methyl halides.



The above reaction is familiar Williamson's synthesis which can even be used for the preparation of unsymmetrical ethers like alkyl aryl ethers. Aryl halides can't be used in the Williamsons synthesis because of their low reactivity towards nucleophilic substitution. For the preparation of any alkyl aryl ether, there can be two combinations of reactants, but one combination can usually be ruled out.



48. Ethyl bromide reacts with sodium methoxide to form ethyl methyl ether. It is an example of

(a) S_N2 reaction (b) S_N1 reaction
(c) S_N1 reaction (d) elimination reaction

49. Decreasing order of reactivity of following alkyl halides in the Williamson's ether synthesis is

$\underset{(A)}{(CH_3)_3CCH_2Br}$; $\underset{(B)}{ClCH_2CH{=}CH_2}$; $\underset{(C)}{ClCH_2CH_2CH_3}$, $\underset{(D)}{BrCH_2CH_2CH_3}$

(a) $B > D > C > A$ (b) $A > B > C > D$
(c) $D > C > B > A$ (d) $C > D > B > A$

50. Williamson's synthesis is an example of

(a) electrophilic addition
(b) electrophilic substitution
(c) nucleophilic addition
(d) nucleophilic substitution reaction

Directions (Q. Nos. 51 to 53) Ethanal is heated with a base in two separate test tubes. In one test tube nothing except the two mentioned reactants were present. In second test tube, malonic acid, $CH_2(COOH)_2$ was also added. The final products of both test tubes easily add 1,3-butadiene molecule. The product obtained in the first test tube can be converted into product, identical in all respect, with that obtained in the second test tube.

51. The respective reaction involved in the two test tubes are

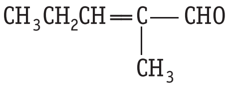
(a) aldol condensation and Cannizaro reaction
(b) aldol condensation and Perkin reaction
(c) aldol condensation and Knoevenagel reaction
(d) aldol condensation and Claisen condensation

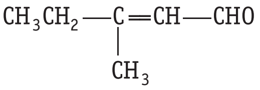
52. Which of the final products can undergo Diels' Alder reaction?

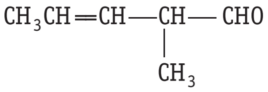
(a) Product from first test tube
(b) Product from second test tube
(c) Products from both test tubes
(d) Neither of the two products

53. What would have been the final product when ethanal of the first test tube is replaced by propanal?

(a) $CH_3CH_2CH{=}CHCH_2CHO$

(b)

$CH_3CH_2CH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CHO$

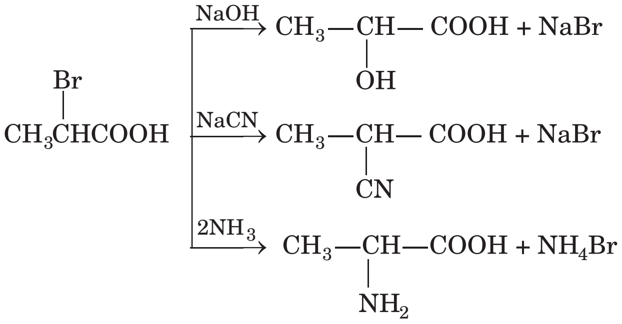
(c)

$CH_3CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH{-}CHO$

(d)

$CH_3CH{=}CH{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CHO$

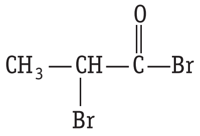
Directions (Q. Nos. 54 to 56) Hell-Volhard-Zelinsky (HVZ) reaction involves the reaction of aliphatic carboxylic acid with bromine in the presence of a trace of PBr_3 to form α-bromocarboxylic acid.

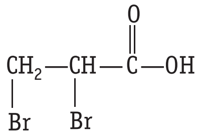
$$CH_3CH_2COOH \xrightarrow{Br_2/PBr_3} CH_3CH_2COBr \longrightarrow$$
$$CH_3CHBrCOOH \xleftarrow{H_2O} CH_3CHBrCOBr$$

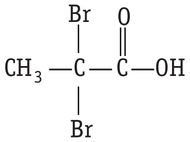
α-halogenated acids are infact good starting material for preparing other α-substituted acids as;


$$\underset{}{CH_3\overset{\displaystyle Br}{\overset{|}{C}H}COOH}\begin{cases}\xrightarrow{NaOH} CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}COOH + NaBr\\ \xrightarrow{NaCN} CH_3{-}\underset{\displaystyle CN}{\underset{|}{CH}}{-}COOH + NaBr\\ \xrightarrow{2NH_3} CH_3{-}\underset{\displaystyle NH_2}{\underset{|}{CH}}{-}COOH + NH_4Br\end{cases}$$

54. When two equivalents of the reagent are used, the product formed in the above reaction will be

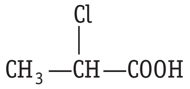
(a)

$CH_3{-}\underset{\displaystyle Br}{\underset{|}{CH}}{-}\overset{\displaystyle O}{\overset{||}{C}}{-}Br$

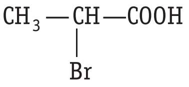
(b)

$\underset{\displaystyle Br}{\underset{|}{CH_2}}{-}\underset{\displaystyle Br}{\underset{|}{CH}}{-}\overset{\displaystyle O}{\overset{||}{C}}{-}OH$

(c)

$CH_3{-}\overset{\displaystyle Br}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{C}}}}{-}\overset{\displaystyle O}{\overset{||}{C}}{-}OH$

(d) Both (b) and (c)

55. What product will be formed when PBr_3 in the given set of reactions is replaced by PCl_3?

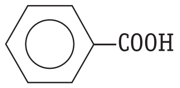
(a)

$CH_3{-}\overset{\displaystyle Cl}{\overset{|}{CH}}{-}COOH$

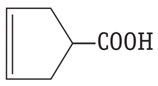
(b)

$CH_3{-}\underset{\displaystyle Br}{\underset{|}{CH}}{-}COOH$

(c) Both (a) and (b) (d) Reaction is not possible

56. Which of the following acid undergoes HVZ reaction?

(a) $CH_3CH{=}CHCOOH$ (b) $CH_3CH_2CBr_2COOH$

(c)


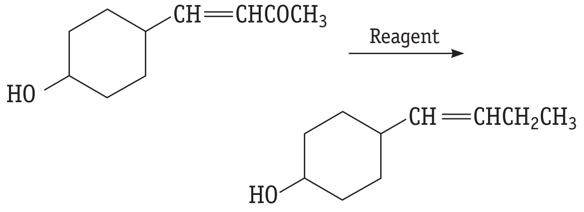
(d)


Previous Years' Questions

57. Iodoform can be prepared from all except [AIEEE 2012]

(a) ethyl methyl ketone (b) isopropyl alcohol
(c) 3-methyl-2-butanone (d) isobutyl alcohol

58. In the given transformation, which of the following is the most appropriate reagent? [AIEEE 2012]



(a) $NH_2NH_2, \overset{\ominus}{O}H$ (b) Zn—Hg/HCl
(c) Na, Liq. NH_3 (d) $NaBH_4$

59. Phenol is heated with a solution of mixture of KBr and $KBrO_3$. The major product obtained in the above reaction is [AIEEE 2011]

(a) 2-bromophenol
(b) 3-bromophenol
(c) 4-bromophenol
(d) 2, 4, 6-tribromophenol

60. Which of the following reagents may be used to distinguish between phenol and benzoic acid ? [AIEEE 2011]

(a) Aqueous NaOH (b) Tollen's reagent
(c) Molisch reagent (d) Neutral $FeCl_3$

61. Trichloroacetaldehyde was subjected to Cannizzaro's reaction by using NaOH. The mixture of the products contains sodium trichloroacetate ion and another compound. The other compound is [AIEEE 2011]

(a) 2, 2, 2-trichloroethanol
(b) trichloromethanol
(c) 2, 2, 2-trichloropropanol
(d) chloroform

62. The strongest acid amongst the following compounds is

(a) CH_3COOH (b) HCOOH
(c) $CH_3CH_2CH(Cl)CO_2H$ (d) $ClCH_2CH_2CH_2COOH$

63. Sodium ethoxide has reacted with ethanoyl chloride. The compound that is produced in the above reaction is [AIEEE 2011]

(a) diethyl ether (b) 2-butanone
(c) ethyl chloride (d) ethyl ethanoate

64. Silver mirror test is given by which one of the following compounds? [AIEEE 2011]

(a) Acetaldehyde (b) Acetone
(c) Formaldehyde (d) Benzophenone

65. The correct order of acid strength of the following compounds is

I. Phenol II. *p*-cresol
III. *m*- nitrophenol IV. *p*- nitrophenol

(a) III > II > I > IV (b) IV > III > I > II
(c) II > IV > I > III (d) I > II > IV > III

66. Consider the following reaction,

$$C_2H_5OH + H_2SO_4 \longrightarrow \text{Product}$$

Among the following, which one cannot be formed as a product under any conditions?

(a) Ethyl hydrogen sulphate
(b) Ethylene
(c) Acetylene
(d) Diethyl ether

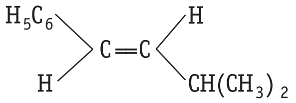
67. From amongst the following alcohols the one that would react fastest with conc. HCl and anhydrous $ZnCl_2$, is

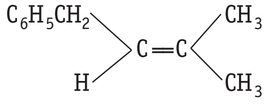
(a) 2-butanol (b) 2-methylpropan-2-ol
(c) 2-methylpropanol (d) 1-butanol

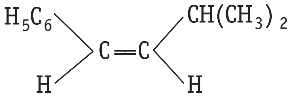
68. The main product of the following reaction is

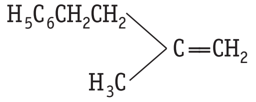
$$C_6H_5CH_2CH(OH)CH(CH_3)_2 \xrightarrow{\text{Conc. } H_2SO_4} ?$$

[AIEEE 2010]

(a) 

(b) 

(c) 

(d) 

69. A liquid was mixed with ethanol and a drop of concentrated H_2SO_4 was added. A compound with a fruity smell was formed. The liquid was [AIEEE 2009]

(a) CH_3OH (b) HCHO
(c) CH_3COCH_3 (d) CH_3COOH

70. The major product obtained on interaction of phenol with sodium hydroxide and carbon dioxide is [AIEEE 2009]

(a) benzoic acid (b) salicylaldehyde
(c) salicylic acid (d) phthalic acid

71. Which of the following on heating with aqueous KOH, produces acetaldehyde?

(a) CH_3COCl (b) CH_3CH_2Cl
(c) CH_2ClCH_2Cl (d) CH_3CHCl_2

72. In Cannizzaro reaction given below

$$2PhCHO \xrightarrow{OH^{\ominus}} PhCH_2OH + PhCO_2^{\ominus}$$ [AIEEE 2009]

the slowest step is

(a) the attack of : : $OH^{\ominus}$ at the carboxyl group
(b) the transfer of hydride to the carbonyl group
(c) the abstraction of proton from the carboxylic group
(d) the deprotonation of $PhCH_2OH$

73. Phenol, when it first reacts with concentrated sulphuric acid and then with concentrated nitric acid, gives [AIEEE 2008]

(a) 2, 4, 6-trinitrobenzene
(b) *o*-nitrophenol
(c) *p*-nitrophenol
(d) nitrobenzene

74. In the following sequence of reactions,

$$CH_3CH_2OH \xrightarrow{P + I_2} A \xrightarrow[\text{ether}]{Mg} B \xrightarrow{HCHO} C \xrightarrow{H_2O} D$$

the compound '*D*' is [AIEEE 2007]

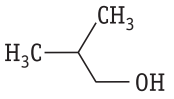
(a) butanal (b) *n*-butyl alcohol
(c) *n*-propyl alcohol (d) propanal

75. The compound formed as a result of oxidation of ethyl benzene by $KMnO_4$ is [AIEEE 2007]

(a) benzophenone
(b) acetophenone
(c) benzoic acid
(d) benzyl alcohol

76. Among the following the one that gives positive iodoform test upon reaction with I_2 and NaOH is [AIEEE 2006]

(a) $CH_3CH_2CH(OH)CH_2CH_3$ (b) $C_6H_5CH_2CH_2OH$

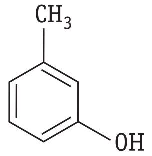
(c) 

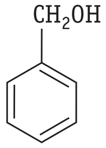
(d) $PhCHOHCH_3$

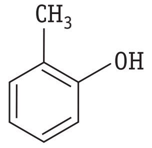
77. Phenyl magnesium bromide reacts with methanol to give [AIEEE 2006]

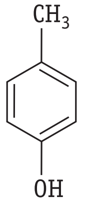
(a) a mixture of anisol and Mg(OH)Br
(b) a mixture of benzene and Mg(OMe)Br
(c) a mixture of toluene and Mg(OH)Br
(d) a mixture of phenol and Mg(Me)Br

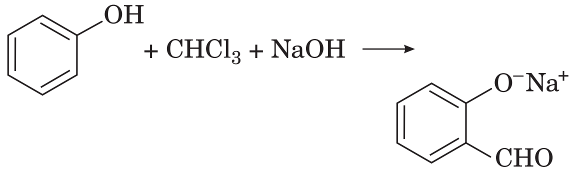
78. The structure of the compound that gives a tribromo derivative on treatment with bromine water is [AIEEE 2006]

(a) 

(b) 

(c) 

(d) 

79. 

The electrophile involved in the above reaction is [AIEEE 2006]

(a) dichloromethyl cation ($\overset{\oplus}{C}HCl_2$)
(b) dichlorocarbene ($:CCl_2$)
(c) trichloromethyl anion ($\bar{C}Cl_3$)
(d) formyl cation ($\overset{\oplus}{C}HO$)

80. The increasing order of the rate of HCN addition to compounds I-IV is [AIEEE 2006]

I. HCHO
II. CH_3COCH_3
III. $PhCOCH_3$
IV. PhCOPh

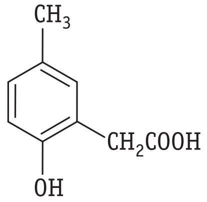
(a) I < II < III < IV
(b) IV < II < III < I
(c) IV < III < II < I
(d) III < IV < II < I

81. Acid catalysed hydration of alkenes except ethene leads to the formation of [AIEEE 2005]

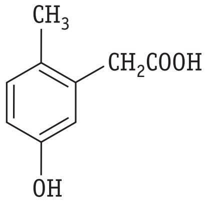
(a) mixture of secondary and tertiary alcohols
(b) mixture of primary and secondary alcohols
(c) secondary or tertiary alcohol
(d) primary alcohol

82. *p*-cresol reacts with chloroform in alkaline medium to give the compound *A* which adds hydrogen cyanide to form the compound *B*. The latter, on acidic hydrolysis gives chiral carboxylic acid. The structure of the carboxylic acid is [AIEEE 2005]

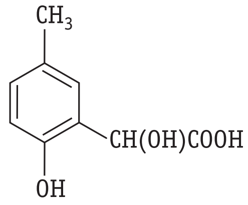
(a)



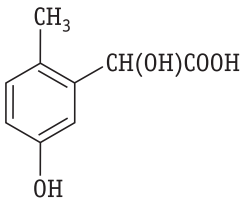
(b)



(c)



(d)



83. The best reagent to convert pent-3-en-2-ol into pent-3-en-2-one is **[AIEEE 2005]**

(a) pyridinium chloro-chromate
(b) chromic anhydride in glacial acetic acid
(c) acidic dichromate
(d) acidic permanganate

84. Which one of the following undergoes reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid ? **[AIEEE 2004]**

(a) Phenol (b) Benzaldehyde
(c) Butanal (d) Benzoic acid

85. Consider the acidity of the carboxylic acids :

I. PhCOOH II. *o*-$NO_2C_6H_4COOH$
III. *p*-$NO_2C_6H_4COOH$ IV. *m*-$NO_2C_6H_4COOH$

Which of the following order is correct? **[AIEEE 2004]**

(a) I > II > III > IV (b) II > IV > III > I
(c) II > IV > I > III (d) II > III > IV > I

86. During dehydration of alcohols to alkenes by heating with concentrated H_2SO_4, the initiation step is **[AIEEE 2003]**

(a) protonation of alcohol molecule
(b) formation of carbocation
(c) elimination of water
(d) formation of an ester

87. The general formula $C_nH_{2n}O_2$ could be for open chain **[AIEEE 2003]**

(a) diketones (b) carboxylic acids
(c) diols (d) dialdehydes

88. When $CH_2{=}CH{-}COOH$ is reduced with $LiAlH_4$, the compound obtained will be **[AIEEE 2003]**

(a) $CH_3{-}CH_2{-}COOH$
(b) $CH_2{=}CH{-}CH_2OH$
(d) $CH_2{=}CH{-}CH_2OH$
(c) $CH_3{-}CH_2{-}CHO$

Answers

Round I

1. (a) **2.** (d) **3.** (a) **4.** (d) **5.** (a) **6.** (a) **7.** (d) **8.** (d) **9.** (a) **10.** (c)
11. (c) **12.** (d) **13.** (c) **14.** (c) **15.** (a) **16.** (b) **17.** (a) **18.** (c) **19.** (c) **20.** (d)
21. (d) **22.** (b) **23.** (b) **24.** (d) **25.** (c) **26.** (c) **27.** (b) **28.** (b) **29.** (d) **30.** (a)
31. (b) **32.** (d) **33.** (c) **34.** (d) **35.** (b) **36.** (c) **37.** (b) **38.** (c) **39.** (d) **40.** (b)
41. (a) **42.** (b) **43.** (b) **44.** (c) **45.** (d) **46.** (a) **47.** (a) **48.** (b) **49.** (a) **50.** (b)
51. (d) **52.** (c) **53.** (c) **54.** (a) **55.** (a) **56.** (b) **57.** (d) **58.** (a) **59.** (c) **60.** (a)
61. (c) **62.** (a) **63.** (a) **64.** (a) **65.** (a) **66.** (c) **67.** (c) **68.** (b) **69.** (b) **70.** (c)
71. (b) **72.** (b) **73.** (b) **74.** (c) **75.** (a) **76.** (c) **77.** (b) **78.** (a) **79.** (b) **80.** (c)

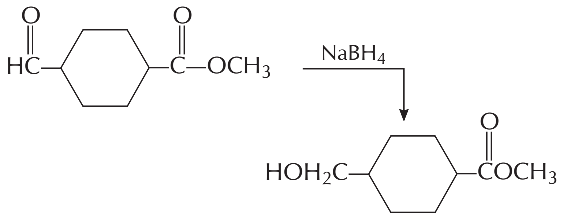
Round II

1. (b) **2.** (d) **3.** (c) **4.** (b) **5.** (c) **6.** (a) **7.** (b) **8.** (c) **9.** (d) **10.** (c)
11. (d) **12.** (c) **13.** (c) **14.** (c) **15.** (c) **16.** (b) **17.** (c) **18.** (d) **19.** (a) **20.** (a)
21. (c) **22.** (a) **23.** (c) **24.** (b) **25.** (a) **26.** (d) **27.** (b) **28.** (c) **29.** (c) **30.** (b)
31. (a) **32.** (d) **33.** (c) **34.** (c) **35.** (d) **36.** (a) **37.** (b) **38.** (a,b,c) **39.** (a,b,c) **40.** (b,d)
41. (b,d) **42.** (a,b,c) **43.** (b) **44.** (c) **45.** (c) **46.** (a) **47.** (d) **48.** (a) **49.** (d) **50.** (d)
51. (c) **52.** (c) **53.** (b) **54.** (c) **55.** (b) **56.** (d) **57.** (d) **58.** (a) **59.** (d) **60.** (d)
61. (a) **62.** (b) **63.** (d) **64.** (a,c) **65.** (b) **66.** (c) **67.** (b) **68.** (a) **69.** (d) **70.** (c)
71. (d) **72.** (b) **73.** (b) **74.** (c) **75.** (c) **76.** (d) **77.** (b) **78.** (a) **79.** (b) **80.** (c)
81. (c) **82.** (c) **83.** (b) **84.** (b) **85.** (d) **86.** (a) **87.** (b) **88.** (b)

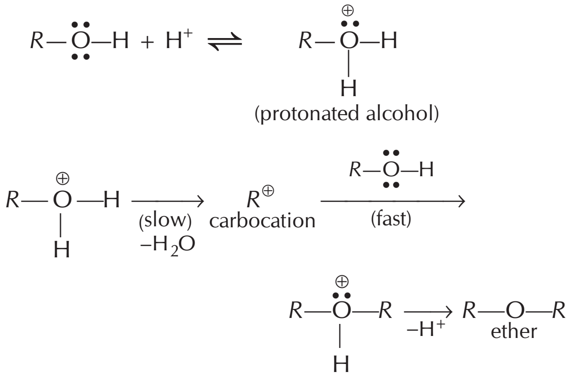
the Guidance

Round I

1.



2. Alcohol is initially protonated by the acid to form protonated alcohol or oxonium ion. It is then attacked by a second molecule of alcohol which acts as nucleophile.

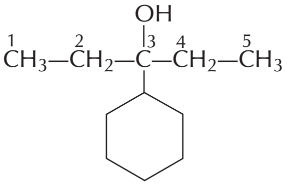


$$R-\ddot{O}-H + H^+ \rightleftharpoons R-\overset{\oplus}{O}(H)-H$$

(protonated alcohol)

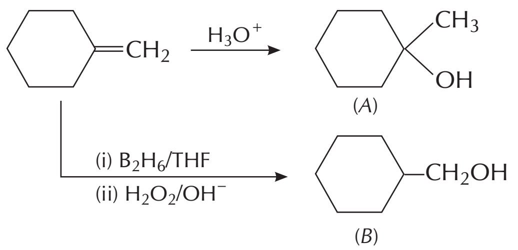
$$R-\overset{\oplus}{O}(H)-H \xrightarrow[-H_2O]{(slow)} \underset{\text{carbocation}}{R^{\oplus}} \xrightarrow[(fast)]{R-\ddot{O}-H} R-\overset{\oplus}{\ddot{O}}(H)-R \xrightarrow{-H^+} \underset{\text{ether}}{R-O-R}$$

3.

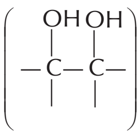


3-cyclohexylpentan-3-ol

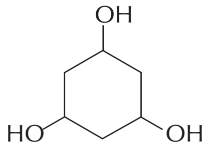
4.



5. All those compounds which have



groups are oxidised by periodic acid (HIO_4). Thus,

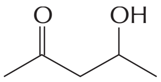


is not oxidised.

6. Alcohols are more acidic than alkynes but less acidic than water thus, the correct order of acidity is

$$H_2O > 1° > 2° > 3° > RC\equiv CH$$

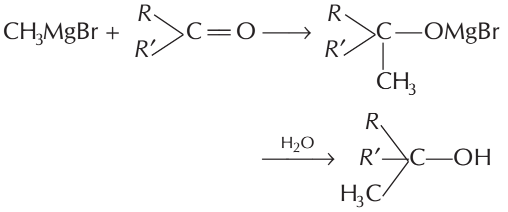
9. Greater the conjugation, greater the stability and hence, easier the dehydration. Thus, in acidic condition



will most readily be dehydrated.

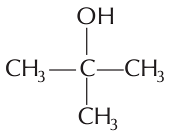
10. The order of reactivity depends upon the stability of the carbocation formed *i.e.*, $FCH_2\overset{+}{C}HCH_3$, $FCH_2CH_2\overset{+}{C}HCH_3$, $CH_3\overset{+}{C}HCH_3$ and $Ph\overset{+}{C}H_2$. The stability order of carbocations is $Ph\overset{+}{C}H_2 > CH_3\overset{+}{C}HCH_3 > FCH_2CH_2\overset{+}{C}HCH_3 > FCH_2\overset{+}{C}HCH_3$. Thus, the order of reactivity follows the order IV > III > II > I.

11. Since carbonyl compounds give alcohols with Grignard regent, so we take a general carbonyl compound $R_2C=O$.



$$CH_3MgBr + \begin{matrix}R\\R'\end{matrix}\!\!>C=O \longrightarrow \begin{matrix}R\\R'\end{matrix}\!\!>C(CH_3)-OMgBr \xrightarrow{H_2O} R'(R)(H_3C)C-OH$$

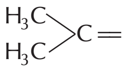
The structure of 2-methyl propan-2-al is



$$CH_3-C(OH)(CH_3)-CH_3$$

Thus, R and R' must be CH_3.

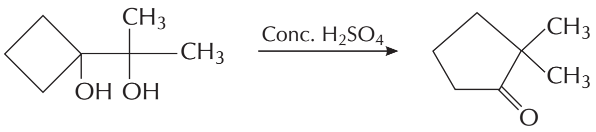
Therefore, X is



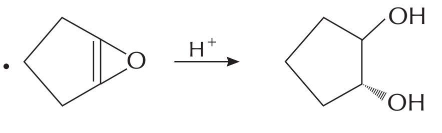
(propanone)

$$\begin{matrix}H_3C\\H_3C\end{matrix}\!\!>C=O$$

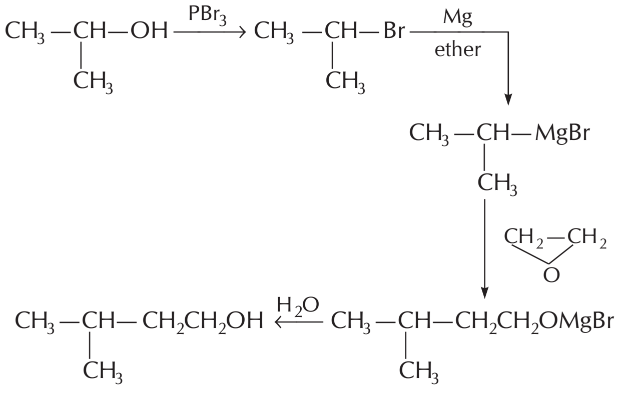
12. The pinacol-pinacolone rearrangement involves dehydration of diols through the formation of carbocation intermediate which rearranges to more stable compound.



13.



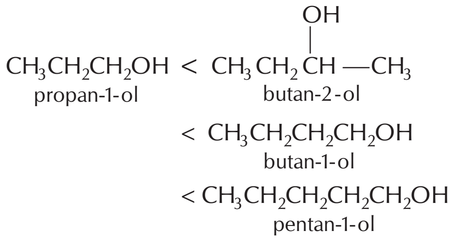
14.



3-methylbutanol

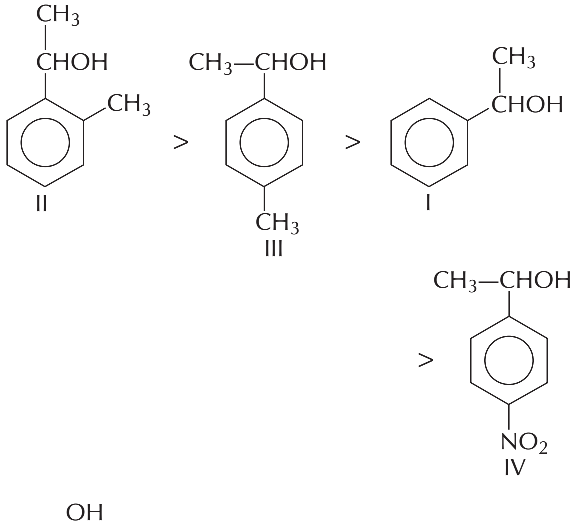
15. Boiling points of alcohols increases with molecular weight. Alcohols with same molecular weight are expected to have almost same boiling point however two more factor other than molecular weight are important, they are namely H-bonding and surface area. Both these factors are least in 3° alcohols and maximum in 1° alcohols.

Therefore, the correct order of boiling points of alcohols will be

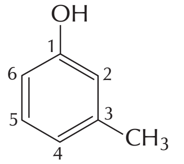


$$\underset{\text{propan-1-ol}}{CH_3CH_2CH_2OH} < \underset{\text{butan-2-ol}}{CH_3CH_2\overset{OH}{\overset{|}{C}H}—CH_3} < \underset{\text{butan-1-ol}}{CH_3CH_2CH_2CH_2OH} < \underset{\text{pentan-1-ol}}{CH_3CH_2CH_2CH_2CH_2OH}$$

16. In the given compounds, correct order of dehydration is

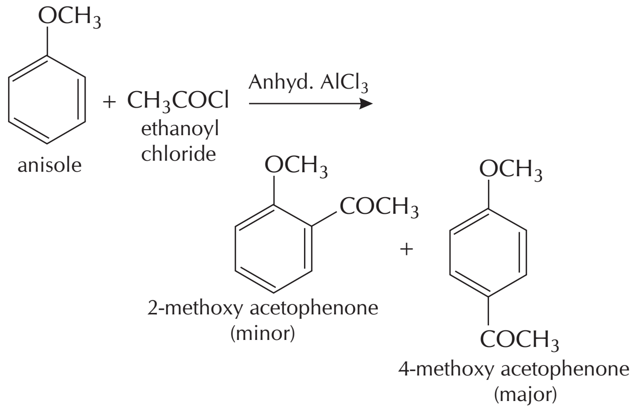


17.

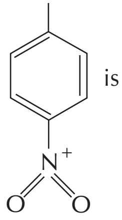


IUPAC name is 3-methylphenol.

18. Friedel–Crafts acetylation of anisole



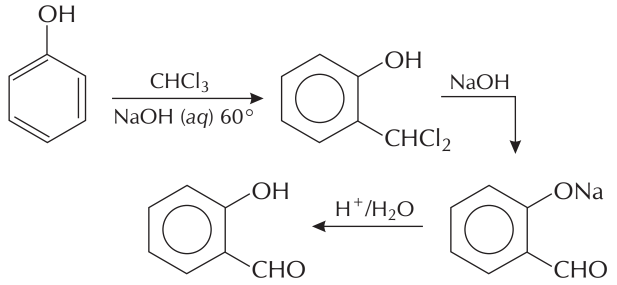
19.



is not a resonating structure of *p*-nitrophenoxide.

Since, N being an element of second period can't contain more than 10 electrons in its valence shell.

20. Phenol, on refluxing with chloroform and sodium hydroxide followed by hydrolysis yields *o*-hydroxy benzaldehyde.



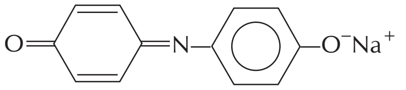
salicylaldehyde

21. Phenol gives Libermann's nitroso reaction.

$$\text{Phenol in conc. } H_2SO_4 \xrightarrow[\text{excess of water}]{NaNO_2} \text{Red colour}$$

$$\xrightarrow[\text{(Excess)}]{NaOH} \text{Blue colour}$$

This blue colour is formed due to the formation of



22. Phenols are acidic in nature due to resonance stabilisation of phenoxide ion. Presence of electron withdrawing groups (such as $—NO_2$, $—X$, $—NR_3^+$, $—CHO$, $—COX$, $—COOR$, $—CN$) in the ring stabilise phenoxide ion and increases the acidic nature of phenols. On the other hand, presence of electron releasing groups (such as $—CH_3$, $—OR$) in the ring destabilises the phenoxide ion and decreases the acidic nature of phenols.

Furthermore *meta*-isomer is less acidic than *p*-and *o*-isomers because it is stabilised by inductive effect only.

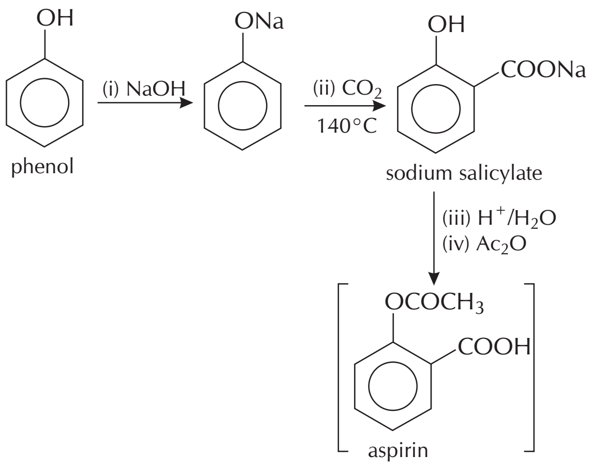
Thus, correct order of acidic strength is II > IV > I > III > V.

23. $C_6H_5O^-$ is a weaker nucleophile than $C_2H_5O^-$. Therefore, the better nucleophile, *i.e.*, $C_2H_5O^-$ will attack C_2H_5I to form diethyl ether.

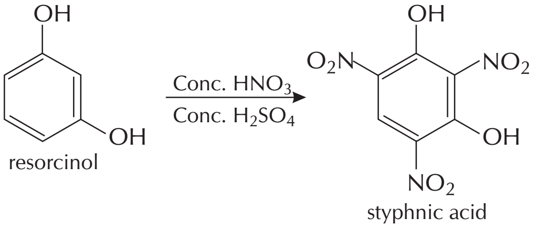
$$C_6H_5OH + \underset{\substack{\text{stronger}\\ \text{nucleophile}}}{C_2H_5O^-} \longrightarrow \underset{\substack{\text{weak}\\ \text{nucleophile}}}{C_6H_5O^-} + C_2H_5OH$$

$$C_2H_5O^- + CH_3-\overset{+\delta}{CH_2}-\overset{-\delta}{I} \longrightarrow \underset{\text{diethyl ether}}{CH_3CH_2-O-CH_2CH_3} + I^-$$

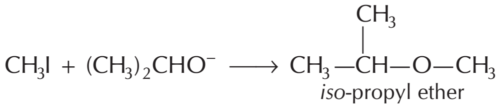
24.



27.



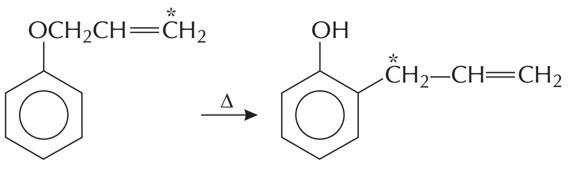
28.



$$CH_3I + (CH_3)_2CHO^- \longrightarrow \underset{\textit{iso}\text{-propyl ether}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-O-CH_3}$$

29. In the presence of air and light, ether form peroxides which cause explosion during distillation.

31.



32. Bulkier the alkyl groups in the ether, greater is the C—O—C bond angle due to steric factor.

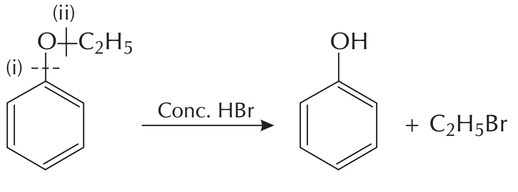
33. 1° alkyl halides on treatment with an alkoxide ion tend to undergo substitution to form ethers. So, sodium tert butoxide and ethyl bromide reagent is used.

34. Peroxide will oxidise Fe^{2+} to Fe^{3+} which gives a blood red colour with KCNS.

$$O_2^{2-} + 2Fe^{2+} + 4H^+ \longrightarrow 2Fe^{3+} + 2H_2O$$

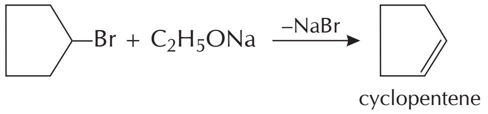
$$Fe^{3+} + 3KCNS \longrightarrow \underset{\text{(blood red colour)}}{Fe(CNS)_3} + 3K^+$$

35.

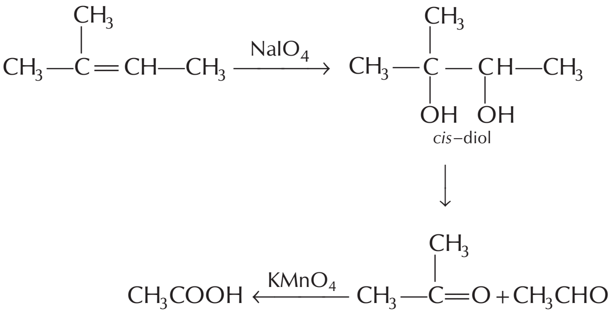


Breaking bond (i) is difficult as this bond has a partial double bond character due to resonance.

36. 2° cyclic alkyl halides tend to undergo elimination. Thus, bromocyclopentane on treatment with sodium ethoxide (a strong base) gives cyclopentane rather than cyclophenyl ethyl ether.



37.



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_3 \xrightarrow{NaIO_4} CH_3-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_3$$

cis–diol

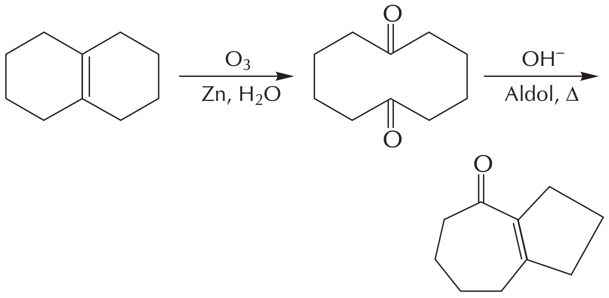
$$\downarrow$$

$$CH_3COOH \xleftarrow{KMnO_4} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=O + CH_3CHO$$

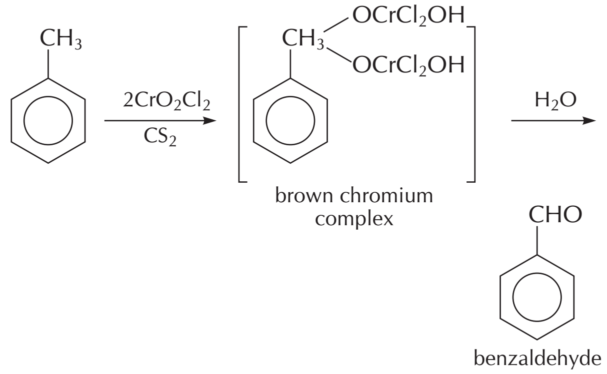
38. Boiling point is related to attractive forces. Stronger the attractive forces, higher is the boiling point. Hydrocarbons are non-polar having weakest attractive forces; Ethers are polar (dipolar forces); Aldehydes have stronger dipolar interactions; Alcohols have maximum inter molecular forces due to hydrogen bonding. Thus the order of boiling point is

$$CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$$

39.



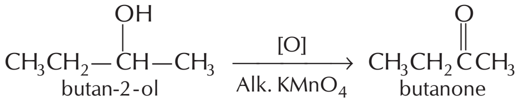
41. Toluene can be oxidised to benzaldehyde with a solution of chromyl chloride (CrO_2Cl_2) in CS_2 or CCl_4. This is known as Etard's reaction.



Further oxidation of benzaldehyde to benzoic acid is avoided by protection of carbonyl group.

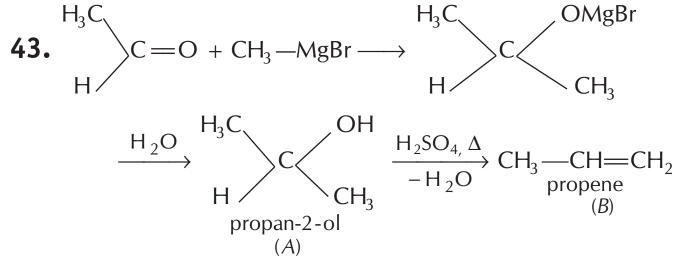
42. Alkaline $KMnO_4$ is a strong oxidising agent. It oxidises primary alcohols into aldehydes and secondary alcohols into ketones.

$$\underset{\text{butan-1-ol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[\text{Alk. }KMnO_4]{[O]} \underset{\text{butanal}}{CH_3CH_2CH_2CHO}$$



$$\underset{\text{butan-2-ol}}{CH_3CH_2—\overset{\overset{OH}{|}}{C}H—CH_3} \xrightarrow[\text{Alk. }KMnO_4]{[O]} \underset{\text{butanone}}{CH_3CH_2\overset{\overset{O}{\|}}{C}CH_3}$$

43.

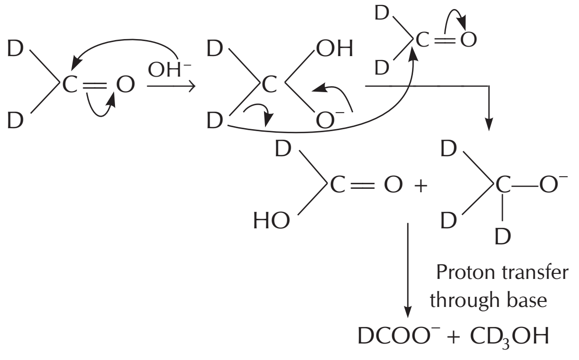


$$\underset{(B)}{6CH_3—CH=CH_2} + B_2H_6 \xrightarrow[\text{oxidation}]{\text{Hydroboration}}$$

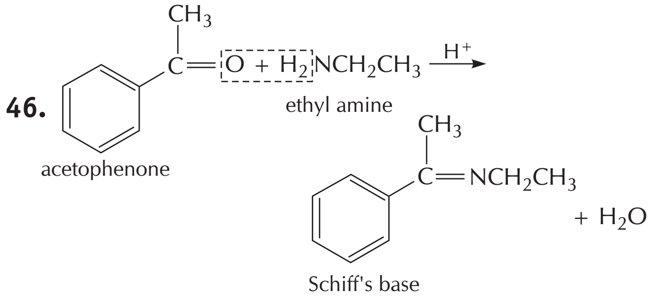
$$\underset{\text{tripropyl borane}}{(2CH_3CH_2CH_2)_3B} \xrightarrow[-2H_3BO_3]{6H_2O_2} \underset{\substack{\text{propan-1-ol}\\(C)}}{6CH_3CH_2CH_2OH}$$

It is clear that compound (*A*) and (*C*) are position isomers.

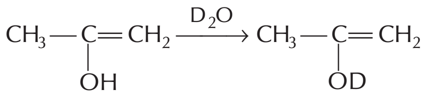
45. Cannizzaro reaction takes place as,



46.

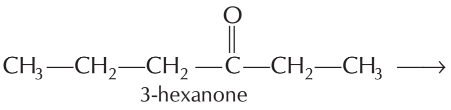


47. After treatment with D_2O, the H^+ ion of —OH group is replaced by D^+ ion, because of being more reactive than deuterium.



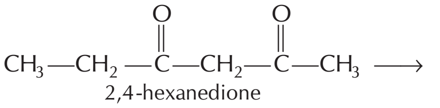
$$CH_3—\underset{\underset{OH}{|}}{C}=CH_2 \xrightarrow{D_2O} CH_3—\underset{\underset{OD}{|}}{C}=CH_2$$

48. A compound that contains a —CH_2— or —CH— group flanked by two electron-withdrawing group such as C=O group, becomes acidic compound and hydrogen atoms are called acidic hydrogen.



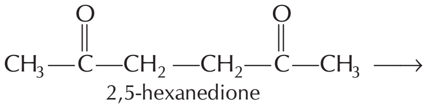
$$\underset{\text{3-hexanone}}{CH_3—CH_2—CH_2—\overset{\overset{O}{\|}}{C}—CH_2—CH_3} \longrightarrow$$

(contains no acidic hydrogen)



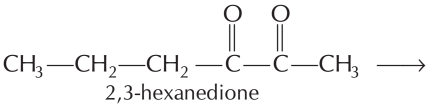
$$\underset{\text{2,4-hexanedione}}{CH_3—CH_2—\overset{\overset{O}{\|}}{C}—CH_2—\overset{\overset{O}{\|}}{C}—CH_3} \longrightarrow$$

(contains 2 acidic hydrogen)



$$\underset{\text{2,5-hexanedione}}{CH_3—\overset{\overset{O}{\|}}{C}—CH_2—CH_2—\overset{\overset{O}{\|}}{C}—CH_3} \longrightarrow$$

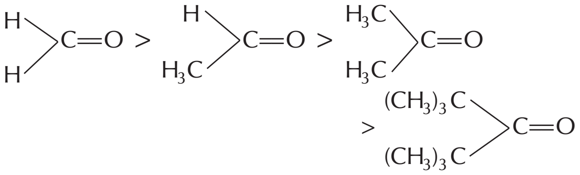
(contains no acidic hydrogen)



$$\underset{\text{2,3-hexanedione}}{CH_3—CH_2—CH_2—\overset{\overset{O}{\|}}{C}—\overset{\overset{O}{\|}}{C}—CH_3} \longrightarrow$$

(contains no acidic hydrogen)

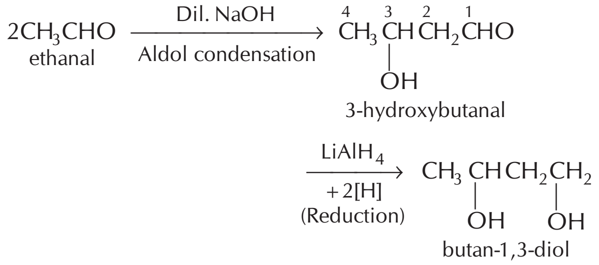
49. As the number and the size of the alkyl groups increases, reactivity decreases. Hence, the reactivity order is



50. When addition of HCN takes place at α, β-unsaturated carbonyl compounds, it gives β-cyano compounds.

$$CH_2=CH—\overset{\overset{O}{\|}}{C}—CH_3 + HCN \xrightarrow{OH^-} NC—CH_2CH_2\overset{\overset{O}{\|}}{C}CH_3$$

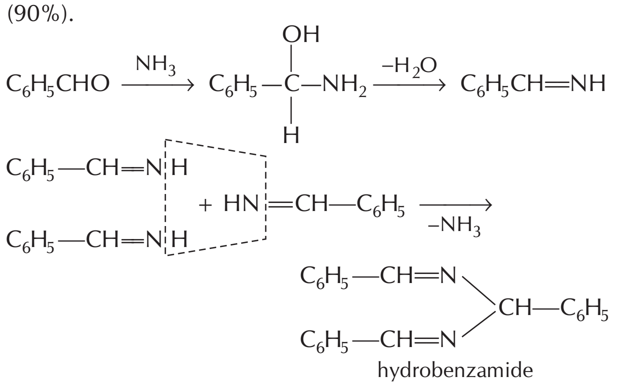
51. Ethanal to butane-1,3-diol



$$\underset{\text{ethanal}}{2CH_3CHO} \xrightarrow[\text{Aldol condensation}]{\text{Dil. NaOH}} \underset{\text{3-hydroxybutanal}}{\overset{4}{C}H_3\overset{3}{C}H(OH)\overset{2}{C}H_2\overset{1}{C}HO}$$

$$\xrightarrow[\substack{+2[H] \\ \text{(Reduction)}}]{\text{LiAlH}_4} \underset{\text{butan-1,3-diol}}{CH_3CH(OH)CH_2CH_2OH}$$

53. Benzaldehyde does not yield a simple addition product with ammonia, but forms a complex product, hydrobenzamide (90%).



$$C_6H_5CHO \xrightarrow{NH_3} C_6H_5-\underset{H}{\overset{OH}{C}}-NH_2 \xrightarrow{-H_2O} C_6H_5CH{=}NH$$

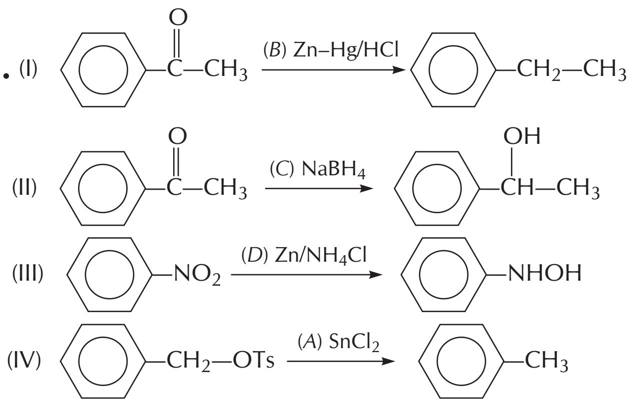
$$2\,C_6H_5-CH{=}NH + HN{=}CH-C_6H_5 \xrightarrow[-NH_3]{} (C_6H_5-CH{=}N)_2CH-C_6H_5$$

hydrobenzamide

54. In Cannizzaro reaction when formaldehyde reacts with other aldehydes lacking α-hydrogen, it is always oxidised and other aldehyde is reduced.

$$HCHO + C_6H_5CHO \xrightarrow[\Delta]{NaOH} HCOO^-Na^+ + C_6H_5CH_2OH$$

55.

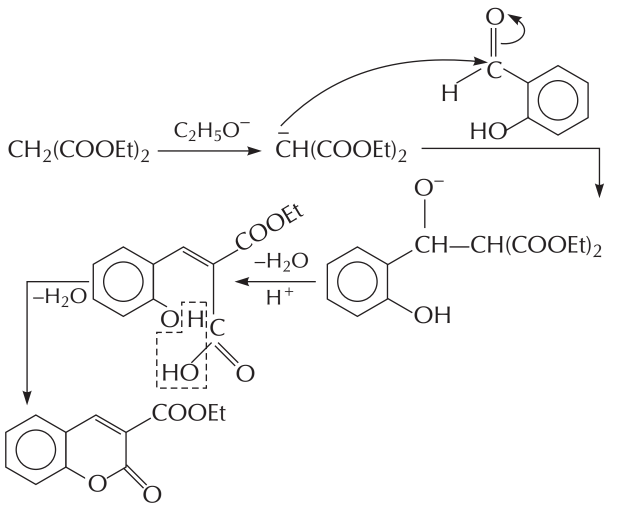


56. Cinnamaldehyde is prepared by the Claisen reaction between benzaldehyde and acetaldehyde.

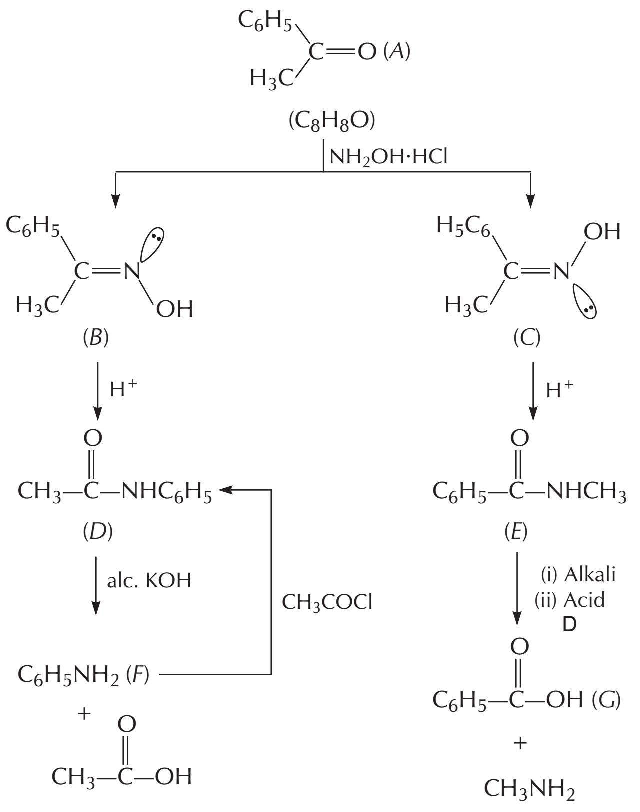
$$C_6H_5CHO + CH_3CHO \xrightarrow{NaOH} \underset{\text{cinnamaldehyde}}{C_6H_5CH{=}CHCHO} + H_2O$$

57. The effect of electron-withdrawing substituent in the benzene ring fastens the Cannizzaro reaction.

58. Formation of α, β-unsaturated carboxylic acid by the action of acetic anhydride and sodium acetate on aromatic aldehyde is known as Perkin reaction. The other Perkin like condensation involve condensation of aromatic aldehyde and α-hydrogen containing compound.



60. The compound is acetophenone.



61. In the carbonyl group, carbon atom is in a state of sp^2 hybridisation. One sp^2 hybrid orbital overlap with a unhybridised *p*-orbital of oxygen to form C—O σ-bond. The remaining two sp^2-orbitals of carbon form σ-bonds with two alkyl groups. Here, all thegroups lie in the same plane.

62. ***Step* I** To determine the molecular formula of the compound.

Element	Percentage	Atomic mass	No. of moles	Simplest molar ratio
C	69.77	12	$\frac{69.77}{12} = 5.81$	$\frac{5.81}{1.16} = 5$
H	11.63	1	$\frac{11.63}{1} = 11.63$	$\frac{11.63}{1.16} = 10$
O	(100 − 69.77 − 11.63) = 18.60	16	$\frac{18.60}{16} = 1.16$	$\frac{1.16}{1.16} = 1$

Empirical formula of the given organic compound = $C_5H_{10}O$.

Molecular formula = $n \times$ (empirical formula)

$$\text{where, } n = \frac{\text{Molecular mass of the compound}}{\text{Empirical formula mass of the compound}}$$

Given, molecular mass = 86

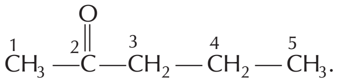
Empirical formula mass of $C_5H_{10}O = (12 \times 5) + (10 \times 1) + (16) = 60 + 10 + 16 = 86$

$$\therefore \quad n = \frac{86}{86} = 1$$

$$\text{Molecular formula} = 1 \times C_5H_{10}O = C_5H_{10}O$$

Thus the structure of the compound can be predicted as

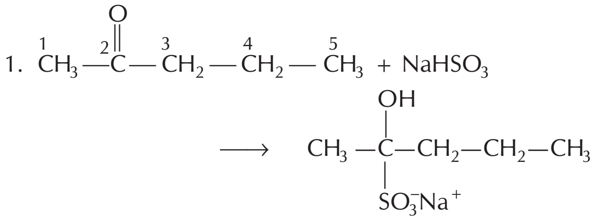
1. Formation of addition compound with $NaHSO_3$ depicts the presence of aldehyde or ketone group.
2. The given compound does not reduce Tollen's reagent but gives positive iodoform test, so it is a methyl ketone.
3. On oxidation, the compound forms a mixture of ethanoic and propanoic acid, so it is



$$\overset{1}{CH_3}-\overset{\overset{O}{\|}}{\underset{2}{C}}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{CH_3}.$$

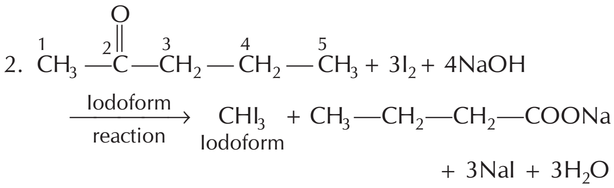
pentan-2-one

The reaction occurring can be shown as

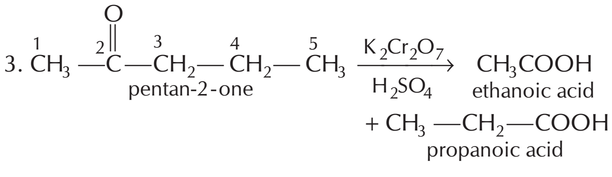


$$1.\ \overset{1}{CH_3}-\overset{\overset{O}{\|}}{\underset{2}{C}}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{CH_3} + NaHSO_3 \longrightarrow CH_3-\underset{SO_3^-Na^+}{\overset{OH}{C}}-CH_2-CH_2-CH_3$$

sodium bisulphite addition product



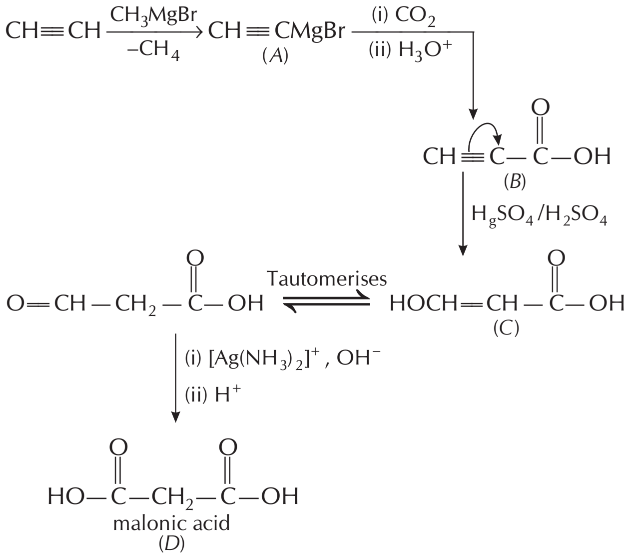
$$2.\ \overset{1}{CH_3}-\overset{\overset{O}{\|}}{\underset{2}{C}}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{CH_3} + 3I_2 + 4NaOH \xrightarrow[\text{reaction}]{\text{Iodoform}} \underset{\text{Iodoform}}{CHI_3} + CH_3-CH_2-CH_2-COONa + 3NaI + 3H_2O$$



$$3.\ \overset{1}{CH_3}-\overset{\overset{O}{\|}}{\underset{2}{C}}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{CH_3} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{ethanoic acid}}{CH_3COOH} + \underset{\text{propanoic acid}}{CH_3-CH_2-COOH}$$

pentan-2-one

64.



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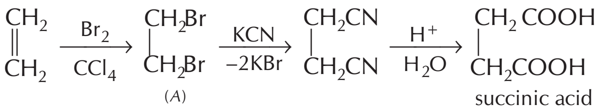
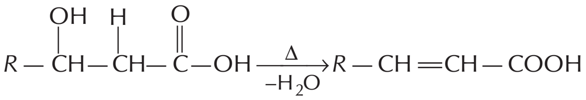


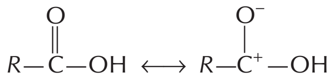
66.



$$R-\overset{OH}{\underset{|}{CH}}-\overset{H}{\underset{|}{CH}}-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[-H_2O]{\Delta} R-CH=CH-COOH$$

67. The reduction of carboxylic acids to alcohols is carried out by $LiAlH_4$ and boranes (BH_3 or B_2H_6) in THF.

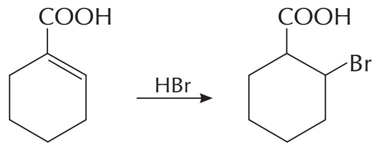
68. In carboxylic acid, the oxygen attached to carboxyl carbon is more electronegative and withdraws the electrons of bond.



$$R-\overset{\overset{O}{\|}}{C}-OH \longleftrightarrow R-\overset{\overset{O^-}{|}}{C^+}-OH$$

Hence, protonation occurs at the carboxyl oxygen.

69. α, β-unsaturated acids add on halogen acids. The mode of addition is contrary to Markownikoff's rule and may be described to the inductive effect of the carboxyl group.



71. Presence of electron withdrawing group (EWG) makes an acid more acidic. As the distance between EWG and —COOH increases, acidity decreases.

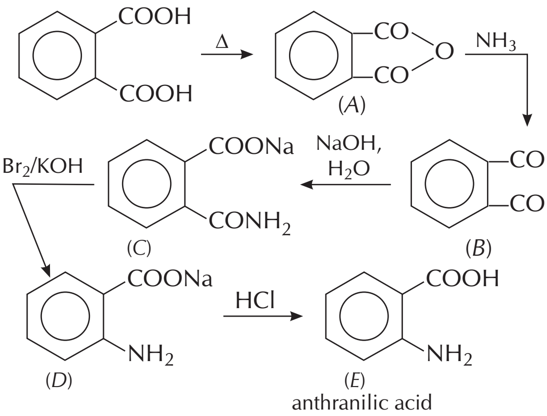
Electron donating group (—OCH_3) decreases the acidic strength. Therefore, increasing order of acidic strength is 4-methoxy benzoic acid < benzoic acid < 4-nitrobenzoic acid < 3,4-dinitrobenzoic acid.

72. Maleic acid contains intramolecular hydrogen bonding while fumaric acid contains intermolecular hydrogen bonding. Thus, maleic acid forms more stable maleate ion after the removal of H^+. Hence, maleic acid is a stronger acid than fumaric acid.

75. β-keto acids are the carboxylic acids that undergo decarboxylation easily.

$$C_6H_5COCH_2\,COOH \xrightarrow{\Delta} C_6H_5COCH_3$$

76.



78. As —CH_3 group has a strong $+I$ effect and —OCH_3 group has a weak $-I$ effect but strong $+R$ effect, hence they increase the electron density on oxygen atom and O—H bond becomes stronger. On the other hand, —NO_2 group has a strong $-I$ and $-R$ effect. It withdraws electrons from benzene ring as well as oxygen atom of —OH group and proton is easily removed. Thus, order of esterification is I > II > III > IV.

79. Carbonic acid is less acidic than carboxylic acids whereas more acidic than phenols and alcohols. Hence, order of acidic strength

$$RCOOH > H_2CO_3 > C_6H_5OH > ROH$$

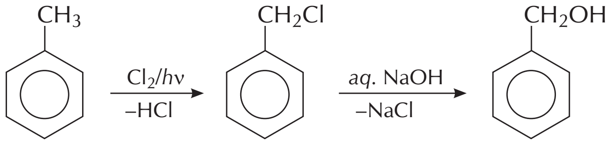
80. In 2,4,6-trinitrobenzoic acid, the decarboxylation takes place most easily, because of $-I$ effect of nitro group, whereas in the dicarboxylic acid with one carbon atom having two carboxylic group it is also easier to remove CO_2. Hence, the order of ease of decarboxylation is

IV > III > II > I

Round II

1. Secondary alcohols give turbidity within 5 min with Lucas reagent.

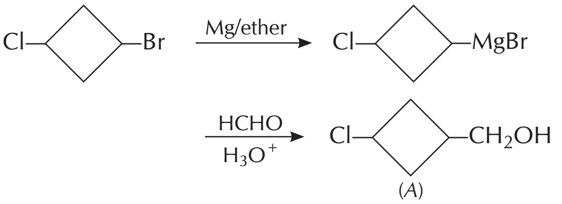
2. On monochlorination in the presence of sunlight, toluene converts into benzyl chloride which on hydrolysis with *aq* NaOH yields benzyl alcohol.



3. Lucas test is used to distinguish between primary, secondary and tertiary alcohols. A mixture of conc HCl + anhy $ZnCl_2$ is called Lucas reagent. In Lucas test, tertiary alcohols immediately give turbidity while secondary alcohols give turbidity after 5 min. Primary alcohols give no reaction with Lucas reagent at room temperature.

Thus, order of reactivity of alcohols is 3° > 2° > 1.

4. C—Br bond is weaker as compared to C—Cl bond.



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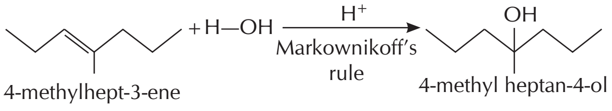

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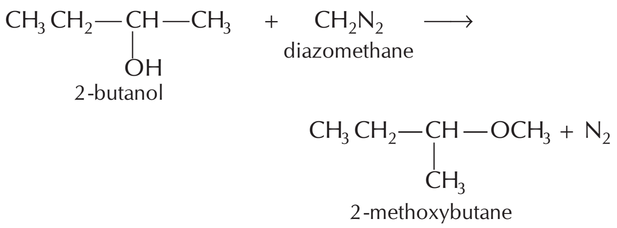
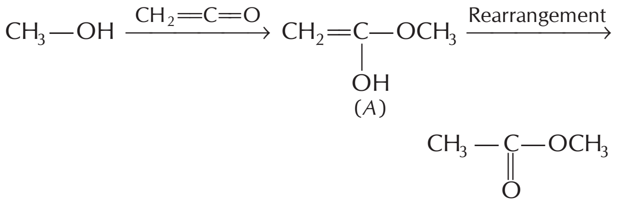


$$CH_3CH_2-\underset{\underset{OH}{|}}{CH}-CH_3 + \underset{\text{diazomethane}}{CH_2N_2} \longrightarrow CH_3CH_2-\underset{\underset{CH_3}{|}}{CH}-OCH_3 + N_2$$

2-butanol

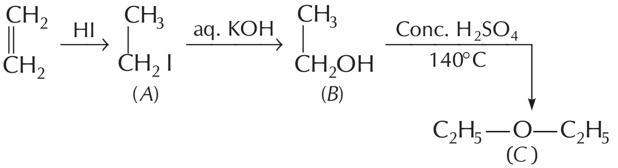
2-methoxybutane

7.



$$CH_3-OH \xrightarrow{CH_2=C=O} \underset{(A)}{CH_2=\underset{\underset{OH}{|}}{C}-OCH_3} \xrightarrow{\text{Rearrangement}} CH_3-\underset{\underset{O}{\|}}{C}-OCH_3$$

8.



$$\begin{array}{c}CH_2\\ \|\\ CH_2\end{array} \xrightarrow{HI} \underset{(A)}{\begin{array}{c}CH_3\\ |\\ CH_2I\end{array}} \xrightarrow{aq.\ KOH} \underset{(B)}{\begin{array}{c}CH_3\\ |\\ CH_2OH\end{array}} \xrightarrow[140^\circ C]{\text{Conc. } H_2SO_4} \underset{(C)}{C_2H_5-O-C_2H_5}$$

Note Ethers are functional isomers of alcohols.

9. Alcohols (—OH) react with sodium and carbonyl compounds ($>C=O$) give precipitate with semicarbazide.

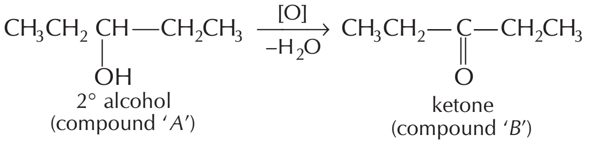
Since, the compound with molecular formula, C_3H_6O does not give precipitate with semicarbazide and does not react with sodium, it is neither a carbonyl compound nor an alcohol. Hence, it must be an ether, *i.e.*, $CH_2=CHOCH_3$

$$CH_2=CHOCH_3 \xrightarrow{Na} \text{no reaction}$$

$$CH_2=CHOCH_3 + \underset{\text{semicarbazide}}{NH_2NHCONH_2} \longrightarrow \text{no reaction}$$

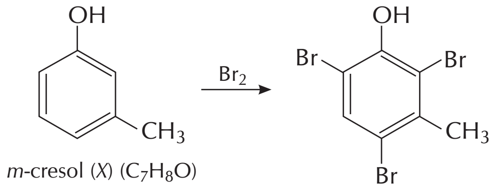
10. Since, the compound '*B*' gave a 2,4-dinitrophenylhydrazine derivative but did not answer haloform test or silver mirrortest, it must contain a $>C{=}O$ group, but it is neither a methyl ketone nor an aldehyde.

Moreover compound '*B*' is obtained by the oxidation of compound *A*, having molecular formula $C_5H_{12}O$, so the compound *A* must be a secondary alcohol.



$$\underset{\substack{\text{2° alcohol}\\\text{(compound 'A')}}}{CH_3CH_2\underset{OH}{\underset{|}{C}H}{-}CH_2CH_3} \xrightarrow[-H_2O]{[O]} \underset{\substack{\text{ketone}\\\text{(compound 'B')}}}{CH_3CH_2{-}\underset{O}{\underset{\|}{C}}{-}CH_2CH_3}$$

11. Compound '*X*' (C_7H_8O) is insoluble in aqueous $NaHCO_3$ but soluble in NaOH, so it is a phenol. Since, the number of carbon atoms remains the same after bromination, the compound must be *meta* cresol and reactions takes place as follows

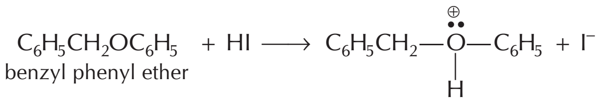


m-cresol (*X*) (C_7H_8O)

2,4,6-tribromo 3-methylphenol

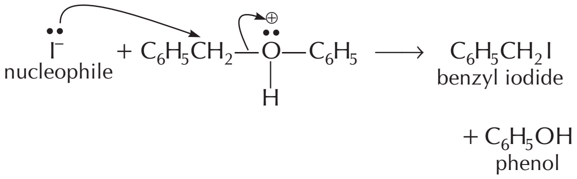
12. Benzyl phenyl ether is an unsymmetrical ether, so halide ion of HI is attached to the simple alkyl group and the reaction takes place by following mechanism :

(i) **Protonation of ether**

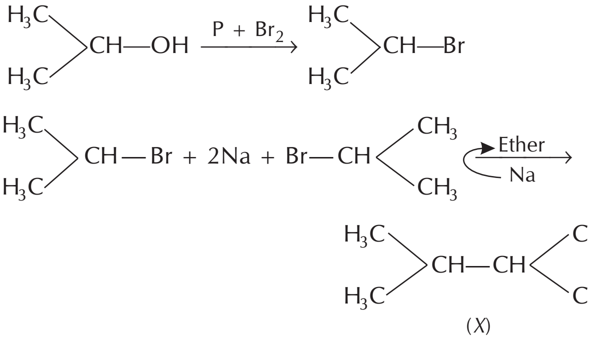


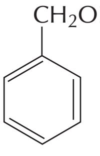
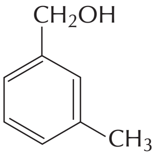
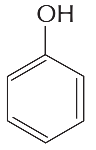
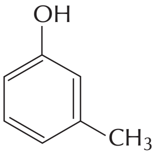
$$\underset{\text{benzyl phenyl ether}}{C_6H_5CH_2OC_6H_5} + HI \longrightarrow C_6H_5CH_2{-}\underset{H}{\underset{|}{\overset{\oplus}{\ddot{O}}}}{-}C_6H_5 + I^-$$

(ii) **Nucleophilic attack**



13.

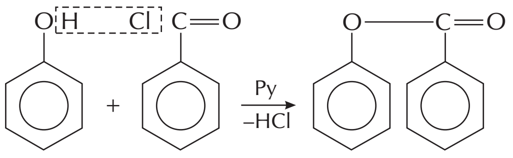


14.  and  are aromatic alcohols due to presence of benzene ring and —OH group is attached with aliphatic carbon.  and  are phenols.

15. In the Rosenmund's reaction, acid chlorides are converted to corresponding aldehydes by catalytic reduction. The reaction is carried out by passing through a hot solution of the acid chloride in the presence of Pd deposited over $BaSO_4$. Here, barium sulphate decrease the activity of palladium.

$$RCOCl + H_2 \xrightarrow{Pd/BaSO_4} RCHO + HCl$$

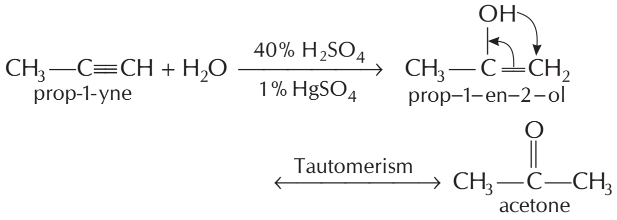
16.



phenol benzoyl chloride phenylbenzoate

17. Acetone (ketone) and benzaldehyde (aromatic aldehyde) both do not react with Fehling solution. With aliphatic aldehydes, Fehling solution give red precipitate of cuprous oxide.

18.



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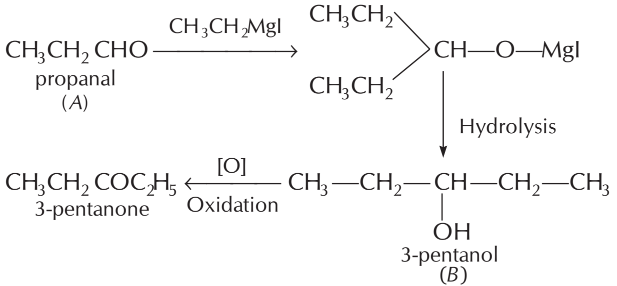

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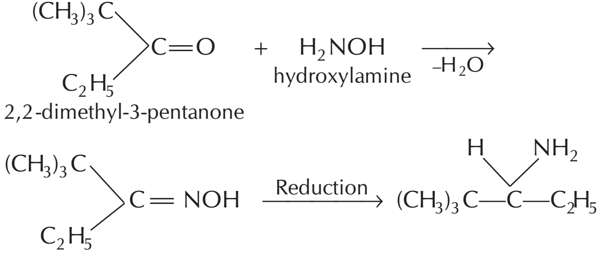
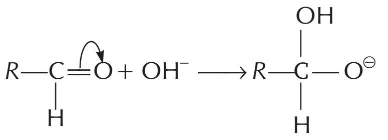
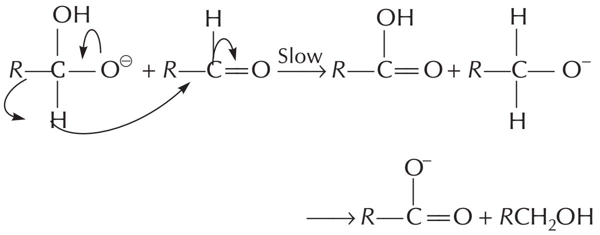


21. Cannizzaro reaction involves oxidation as well as reduction of aldehydes having lack of α-H atom. The mechanism of this reaction is as

(i) Attack of OH^- on carbonyl carbon



(ii) Transfer of hydride ion

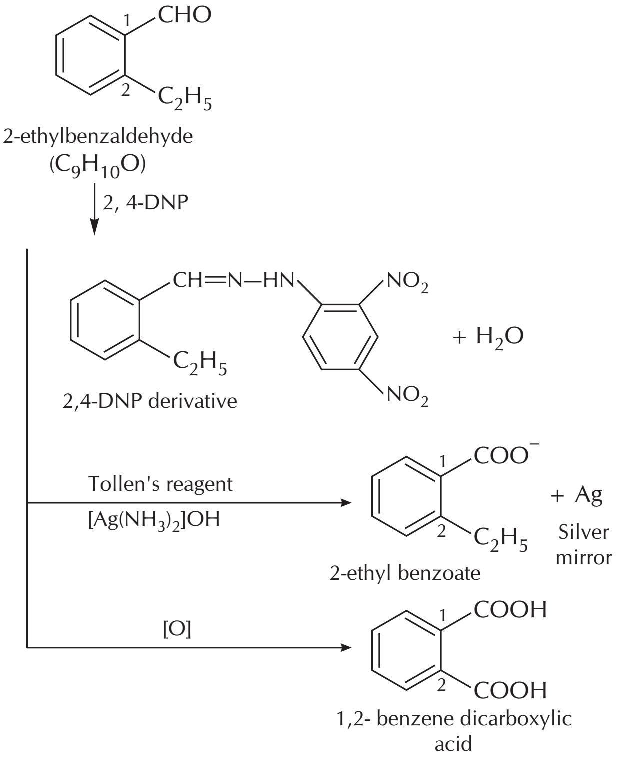


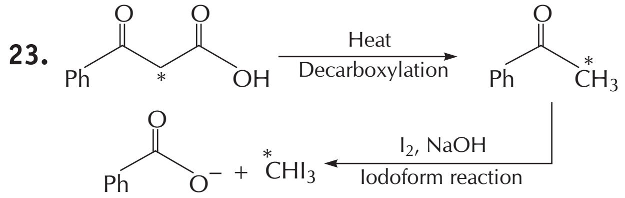
22. (i) The compound with molecular formula $C_9H_{10}O$ forms a 2,4-DNP derivative and reduces Tollen's reagent, so it is an aldehyde.

(ii) It undergoes Cannizzaro reaction, so the aldehyde group should be directly attached to the benzene ring.

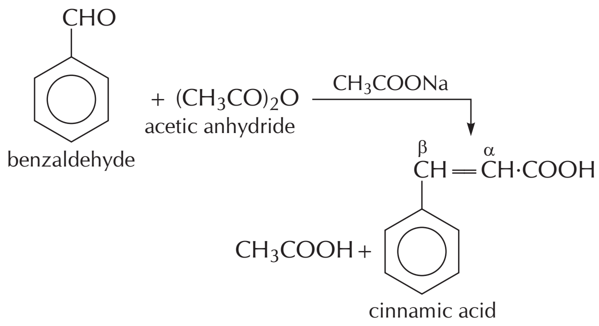
(iii) On vigorous oxidation, it gives 1,2-benzene dicarboxylic acid, so it should be an *ortho* substituted benzaldehyde. For molecular formula $C_9H_{10}O$, the possibility is only *o*-ethyl benzaldehyde.

(iv) The equations for all the reactions are given below

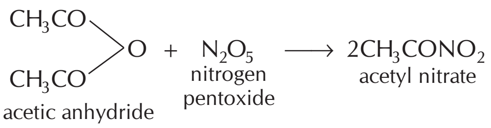


23. 

24. Perkin reaction is the condensation reaction in which aromatic aldehyde is heated with an anhydride of an aliphatic acid in the presence of sodium salt of the same acid to form α, β-unsaturated acid.



25. Acetyl nitrate is formed, when acetic anhydride reacts with nitrogen pentoxide.



$$\underset{\text{acetic anhydride}}{(CH_3CO)_2O} + \underset{\text{nitrogen pentoxide}}{N_2O_5} \longrightarrow \underset{\text{acetyl nitrate}}{2CH_3CONO_2}$$

26. $\underset{\text{acetic acid}}{CH_3COOH} \xrightarrow{NH_3} \underset{\text{ammonium acetate}}{CH_3COONH_4} \xrightarrow[-H_2O]{\Delta} \underset{\text{acetamide}}{CH_3CONH_2}$

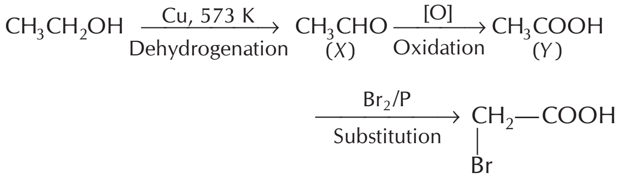
The isomers of CH_3CONH_2 is

(I) NH_2CH_2CHO (II) $CH_3—CH═NOH$

(III) $HCONH—CH_3$

27.

Column I	Column II
(A) CH_3CONH_2 and PCl_5	Acetonitrile
(B) $—NO_2$ group	Acid strengthening
(C) Lactic acid	Optically active compound
(D) CH_3COOH and Na	Hydrogen gas is liberated.

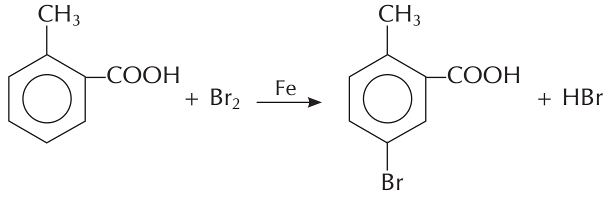
28. 

$$CH_3CH_2OH \xrightarrow[\text{Dehydrogenation}]{\text{Cu, 573 K}} \underset{(X)}{CH_3CHO} \xrightarrow[\text{Oxidation}]{[O]} \underset{(Y)}{CH_3COOH} \xrightarrow[\text{Substitution}]{Br_2/P} \underset{Br}{\underset{|}{CH_2}}—COOH$$

29. $\underset{\text{formic acid}}{2HCOOH} + \underset{\text{sodium carbonate}}{Na_2CO_3} \longrightarrow 2HCOONa + CO_2 + H_2O$

$HCOOH + \underset{\text{Tollen's reagent}}{Ag_2O} \longrightarrow H_2O + CO_2 + \underset{\text{black ppt. (silver mirror)}}{2Ag}$

30. —COOH is *meta*-directing group.

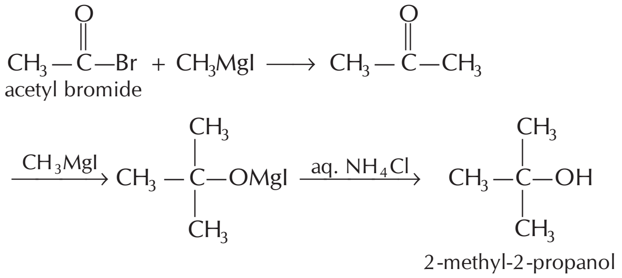


31. Aqueous NaCl is neutral hence, there is no reaction between ethyl acetate and aqueous NaCl.

$$CH_3COOC_2H_5 + NaCl(aq) \longrightarrow \text{No reaction}$$

32. Formic acid has $-\overset{\overset{O}{\|}}{C}-H$ (aldehyde) group. It reduces Tollen's reagent to silver mirror like other aldehydes.

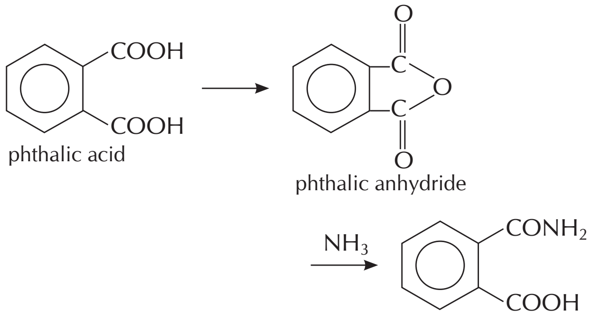
33.



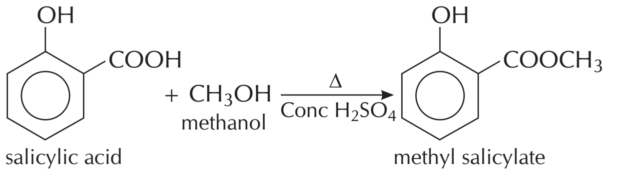
$$\underset{\text{acetyl bromide}}{CH_3-\overset{\overset{O}{\|}}{C}-Br} + CH_3MgI \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

$$\xrightarrow{CH_3MgI} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OMgI \xrightarrow{aq.\ NH_4Cl} \underset{\text{2-methyl-2-propanol}}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH}$$

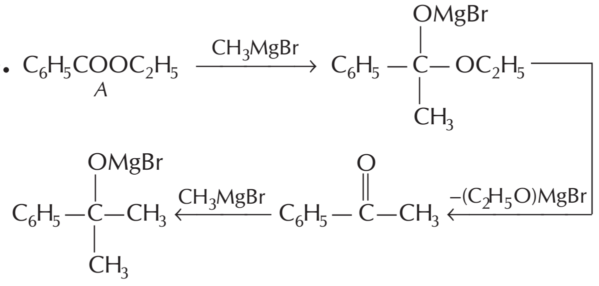
34.



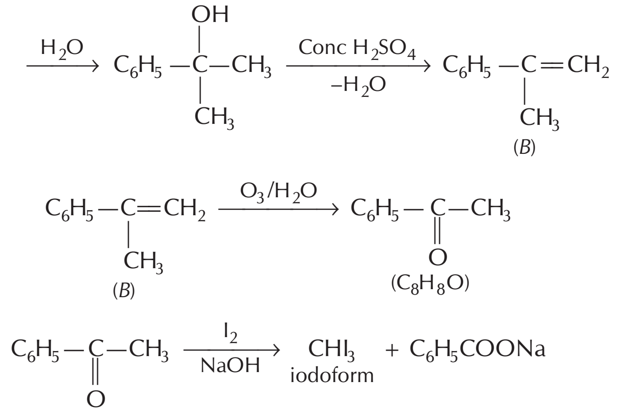
35. Methanol reacts with salicylic acid in the presence of a few drops of conc. H_2SO_4 to give methyl salicylate having the smell of oil of winter green.



36.



$$\underset{A}{C_6H_5COOC_2H_5} \xrightarrow{CH_3MgBr} C_6H_5-\underset{\underset{CH_3}{|}}{\overset{\overset{OMgBr}{|}}{C}}-OC_2H_5 \xrightarrow{-(C_2H_5O)MgBr} C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{CH_3MgBr} C_6H_5-\underset{\underset{CH_3}{|}}{\overset{\overset{OMgBr}{|}}{C}}-CH_3$$

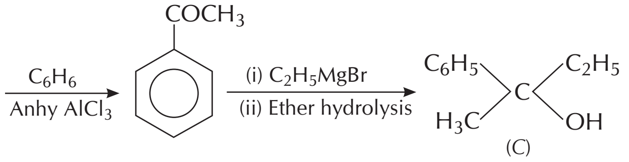


$$\xrightarrow{H_2O} C_6H_5-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3 \xrightarrow[-H_2O]{Conc\ H_2SO_4} \underset{(B)}{C_6H_5-\underset{\underset{CH_3}{|}}{C}=CH_2}$$

$$\underset{(B)}{C_6H_5-\underset{\underset{CH_3}{|}}{C}=CH_2} \xrightarrow{O_3/H_2O} \underset{(C_8H_8O)}{C_6H_5-\underset{\underset{O}{\|}}{C}-CH_3}$$

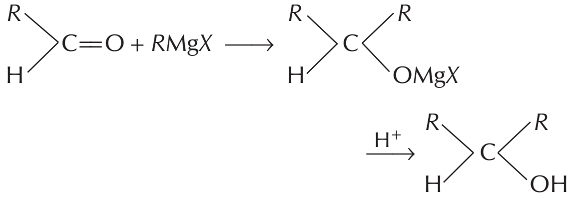
$$C_6H_5-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[NaOH]{I_2} \underset{\text{iodoform}}{CHI_3} + C_6H_5COONa$$

37. $CH_3COOH + PCl_5 \longrightarrow \underset{(A)}{CH_3COCl}$

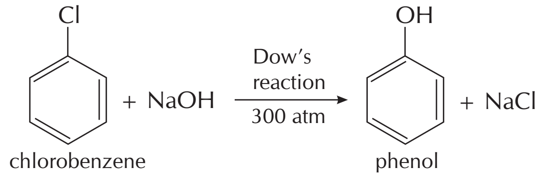


38. $RCHO \xrightarrow{\text{Reduction}} RCH_2OH$

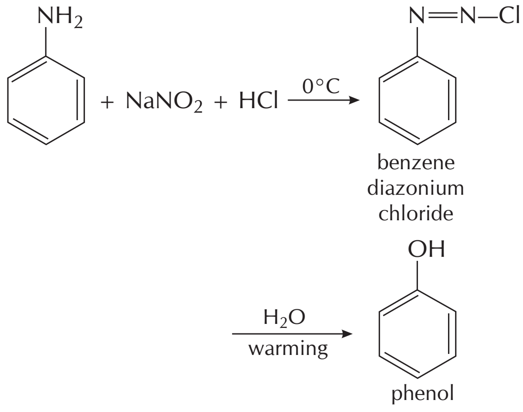
$H_2/Pd, LiAlH_4, NaBH_4$ reduce aldehyde into alcohol having same number of alcohol whereas $RMgX$ followed by hydrolysis reduces aldehyde into alcohol having extra R from Grignard reagent.



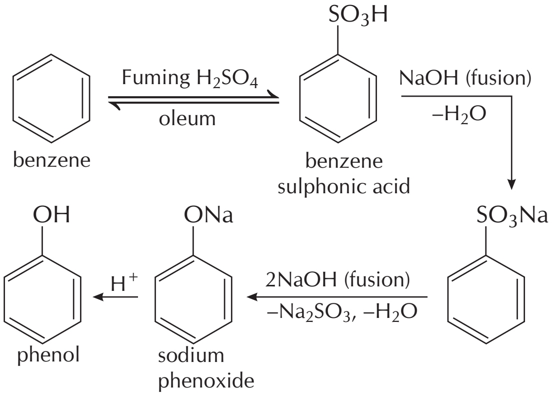
39. (a)



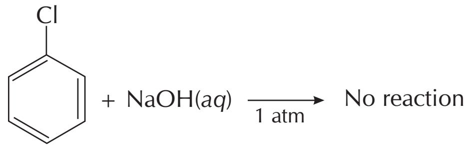
(b)



(c)



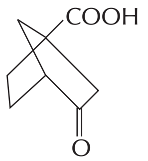
(d)



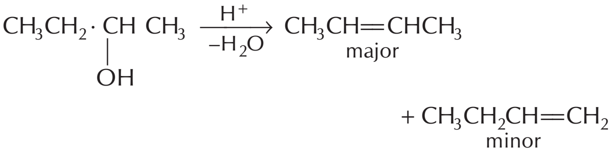
40. Compound having α-H-atom, undergo aldol condensation.

Therefore, CH_3—CHO and $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ cannot show this condensation.

41. In Clemmensen reduction, $>C{=}O$ group of carbonyl compounds is reduced into methylene group (—CH_2—) in the presence of zinc amalgam and conc.HCl.

42. Upon gently heating β-keto acids, *gem*-dicarboxylic acids lose CO_2.  though is a β-keto acid, but it does not lose CO_2 since —COOH group is present at bridge and produces unstable transition state or intermediate (carbanion) after losing CO_2.

43.

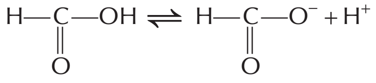


$$CH_3CH_2\cdot\underset{\underset{OH}{|}}{CH}\,CH_3 \xrightarrow[-H_2O]{H^+} \underset{\text{major}}{CH_3CH{=}CHCH_3} + \underset{\text{minor}}{CH_3CH_2CH{=}CH_2}$$

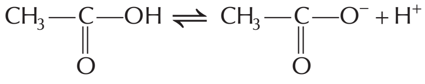
Dehydration leading to conjugation occurs faster.

44. CH_3CO— group in acetophenone being electron withdrawing reduces the electron-density at the benzene ring, thereby preventing further electrophilic substitution.

45. Formic acid is stronger than acetic acid.

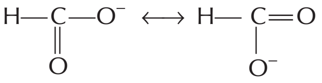


$$H-\underset{\underset{O}{\|}}{C}-OH \rightleftharpoons H-\underset{\underset{O}{\|}}{C}-O^- + H^+$$



$$CH_3-\underset{\underset{O}{\|}}{C}-OH \rightleftharpoons CH_3-\underset{\underset{O}{\|}}{C}-O^- + H^+$$

46. In formate ion, resonance gives rise to identical bond lengths.



$$H-\underset{\underset{O}{\|}}{C}-O^- \longleftrightarrow H-\underset{\underset{O^-}{|}}{C}{=}O$$

47. In ethers, two bond pairs and two lone pairs of electrons on oxygen are arranged approximately in tetrahedral manner. The bond angle is slightly greater than tetrahedral angle due to the repulsive forces between the two bulky alkyl groups.

48. $CH_3CH_2Br + CH_3ONa \longrightarrow CH_3CH_2OCH_3$ is an example of S_N2 reaction.

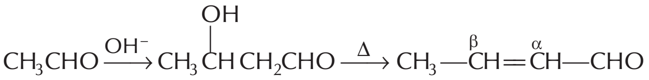
49. Williamson's ether synthesis reaction follows S_N2 mechanism.

Thus, the order of reactivity is

$$\underset{(C)}{ClCH_2CH_3CH_3} > \underset{(D)}{BrCH_2CH_2CH_3} > \underset{(B)}{ClCH_2CH{=}CH_2} > \underset{(A)}{(CH_3)_3CCH_2Br}$$

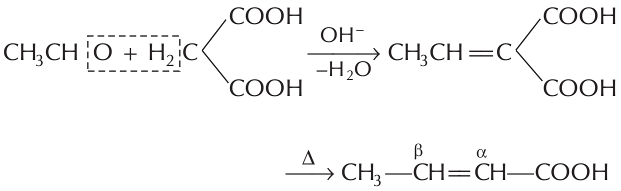
50. Williamson's synthesis is an example of nucleophilic substitution reaction.

51. In first test tube



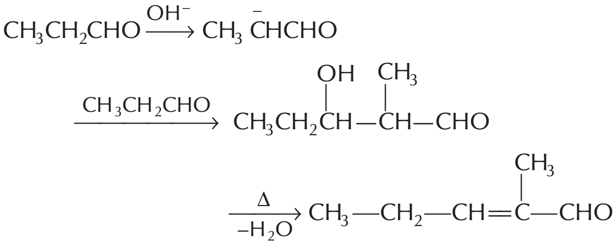
$$CH_3CHO \xrightarrow{OH^-} CH_3\overset{\overset{OH}{|}}{C}H\,CH_2CHO \xrightarrow{\Delta} CH_3-\overset{\beta}{C}H{=}\overset{\alpha}{C}H-CHO$$

In second test tube



52. Diels' Alder reaction is the addition between conjugated dienes (1, 3-butadiene) and a dienophile (compound containing a double bond and a – *M* group in conjugation). Hence, the products from both the test tubes can show Diels'-Alder reaction.

53. Aldol condensation involves only the α-hydrogen of aldehyde.



$$CH_3CH_2CHO \xrightarrow{OH^-} CH_3\overset{-}{C}HCHO \xrightarrow{CH_3CH_2CHO} CH_3CH_2\overset{\overset{OH}{|}}{C}H-\overset{\overset{CH_3}{|}}{C}H-CHO \xrightarrow[-H_2O]{\Delta} CH_3-CH_2-CH{=}\overset{\overset{CH_3}{|}}{C}-CHO$$

54. The HVZ reaction brings about halogenation only at the α- carbon of the fatty acid. In case the acid has two α-hydrogens, α-dihalo product will be formed when 2 equivalents of halogen are used.

55. The α-halogen comes from halogen (Cl_2 or Br_2) whatever might be the nature of PX_3 which is used for converting acid to acid chloride.

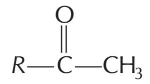
56. To undergo HVZ reaction, the carboxylic acid must have at least one α-hydrogen at sp^3 hybridised α-carbon atom.

57. Iodoform is formed from

(i) CH_3CH_2OH

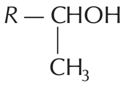
(ii) CH_3CHO

(iii) All carbonyl compounds of the type

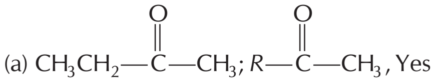


$R—\overset{\overset{O}{\|}}{C}—CH_3$

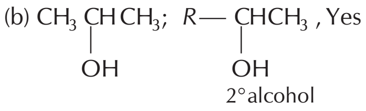
(iv) 2° alcohol



$R—\underset{\underset{CH_3}{|}}{C}HOH$

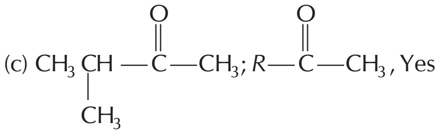


(a) $CH_3CH_2—\overset{\overset{O}{\|}}{C}—CH_3; R—\overset{\overset{O}{\|}}{C}—CH_3$, Yes

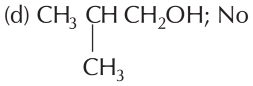


(b) $CH_3\underset{\underset{OH}{|}}{C}HCH_3;\ R—\underset{\underset{OH}{|}}{C}HCH_3$, Yes

2° alcohol

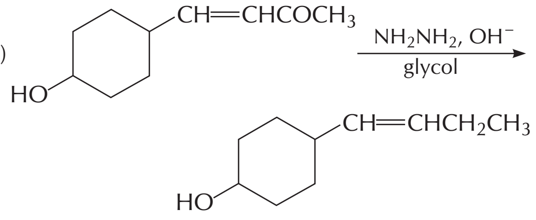


(c) $CH_3\underset{\underset{CH_3}{|}}{C}H—\overset{\overset{O}{\|}}{C}—CH_3; R—\overset{\overset{O}{\|}}{C}—CH_3$, Yes



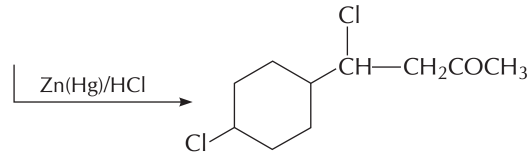
(d) $CH_3\underset{\underset{CH_3}{|}}{C}HCH_2OH$; No

58. (a)



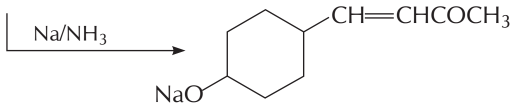
(Wolff-Kishner)

(b)



HCl attacks 2° alcohol as well as (C═C) bond.

(c)

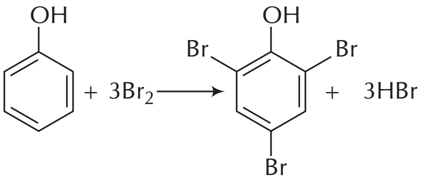


(d) $\xrightarrow{NaBH_4}$ low yield

59. Br_2 is formed by a redox reaction

$$5Br^- + BrO_3^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$$

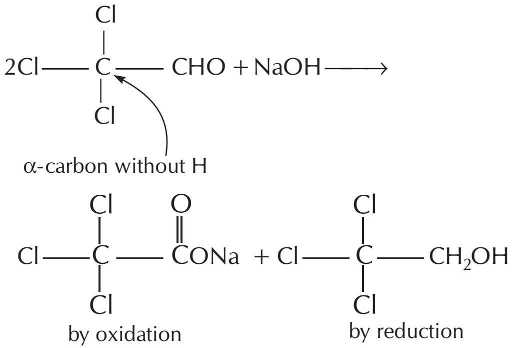
—OH group is the activating group and there is S_E at *o*-and *p*-positions giving yellowish white precipitate of 2,4,6-tribromophenol.



60.

	Reagent	Phenol	Benzoic acid	Conclusion
(a)	Aqueous NaOH	Salt formation	Salt formation	No specific colour change
(b)	Tollen's reagent	No effect	No effect	
(c)	Molisch reagent	No effect	No effect	
(d)	Neutral $FeCl_3$	Violet colour	Buff-coloured precipitate	Thus, $FeCl_3$ can be used to make distinction

61. Cannizzaro's reaction is given by aldehydes (*R*CHO) lacking H at α-carbon or lacking α-carbon (as in HCHO). With NaOH, there is formation of acid salt ($RCOO^-$) by oxidation and alcohol (RCH_2OH) by reduction.



(2,2,2-trichloroethanol)

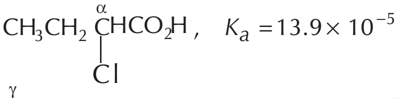
62. Electron withdrawing group (– *I* effect) stabilises the anion, and thus increases acidic nature.

Thus, (c), (d) > (a) acidic

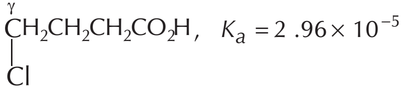
Farther the electron withdrawing group from the —COOH group, acid strength decreases thus (c) with Cl at α-position is stronger than (d) with Cl at γ-position.

CH_3COOH, $K_a = 1.75 \times 10^{-5}$

$HCOOH$, $K_a = 17.7 \times 10^{-5}$

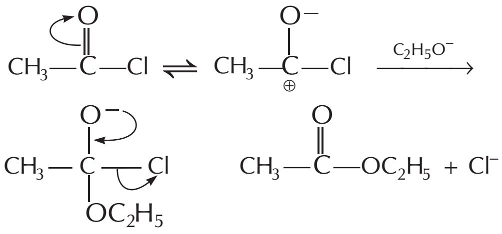


$CH_3CH_2\underset{\underset{Cl}{|}}{\overset{\alpha}{C}}HCO_2H$, $K_a = 13.9 \times 10^{-5}$



$\underset{\underset{Cl}{|}}{\overset{\gamma}{C}}H_2CH_2CH_2CO_2H$, $K_a = 2.96 \times 10^{-5}$

But from the K_a values, it is clear that HCOOH is the strongest acid. This can be explained on the basis of absence of + *I* showing group.

63. 

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl \rightleftharpoons CH_3-\overset{O^-}{\overset{|}{C^{\oplus}}}-Cl \xrightarrow{C_2H_5O^-} CH_3-\overset{O^-}{\overset{|}{\underset{OC_2H_5}{\underset{|}{C}}}}-Cl \quad CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 + Cl^-$$

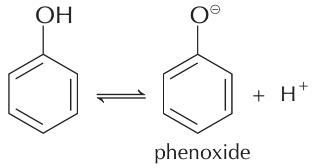
This is by S_N reaction. Cl^- is a better leaving group than $C_2H_5O^-$ and the ethyl ethanoate is formed.

64. All aldehydes including reducing sugar (as glucose, fructose) give **silver-mirror test** (with Tollen's reagent)

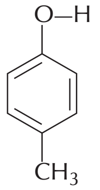
$$RCHO + 2[Ag(NH_3)_2]^+ + 3OH^- \xrightarrow{\Delta} RCOO^- + \underset{\text{silver mirror}}{2Ag\downarrow} + 4NH_3 + 2H_2O$$

$$(R = H, CH_3)$$

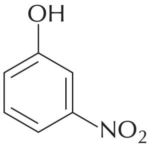
Thus (a) and (c) give silver-mirror test.

65. I. 

Acidic due to resonance stabilisation of phenoxide ion.

II. 

—CH_3 group releases electrons, destabilises the phenoxide ion, thus acidic nature is decreased hence II < I (acidic)

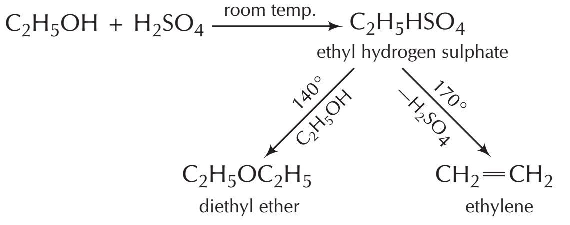
III. 

—NO_2 withdraws electrons, stabilises the phenoxide ion, hence acidity is increased.

IV. Lower acidity in case of *meta*-isomer as compared to *para*-isomer is explained by the fact that *m*-nitrophenoxide is stabilised by inductive effect only and no resonance effect operates with –NO_2 group.

Thus, $\underset{\text{(III)}}{m\text{-nitrophenol}} < \underset{\text{(IV)}}{p\text{-nitrophenol}}$ (acidic)

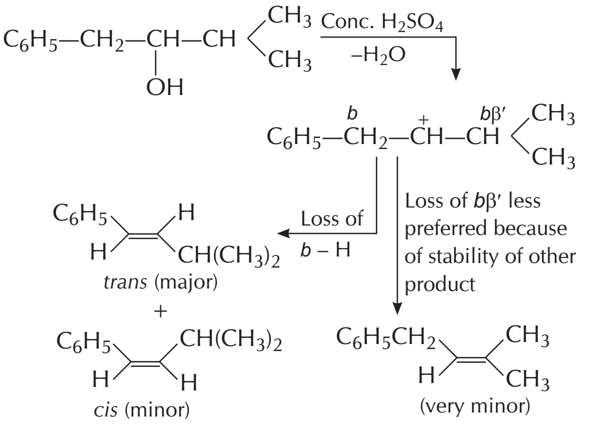
Thus, correct order is IV > III > I > II

66. 

(a), (b), (d) may be formed but (c) is never formed.

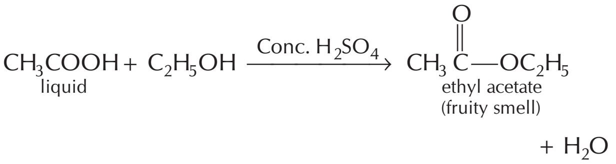
67. The reaction of alcohol with conc. HCl and anhydrous $ZnCl_2$ follows S_N1 pathway, so greater the stability of carbocation formed, faster is the reaction.

2-methylpropan-2-ol gives 3° carbocation. Hence, it reacts rapidly with conc. HCl and anhydrous $ZnCl_2$ (Lucas reagent).

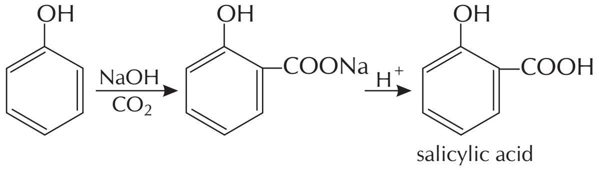
68. 

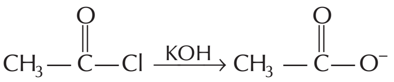
69. A liquid + $C_2H_5OH \xrightarrow{\text{Conc. } H_2SO_4} \underset{\text{(fruity smell)}}{\text{Compound}}$

Fruity smell is the characteristic property of ester, thus reaction can be considered as follows



$$\underset{\text{liquid}}{CH_3COOH} + C_2H_5OH \xrightarrow{\text{Conc. } H_2SO_4} \underset{\substack{\text{ethyl acetate}\\\text{(fruity smell)}}}{CH_3\overset{O}{\overset{\|}{C}}-OC_2H_5} + H_2O$$

70. 

71. 

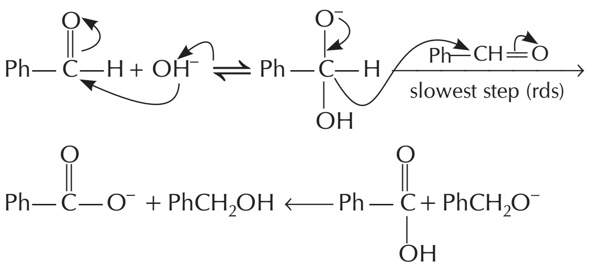
$$CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{KOH} CH_3-\overset{O}{\overset{\|}{C}}-O^-$$

$$CH_3CH_2Cl \longrightarrow CH_3CH_2OH$$

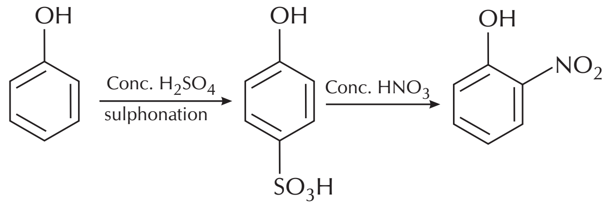
$$ClCH_2-CH_2Cl \longrightarrow HOCH_2-CH_2OH$$

$$CH_3CHCl_2 \longrightarrow \underset{\text{intermediate}}{CH_3-CH(OH)_2} \longrightarrow \underset{\text{acetaldehyde}}{CH_3-CH=O}$$

72. In Cannizzaro reaction, the transfer of H^- to another carbonyl group is difficult and slowest step.

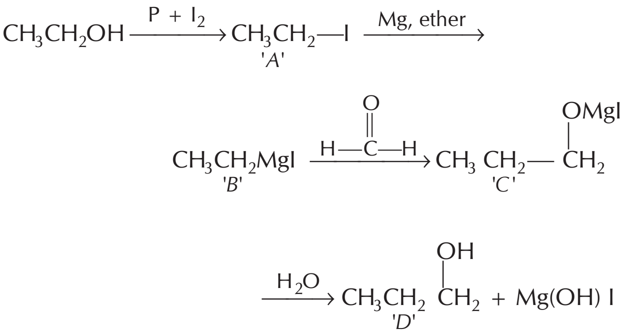


73.



First sulphonation is the means to block *para* position and to reduce the reactivity of phenolic ring against strong oxidising agent HNO_3. (The use of conc. HNO_3 over phenol cause the oxidation of ring mainly). The strong acidic medium in second step cause desulphonation (ipso mechanism) also.

74.



$$CH_3CH_2OH \xrightarrow{P + I_2} \underset{'A'}{CH_3CH_2—I} \xrightarrow{\text{Mg, ether}}$$

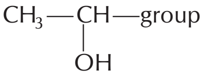
$$\underset{'B'}{CH_3CH_2MgI} \xrightarrow{H—\overset{\overset{O}{||}}{C}—H} \underset{'C'}{CH_3\,CH_2—\overset{\overset{OMgI}{|}}{CH_2}}$$

$$\xrightarrow{H_2O} \underset{'D'}{CH_3CH_2\,\overset{\overset{OH}{|}}{CH_2}} + Mg(OH)\,I$$

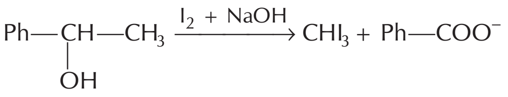
n-propyl alcohol

75. Any aliphatic carbon with hydrogen attached to it, in combination with benzene ring, will be oxidised to benzoic acid by $KMnO_4 / H^+$.

76. For positive iodoform test, alcohol molecule must have

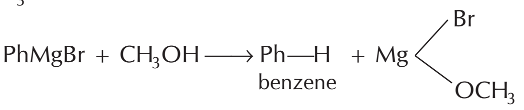


$CH_3—\underset{\underset{OH}{|}}{CH}—\text{group}$



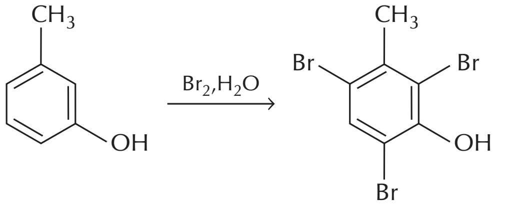
$$Ph—\underset{\underset{OH}{|}}{CH}—CH_3 \xrightarrow{I_2 + NaOH} CHI_3 + Ph—COO^-$$

77. PhMgBr can be protonated by any of the protic solvent e.g., CH_3OH.



$$PhMgBr + CH_3OH \longrightarrow \underset{\text{benzene}}{Ph—H} + Mg\begin{matrix}\diagup Br\\ \diagdown OCH_3\end{matrix}$$

78. *m*-cresol due to phenoxide ion in H_2O solvent, gives tribromo derivative at all *ortho* and *para* positions.

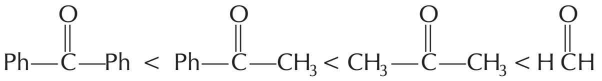


79. $CHCl_3 + OH^{\ominus} \longrightarrow \underset{\text{(unstable)}}{{}^{\ominus}CCl_3} + H_2O$

$${}^{\ominus}CCl_3 \longrightarrow \underset{\text{dichlorocarbene}}{:CCl_2} + Cl^-$$

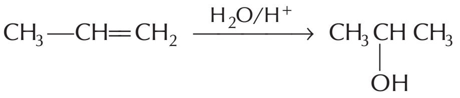
80. Addition of HCN is a nucleophilic reaction. Greater the electron deficiency of carbonyl group, higher the rate of reaction.

Hence,



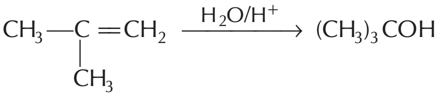
$$Ph—\overset{\overset{O}{||}}{C}—Ph < Ph—\overset{\overset{O}{||}}{C}—CH_3 < CH_3—\overset{\overset{O}{||}}{C}—CH_3 < H\overset{\overset{O}{||}}{C}H$$

81. $CH_2{=}CH_2 \xrightarrow{H_2O/H^+} CH_3CH_2OH$



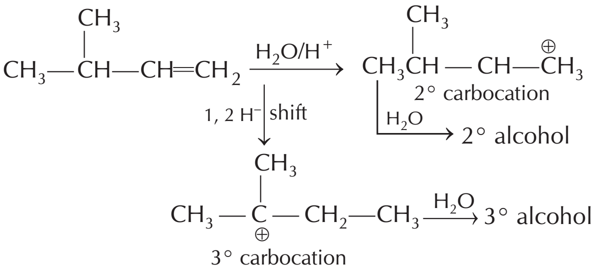
$$CH_3—CH{=}CH_2 \xrightarrow{H_2O/H^+} CH_3\underset{\underset{OH}{|}}{CH}CH_3$$

(2°alcohol) through 2° carbocation $CH_3\overset{\oplus}{C}HCH_3$



$$CH_3—\underset{\underset{CH_3}{|}}{C}{=}CH_2 \xrightarrow{H_2O/H^+} (CH_3)_3COH$$

(3° alcohol) through 3° carbocation $(CH_3)_3\overset{\oplus}{C}$

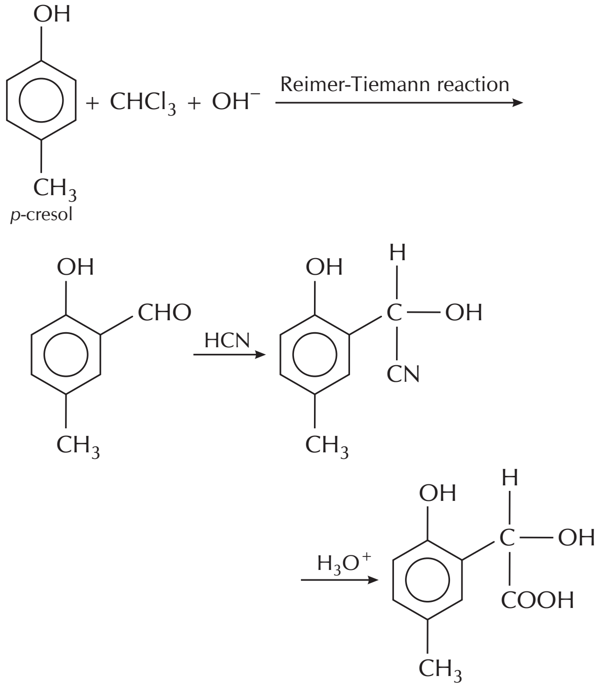


$$CH_3—\overset{\overset{CH_3}{|}}{CH}—CH{=}CH_2 \xrightarrow{H_2O/H^+} CH_3\overset{\overset{CH_3}{|}}{CH}—\underset{2°\text{ carbocation}}{CH}—\overset{\oplus}{CH_3} \xrightarrow{H_2O} 2°\text{ alcohol}$$

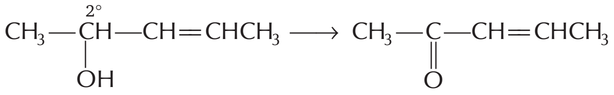
$$\downarrow 1,2\,H^-\text{ shift}$$

$$\underset{3°\text{ carbocation}}{CH_3—\underset{\oplus}{\overset{\overset{CH_3}{|}}{C}}—CH_2—CH_3} \xrightarrow{H_2O} 3°\text{ alcohol}$$

82.



(—OH is more activating than —CH_3 in *o*, *p*- directing, thus —CHO goes to *ortho wrt* —OH).

83. 

$$CH_3-\underset{OH}{\overset{2^\circ}{C}H}-CH=CHCH_3 \longrightarrow CH_3-\underset{O}{\underset{\|}{C}}-CH=CHCH_3$$

Only suitable reagent is chromic anhydride in glacial acetic acid. Other will also affect (C═C) bond.

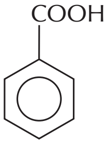
84. $A + NaOH \longrightarrow$ alcohol + acid

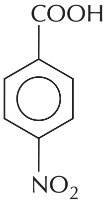
Thus, it is Cannizzaro reaction.

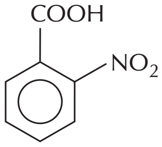
A is thus aldehyde without H at α-carbon.

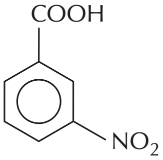
(as C_6H_5CHO, HCHO)

$$2C_6H_5CHO + NaOH \longrightarrow C_6H_5CH_2OH + C_6H_5COONa$$

85. (I) 

(II) 

(III) 

(IV) 

—NO_2 group at any position shows electron withdrawing effect, thus acid strength is increased. But *o*-nitro benzoate ion is stabilised by intramolecular H-bonding like forces, hence its acid strength is maximum. Thus,

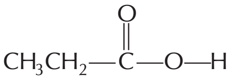
the order of acid strength is (II) > (III) > (IV) > (I)

The effect is more at *para* position than *meta*.

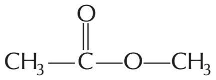
86. Protonation of —OH is the first step. It involves conversion of poor leaving group (—OH) into good leaving group $(—\overset{+}{O}H_2)$.

87. $C_nH_{2n}O_2$ is general formula for open chain acids and esters.

$n = 3$ $C_3H_6O_2$

Acid, 

$$CH_3CH_2-\overset{O}{\overset{\|}{C}}-O-H$$

Ester, 

$$CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3$$

88. $LiAlH_4$ reduces —COOH to —CH_2OH without affecting C═C bond.

12

Organic Compounds Containing Nitrogen

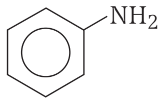
JEE Main MILESTONE

- General Characteristics of Amines
- Methods of Preparation of Aliphatic Amines
- Properties of Aliphatic Amines
- Methods of Preparation of Aromatic Amines
- Properties of Aromatic Amines
- Uses of Amines

12.1 General Characteristics of Amines

Aliphatic and aromatic amines are alkyl and aryl derivatives of ammonia in which one or more hydrogen atoms of ammonia have been replaced by alkyl and aryl groups respectively, *e. g.*,

CH_3NH_2
aliphatic amine



aromatic amine

They occur in nature in protiens, vitamins, hormones and alkaloids. Their synthetic examples include drugs, dyes and polymers.

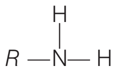
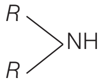
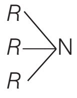
Amines, diazonium salts, nitro compounds, cyanides all are included in nitrogen containing organic compounds. These are obtained by replacing one or more H*-atoms of hydrocarbons with different groups like* $-NH_2$, $-N_2Cl$, $-NO_2$ *or* $-CN$ *group.*

Classification of Amines

Depending upon the number of alkyl or aryl groups attached to the nitrogen atom, the aliphatic or aromatic amines are classified as primary (1°), secondary (2°) and tertiary (3°) amines. If number of H-atoms attached to the N atoms is n, the degree of amines is obtained by the following formula

Degree of amine = $(3 - n)°$

Table 12.1 **Degree and Functional Group of Various Amines**

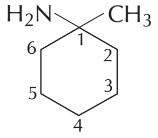
S. N.	Amine	n (no. of H-atoms attached to N)	Degree	Functional group
1.	 $R-\overset{\overset{H}{\vert}}{N}-H$	2	$(3-2)° = 1°$ (primary)	$-NH_2$
2.		1	$(3-1)° = 2°$ (secondary)	$-NH-$
3.		$n = 0$	$(3-0)° = 3°$ (tertiary)	

Quaternary ammonium salts ($R_4N^+X^-$) are the ammonium compounds formed by the replacement of all the four hydrogen atoms with either alkyl or aryl groups. Here X is normally a halogen atom or hydroxyl group. Ammonium salts are quite different from amines in the sense that amines are of basic nature, the salts are not.

Sample **Problem 1** *Which of the following is a* 3° amine? **[NCERT Exemplar]**

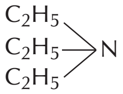
- (a) 1-*methylcyclohexylamine*
- (b) *Triethylamine*
- (c) *tert-butylamine*
- (d) *N-methylaniline*

Interpret (*b*) In order to solve such problems, first draw the structures of the given compounds and then find whether it contains N⩽ group or not. If such a group is present, the amine is tertiary.

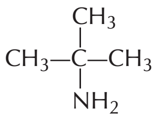


1-methylcyclohexylamine
(—NH_2 group, so 1° amine)

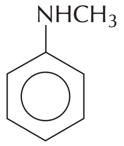
$(C_2H_5)_3N$ or



(>N group, so 3° amine)



tertiary-butylamine
(—NH_2 group, so 1° amine)

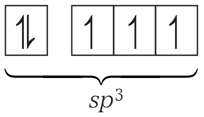


N-methylaniline
(>NH group, so 2° amine)

Hence, among the given compounds, only triethylamine is a 3° (tertiary,) amine.

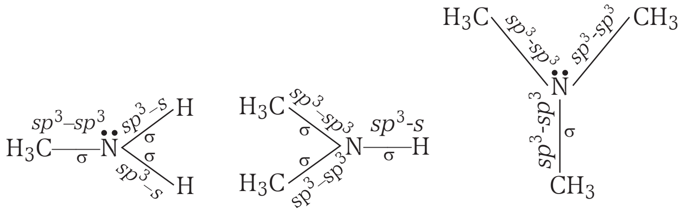
Structure of Amines

$$N_7 = 1s^2, 2s^2\, 2p^3$$



Nitrogen atom possesses four sp^3 hybridised orbitals. In amines, out of these four, three sp^3 hybridised orbitals, overlap either with the sp^3 hybridised orbitals of —CH_3 group (alkyl group) or with the s orbital of –H atom or with both to form three σ bonds. The remaining fourth sp^3 hybridised orbital, being completely filled, does not take part in bond formation. Here it is obvious that there are three σ bonds and one lone pair over nitrogen in amines. Thus, all amines, *i.e.*, 1°, 2° and 3° have pyramidal geometry.

The structures of the amines can be shown as



(primary amine) (secondary amine) (tertiary amine)

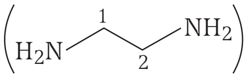
Caution Point *Tertiary amines having three different alkyl groups, generally exist in the form of racemic mixture that cannot be resolved into enantiomers because of the rapid inversion of an enantiomer to its mirror image. This inversion is called amine inversion or nitrogen inversion or flipping.*

Nomenclature of Amines

IUPAC system propossed following rules for nomenclature of amines.

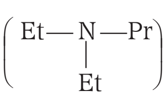
(a) For Alkyl Amine

According to IUPAC system, amines are named as alkanamines, derived by the replacement of '*e*' of alkane by the word amines *e.g.*, CH_3NH_2 is named as methanamine, $C_2H_5NH_2$ as ethanamine and $C_3H_7NH_2$ as propanamine. In case more than one amino groups are present at different positions in the parent chain, their positions are mentioned by giving numbers to the C atom bearing (—NH_2) groups and suitable prefix such as di, tri, etc., is attached to the amine. The word 'e' of alkane is retained, *e.g.*,



is named ethane-1,2-diamine.

Common name An aliphatic amine is named by prefixing alkyl group to amine, *i.e.*, alkylamine as one word, *e.g.*, methylamine. 2° and 3° amines, containing same two or more groups, are named by prefix *di* of *tri* attached before the name of the alkyl group, *e.g.*,



$$\left(\begin{array}{c}\text{Et—}\underset{\displaystyle\text{Et}}{\underset{|}{\text{N}}}\text{—Pr}\end{array}\right)$$

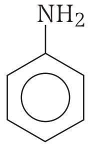
is named diethyl propyl amine.

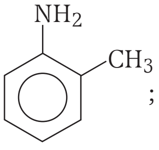
(b) For Aromatic Amines

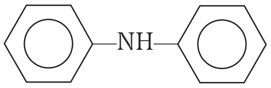
When an (—NH_2) group is directly attached to the benzene ring, the compound formed is called an arylamine; (Ph—NH_2) is the simplest example of arylamine. In the common system, it is called aniline, also an accepted IUPAC name.

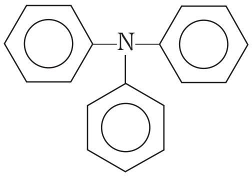
According to IUPAC system, suffix '*e*' of arene is replaced with 'amine'. *e.g.*, (Ph—NH_2) is named benzenamine.

Common names of some aromatic amines are as


aniline
(phenyl amine)


o-toluidine


diphenyl amine


triphenyl amine

Sample Problem 2 *The correct IUPAC name for* $CH_2{=}CHCH_2NHCH_3$ *is* **[NCERT Exemplar]**

(*a*) *Allylmethylamine* (*b*) *2-amino-4-pentene*
(*c*) *4-aminopent-1-ene* (*d*) *N-methylprop-2-en-1-amine*

Interpret (*d*) $H_2\overset{3}{C}{=}\overset{2}{C}H\overset{1}{C}H_2NHCH_3$

[preference order > NH > =]
N-methylprop-2-en-1-amine

Isomerism in Amines

Amines exhibit chain, position, functional isomerism and metamerism, (For their details see chapter isomerism).

Hot Spot 1

BASIC CHARACTER of Amines

It is a very important topic of this chapter from JEE Main point of view. The question is generally based on 'order of basicity'. The level of question varies from easy to difficult.

All amines are basic due to the presence of lone pair of electron for protonation. Their basicity, *i.e.,* availability of lone pair for protonation is affected by the following three factors

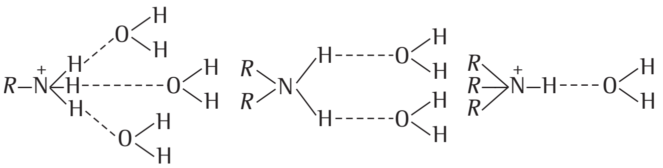
(i) Alkyl group substitution (+ *I* effect)
(ii) Steric effect
(iii) Solvation effect

Alkyl group have +*I* effect, thus as their number increases, the electron density over nitrogen increases. Hence, the lone pair will become more available for protonation and results in increased basicity. An evidence in support of this is that in the gas phase, the basicity of the following amines increases with increase in the number of methyl groups.

$$(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$$

However, in aqueous solution, the third methyl group decreases the basic strength due to steric effect. This is because the size of the methyl group is more than that of hydrogen so it hinders the attack of the acid on the amine and thus, the basic strength tends to decrease. **Greater the number of methyl groups, lesser will be basic strength.** In this case, trimethylamine is expected to be the least basic.

Solvation Effect also affect basicity as amine gets protonated by accepting a H^+ ion from aqueous solution. The protonated amine forms hydrogen bonds with H_2O molecules and gets solvated. Consequently, the cation is stabilised in aqueous solution. **[Greater the solvation of cation, more will be the tendency of amine to change to cation by releasing the electron pair on nitrogen atom. Thus, more will be the basic strength of the amine.]** Since solvation is maximum in primary amine, it is expected to be maximum basic while tertiary amine is the least basic.


Tendency for solvation decreases

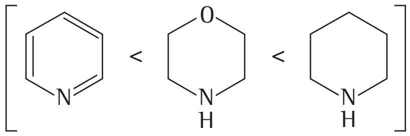
From the above discussion it is clear that the order of basic character in aqueous solution (where steric and solvation effects also work), is

$$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$$

Presence of an electron withdrawing group (like —CN, >CO etc.) decreases the electron density and thus also the availability of lone pair for donation over nitrogen decreases.

The order of basic strength of other compounds is

(i) $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$
(ii) $(CH_3)_2CHNH_2 > NH_3 > [(CH_3)_2CH]_2NH > [(CH_3)_2CH]_3N$
(iii) aniline < CH_3NH_2 (due to resonance effect in aniline)
(iv) pyrrole < aniline < pyridine
(v) diphenylamine < aniline < cyclohexylamine
(vi) pyridine < morpholine (– *I* effect of O atom) < piperidine (non-aromatic and sp^3 hybridised)



The basic character of amines can be explained in terms of their K_b or pK_b values. **Larger the K_b or smaller the value of pK_b, stronger is the base.** The pK_b value of NH_3 is 4.75. Aliphatic amines are stronger bases then NH_3, due to the $+I$ effect of alkyl groups leading to high electron density on the N atom. Aromatic amines are weaker bases than NH_3 due to the electron-withdrawing nature of aryl group.

Table 12.2 **pK_b Values of Substituted Anilines**
(pK_b of aniline $= 9.38$)

Substituent	pK_b	Substituent	pK_b
o-CH_3	9.62	*o*-OCH_3	9.51
p-CH_3	9.00	*p*-OCH_3	8.71
m-CH_3	9.33	*m*-OCH_3	9.80
o-OH	9.28	*o*-Cl	13.30
p-OH	8.50	*p*-Cl	10.00
m-OH	9.83	*m*-Cl	11.52
o-NH_2	9.52	*o*-NO_2	14.28
p-NH_2	7.86	*p*-NO_2	13.02
m-NH_2	9.00	*m*-NO_2	11.55

The relative base strength of various aromatic amines in the decreasing order is as

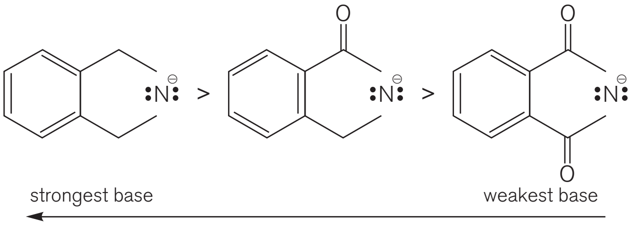
(i) *p*-toluidine > *m*-toluidine > aniline > *o*-toluidine
(ii) aniline > *m*-nitroaniline > *p*-nitroaniline > *o*-nitroaniline
(iii) *p*-methoxyaniline > aniline > *o*-methoxyaniline > *m*-methoxyaniline

The basicity of *o*-substituted anilines (whether the substitutent is electron releasign or electron withdrawing) is generally lower as compared to aniline. This is due to *ortho* effect in which the substituent at the *o*-position hinders the attack of the acid on the amino group.

In general, **more the *s*-character of the hybrid orbital containing lone pair of electrons, lesser is the basic character.** For example, out of , $R\ddot{N}H_2(sp^3)$, $R\ddot{N}{=}CHR_2(sp^2)$ and $RC{\equiv}\ddot{N}(sp)$, RNH_2 is most basic (25% *s*-character of hybrid orbital containing lone pair of electrons) and $RC{\equiv}\ddot{N}$ is least basic (50% *s*-character of the hybrid orbital containing lone pair of electron). Therefore, decreasing order of basicity of these compound is

$$\underset{(25\%\ s\text{-character})}{R\ddot{N}H_2} > \underset{(33.33\%\ s\text{-character})}{R\ddot{N}{=}CHR'} > \underset{(50\%\ s\text{-character})}{RC{\equiv}N\colon}$$

Caution Point *A carbonyl group attached to the nitrogen stabilises its negative charge. The strongest base is the anion that has no carbonyl groups on nitrogen; the weakest base is the phthalimide anion which has two carbonyl groups.*

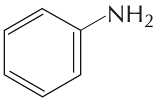


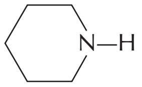
Sample Problem 3 *Amongst the following, the strongest base in aqueous medium is* **[NCERT Exemplar]**

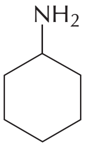
(a) CH_3NH_2 (b) $NCCH_2NH_2$
(c) $(CH_3)_2NH$ (d) $C_6H_5NHCH_3$

Interpret (c) In aqueous medium, basic tendency is affected by $+I$ effect of alkyl group as well as steric effect. Among the given, $(CH_3)_2NH$ is most basic because of the presence of two electron donating $—CH_3$ groups which increase electron density over N of $—NH_2$ group and thus, facilitate the removal of its lone pair.

Sample Problem 4 *Which of the following is the weakest Bronsted base?* **[NCERT Exemplar]**

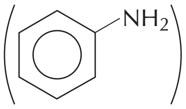
(a) 

(b) 

(c) 

(d) CH_3NH_2

Interpret (a) Basic tendency of a Bronsted base is infact the tendency of accepting a proton by donating its lone pair to the proton.

Among the given, aniline  is least basic because of the involvement of its lone pair is resonance and hence its less availability for donation.

12.2 Methods of Preparation of Aliphatic Amines

Several methods can be used to prepare aliphatic amines, out of which some are specific for 1°, 2° and 3° amines while some gives mixtures of all the three.

Methods for Mixtures of Amines

With the help of following methods, mixture of amines can be obtained.

(a) Hofmann's Ammonolysis Method

When alkyl halide is heated with alcoholic solution of ammonia in a sealed tube at about 393 K, a mixture of amines is obtained. This reaction is called Hofmann's ammonolysis method.

$$RI \xrightarrow[-HI]{NH_3/393\ K} \underset{(1^\circ)}{R\ddot{N}H_2} \xrightarrow[-HI]{RI} \underset{(2^\circ)}{R_2\ddot{N}H} \xrightarrow[-HI]{RI} \underset{(3^\circ)}{R_3\ddot{N}}$$
$$\xrightarrow[-HI]{RI} \underset{\substack{\text{quaternary}\\ \text{ammonium}\\ \text{salt}}}{[R_4\overset{+}{N}]I^-}$$

This reaction follows the S_N2 mechanism.

Primary amine is the main product, if excess of ammonia is used.

Caution Point *Aniline is not obtained by this method as* C—*X bond in alkyl halide is quite strong and does not cleave easily. However aryl halides activated by electron withdrawing group at ortho/para position, gives this reaction.*

But when vapours of ammonia are passed through a mixture of chlorobenzene and cuprous oxide at 473 *K under* 60 *atmospheric pressure, aniline is formed.*

$$C_6H_5Cl + 2NH_3 + Cu_2O \xrightarrow{473\ K,\ 60\ atm} C_6H_5NH_2 + Cu_2Cl_2 + H_2O$$

This method is fully described in properties of alkyl halides.

Sample Problem 5 *Benzylamine may be alkylated as shown in the following equation*

$$C_6H_5CH_2NH_2 + R-X \longrightarrow C_6H_5CH_2NHR$$

Which of the following alkyl halides is best suited for this reaction through S_N1 *mechanism?* **[NCERT Exemplar]**

(*a*) CH_3Br (*b*) C_6H_5Br
(*c*) $C_6H_5CH_2Br$ (*d*) C_2H_5Br

Interpret (*c*) S_N1 mechanism involves cleavage of C—*X* bond to give a carbocation intermediate. Thus, the halide that gives more stable carbocation is best suited for the reaction.

The stability order of carbocation obtained from the given halides is

$$C_6H_5CH_2^+ > C_2H_5^+ > CH_3^+ > C_6H_5^+$$

Thus, $C_6H_5CH_2Br$ is best suited for the given reaction.

(b) Reaction of Alcohols with Ammonia

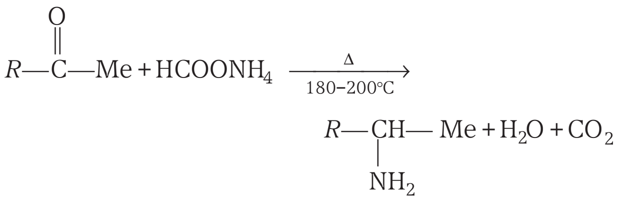
When vapours of a mixture of alcohol and ammonia are passed over heated alumina or thoria (ThO_2) at 620 K, a mixture of amines is obtained, *i.e.*,

$$ROH + NH_3 \xrightarrow[620\ K]{Al_2O_3} RNH_2 + H_2O$$
$$RNH_2 + ROH \longrightarrow R_2NH + H_2O$$
$$R_2NH + ROH \longrightarrow R_3N + H_2O$$
$$R_3N + ROH \longrightarrow R_4\overset{+}{N}OH^-$$

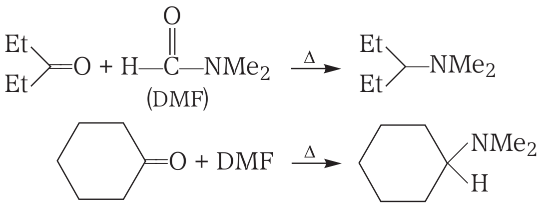
If NH_3 is taken in large excess, RNH_2 is obtained as main product.

(c) Leuckart Reaction

Ketones on reductive amination with $HCOONH_4$ (ammonium formate) or with DMF (dimethylformamide, $H-\overset{\overset{\large O}{\|}}{C}-NMe_2$) give amines. This reaction is called Leuckart reaction.



$$R-\overset{\overset{O}{\|}}{C}-Me + HCOONH_4 \xrightarrow[180-200^\circ C]{\Delta} R-\underset{\underset{NH_2}{|}}{CH}-Me + H_2O + CO_2$$



Methods for Primary Amines Only

With the help of the following methods, only primary amines can be prepared.

(a) Reduction

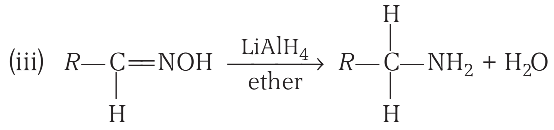
Alkyl nitriles, nitroalkanes, oximes and amides, all on reduction give primary amines as

(i) $$RC\equiv N \xrightarrow[LiAlH_4]{Reduction} RCH_2NH_2$$

(Reduction of nitriles to primary amines by using Na and alcohol is called **Mendius reaction**).

Caution Point *Mendius reaction helps in increasing number of carbon atom in the main chain.*

(ii) $$RNO_2 + 3H_2 \xrightarrow[\substack{\text{or LAH, or } H_2/Pt\\ \text{or metal/acid}}]{Ni/250^\circ} RNH_2 + 2H_2O$$



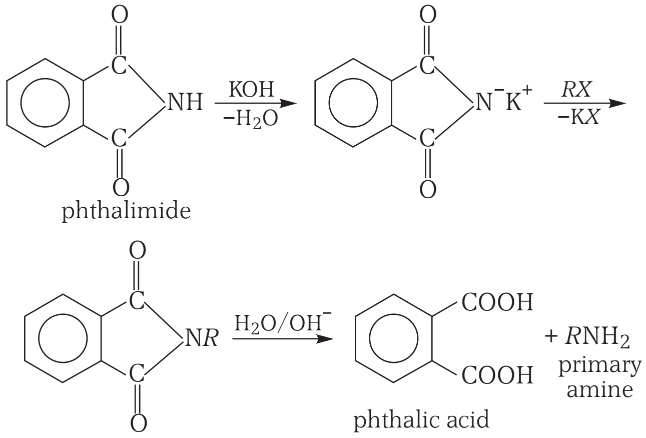
$$\text{(iii)}\quad R\text{—}\underset{\substack{|\\ H}}{C}\text{=NOH} \xrightarrow[\text{ether}]{\text{LiAlH}_4} R\text{—}\overset{\substack{H\\ |}}{\underset{\substack{|\\ H}}{C}}\text{—NH}_2 + H_2O$$

(The best reducing agent for the purpose is LAH but Na/alcohol or H_2 + Ni can also be used).

(iv) $RCONH_2 \xrightarrow{\text{LiAlH}_4} RCH_2NH_2 + H_2O$

(b) Gabriel Phthalimide Synthesis

This reaction is used for the preparation of 1° amine (aliphatic as well as aromatic amines having electron withdrawing group at *o*-and *p*-positions, *e.g.*, —NO_2 group). In this reaction, phthalimide on treatment with ethanolic KOH forms potassium salt of phthalimide which on heating with *RX* followed by either alkaline hydrolysis or hydrazinolysis with hydrazine ($H_2N \cdot NH_2$) produces the corresponding 1° amine. 1° atomatic amine (except those containing electron withdrawing group at *o*- and *p*-positions, *e.g.*, —NO_2 group) cannot be synthesised by this method because Ar*X* does not undergo S_N reaction with anion formed by phthalimide.



Sample **Problem 6** *Which of the following cannot be prepared by Gabriel method from their corresponding halides of tosylates?*

I. t-butylamine,	*II. Neopentylamine*
III. Diethylamine,	*IV. p-toluidine*
V. m-nitroaniline	*VI. Vinylamine,*
VII. p-nitroaniline	*VIII. o-nitroaniline, and*
IX. Allylamine	

The correct answer is

(a) I, II, III, IV, V, VI	*(b) I, II, VI, VII, VIII*
(c) II, III, IV, V, VI, VIII	*(d) All of these*

Interpret (*a*) Halides or tosylates which are unreactive in S_N2 cannot be used.

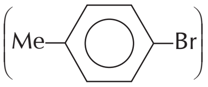
(I) to (VI) cannot be prepared but (VII) to (IX) can be prepared.

I. It cannot be prepared since Me_3C—X is a 3° halide.

II. It cannot be prepared since Me_3C—CH_2—*X* is neopentyl halide and does not undergo S_N2 reaction due to steric hindrance.

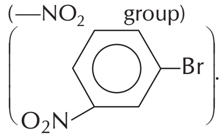
III. It cannot be prepared since 2° amine gives poor yield due to elimination.

IV. It cannot be prepared, since arylhalide



is not activated by electron donating group (Me group). ArSN reaction takes place only when the benzene ring is activated by electron withdrawing group present at *o* - and *p*-positions.

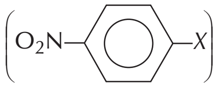
V. It cannot be prepared, since electron with drawing group (—NO_2 group) is present at *m*-position



. ArS_N reaction does not take place.

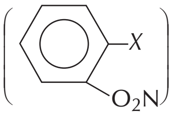
VI. It cannot be prepared, since vinyl halides (CH_2=CH—*X*) are unreactive in S_N2 reactions.

VII. It can be prepared, since benzene ring



is activated by electron withdrawing group (—NO_2 group) at *p*-position and hence ArS_N reaction takes place.

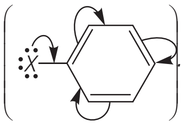
VIII. It can be prepared, since benzene ring



is activated by electron with drawing group (—NO_2 group) at *o*-position and hence ArS_N reaction takes place.

IX. It can be prepared, since allyl halides (CH_2=$CHCH_2X$) can undergo S_N2 reaction.

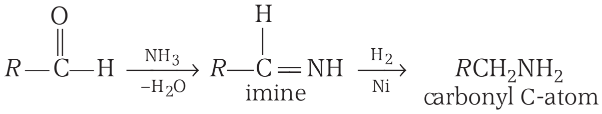
Caution Point *Aryl halides are unreactive towards* S_N2 *reaction, due to resonance stabilisation*



. But, Ar*X containing electron-withdrawing groups at o-and p-positions activates the benzene ring for* ArS_N *reaction. That is why o-and p-nitroaniline can be prepared but* Ar*X containing e-donating groups cannot be used for the preparation of corresponding amines.*

(c) Reductive Amination of Carbonyl Compounds

When a mixture of carbonyl compound, hydrogen and ammonia is passed over Ni catalyst at high temperature, primary amine is formed. The reaction probably goes through the formation of an imine as

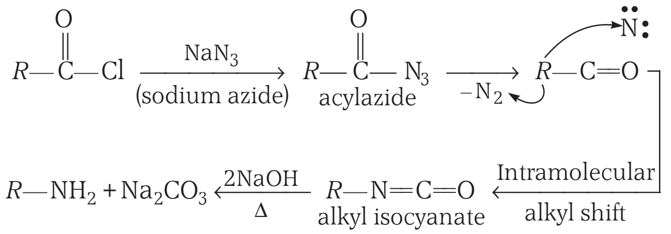


$$R\text{—}\overset{\substack{O\\ \|}}{C}\text{—H} \xrightarrow[-H_2O]{NH_3} \underset{\text{imine}}{R\text{—}\overset{\substack{H\\ |}}{C}\text{=NH}} \xrightarrow[\text{Ni}]{H_2} \underset{\text{carbonyl C-atom}}{RCH_2NH_2}$$

The other catalyst used in place of Ni can be $NaBH_3CN$ (sodium cyanoborohydride).

(d) Curtius Method

In this method, acyl chloride is used to prepare primary amine through acyl azide formation as



$$R-\overset{\overset{\large O}{\|}}{C}-Cl \xrightarrow[\text{(sodium azide)}]{NaN_3} R-\overset{\overset{\large O}{\|}}{C}-N_3 \xrightarrow[-N_2]{} R-C{=}O \xrightarrow{\text{Intramolecular alkyl shift}} R-N{=}C{=}O \xrightarrow[\Delta]{2NaOH} R-NH_2 + Na_2CO_3$$

(e) Hofmann Bromamide Degradation Reaction

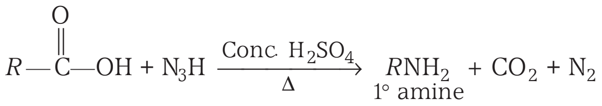
Amides on reaction with Br_2 in an aqueous or ethanolic solution of NaOH give 1° amine with one C atom less than that present in the amide.

$$RCONH_2 + Br_2 + 4KOH \xrightarrow{\Delta} \underset{1^\circ \text{ amine}}{RNH_2} + 2KBr + K_2CO_3 + 2H_2O$$

(The mechanism of this reaction is completely described in the properties of acid amide).

(f) Schmidt Rearrangement

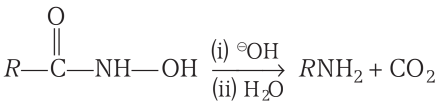
Carboxylic acid, when warmed with hydrazoic acid (N_3H) in the presence of concentrated sulphuric acid, gives a high yield of primary amines.



$$R-\overset{\overset{\large O}{\|}}{C}-OH + N_3H \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} \underset{1^\circ \text{ amine}}{RNH_2} + CO_2 + N_2$$

(g) Lossen Rearrangement Reaction

Hydroxamic acid on reaction with a base followed by hydrolysis gives 1° amine.



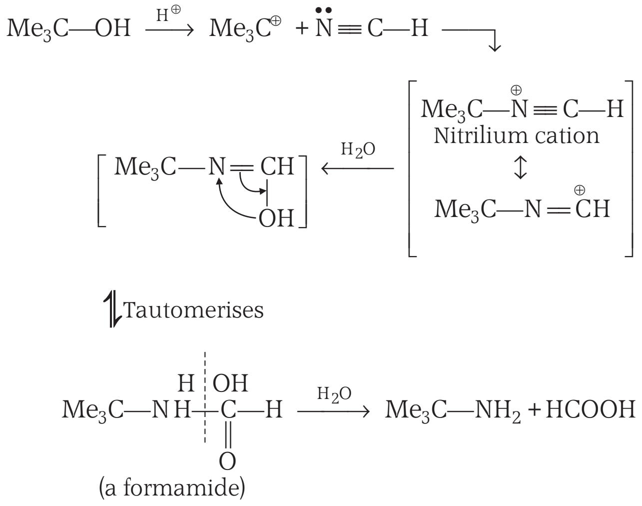
$$R-\overset{\overset{\large O}{\|}}{C}-NH-OH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } ^{\ominus}OH} RNH_2 + CO_2$$

(h) Ritter Reaction

Primary amines having tertiary alkyl group are prepared from tertiary alcohol by using Ritter reaction. In this reaction, Me_3C-OH or $Me_2C{=}CH_2$ is reacted with conc. H_2SO_4 and HCN. In conc. H_2SO_4, these substrates are converted to $Me_3C^{\oplus}$ which then react with HCN.

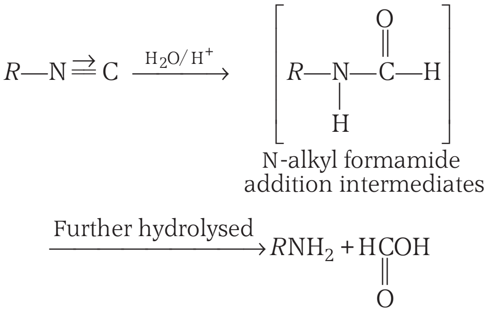
$$Me_3C-OH + HCN + H_2SO_4 \longrightarrow Me_3C-NH_2$$

Mechanism

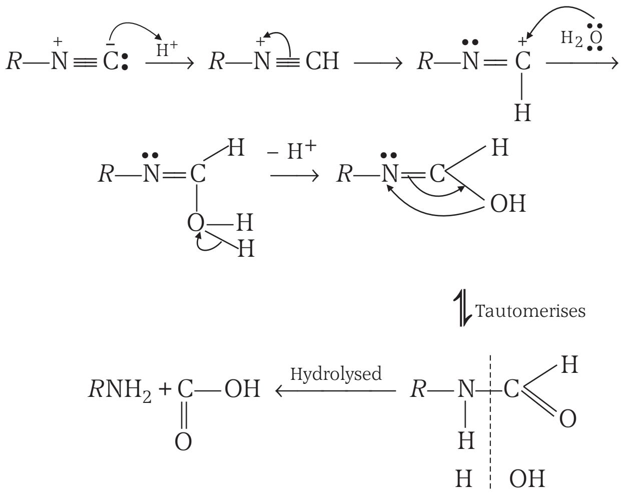


(i) Hydrolysis of Isocyanides

Isocyanides are hydrolysed by dilute acids (but not by alkali) to form a primary amine and formic acid



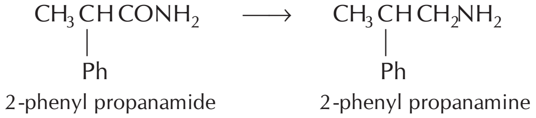
Mechanism



Sample Problem 7 *The best reagent for converting 2-phenylpropanamide into 2-phenylpropanamine is* [**NCERT** Exemplar]

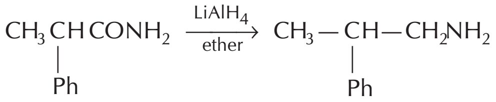
(a) *excess* H_2
(b) Br_2 *in aqueous* NaOH
(c) *iodine in the presence of red phosphorus*
(d) $LiAlH_4$ *in ether*

Interpret (d) First write the conversion in equation form



$$\underset{\text{2-phenyl propanamide}}{CH_3\underset{\substack{|\\ Ph}}{C}HCONH_2} \longrightarrow \underset{\text{2-phenyl propanamine}}{CH_3\underset{\substack{|\\ Ph}}{C}HCH_2NH_2}$$

Find what is converting and into which group, *e.g.*, here $-\overset{\overset{O}{\|}}{C}-$ group is converted into $>CH_2$ group. Now, think about the reagent which bring about this conversion, *e.g.*, For the above conversion, $LiAlH_4$ in ether can be used.



$$CH_3\underset{\substack{|\\ Ph}}{C}HCONH_2 \xrightarrow[\text{ether}]{LiAlH_4} CH_3-\underset{\substack{|\\ Ph}}{C}H-CH_2NH_2$$

Note Br_2 in aqueous NaOH cannot be used as it gives an amine with one less carbon than the parent amide.

Methods for Secondary Amines Only

Following methods are employed for the preparation of secondary amines.

(a) Reaction of *RX* with 1° Amines

Primary amine when heated with an alkyl halide resulting to dialkyl ammonium salt which on treatment with NaOH yields secondary amine.

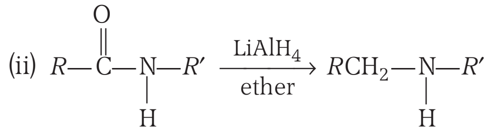
$$RNH_2 + RX \longrightarrow R_2\overset{+}{N}H_2X^- \xrightarrow{NaOH} R_2NH + NaX + H_2O$$

(b) Reduction

Isocyanides and substituted amides on complete reduction give N-substituted amines.

(i) $$\underset{\text{alkyl isocyanide}}{RN\overrightarrow{=}C} + 2H_2 \xrightarrow{\text{Ni or Pt}} \underset{2^\circ\ \text{amine}}{RNHCH_3}$$

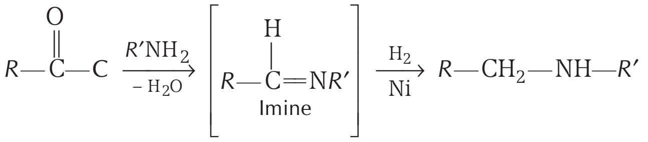
(ii)



$$R-\overset{\overset{O}{\|}}{C}-\underset{\substack{|\\ H}}{N}-R' \xrightarrow[\text{ether}]{LiAlH_4} RCH_2-\underset{\substack{|\\ H}}{N}-R'$$

(c) Reductive Amination of Carbonyl Compounds

A mixture of carbonyl compound, hydrogen and primary amine when passed over Ni catalyst at high temperature, yields secondary amine.



$$R-\overset{\overset{O}{\|}}{C}-C \xrightarrow[-H_2O]{R'NH_2} \left[\underset{\text{Imine}}{R-\overset{\overset{H}{|}}{C}=NR'}\right] \xrightarrow[Ni]{H_2} R-CH_2-NH-R'$$

Caution Point *Reduction of imine is more rapid than that of the starting carbonyl compound.*

Sample Problem 8 *Amongst the given set of reactants, the most appropriate for preparing* 2° *amine is* [**NCERT** Exemplar]

(a) $2^\circ\ R-Br + NH_3$
(b) $2^\circ\ R-Br + NaCN$ *followed by* H_2/Pt
(c) $1^\circ\ R-NH_2 + RCHO$ *followed by* H_2/Pt
(d) $1^\circ\ R-Br$ (2 *mol*) + *potassium phthalimide followed by* H_3O^+/*heat*.

Interpret (c) (a) $2^\circ\ R-Br + NH_3 \longrightarrow \underset{\substack{1^\circ\ \text{amine}\\ \text{(here } R \text{ is } 2^\circ \text{ but}\\ \text{N is not)}}}{2^\circ\ R-NH_2} + HBr$

(b) $2^\circ\ R-Br + NaCN \xrightarrow[-NaBr]{} 2^\circ\ R-CN \xrightarrow{H_2/Pt} \underset{(1^\circ\ \text{amine})}{2^\circ\ R-CH_2NH_2}$

(c) $1^\circ\ RNH_2 + RCHO \longrightarrow RN{=}CHR \xrightarrow{\text{Reduction}} \underset{2^\circ\ \text{amine}}{RNHCH_2R}$

(d) Gabriel phthalimide reaction always gives 1° amine.

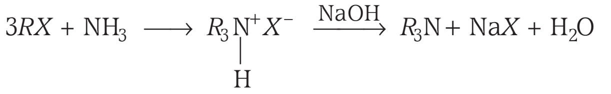
Thus, method given in option (b) is most appropriate to synthesise 2° amine.

Methods for Tertiary Amines Only

Methods for preparation of tertiary amines only are discussed below.

(a) Reaction of *RX* with NH_3

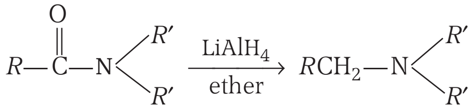
Here, alcoholic NH_3 solution is heated with excess of alkyl halide resulting to trialkyl ammonium halide which on treatment with NaOH gives tertiary amine as



$$3RX + NH_3 \longrightarrow R_3\underset{\substack{|\\ H}}{N^+}X^- \xrightarrow{NaOH} R_3N + NaX + H_2O$$

(b) Reduction of N,N-Disubstituted Amides

N, N-dialkyl alkanamide when reduced from $LiAlH_4$, in the presence of ether, gave a tertiary amine.



$$R-\overset{\overset{O}{\|}}{C}-N\begin{matrix}\diagup R'\\ \diagdown R'\end{matrix} \xrightarrow[\text{ether}]{LiAlH_4} RCH_2-N\begin{matrix}\diagup R'\\ \diagdown R'\end{matrix}$$

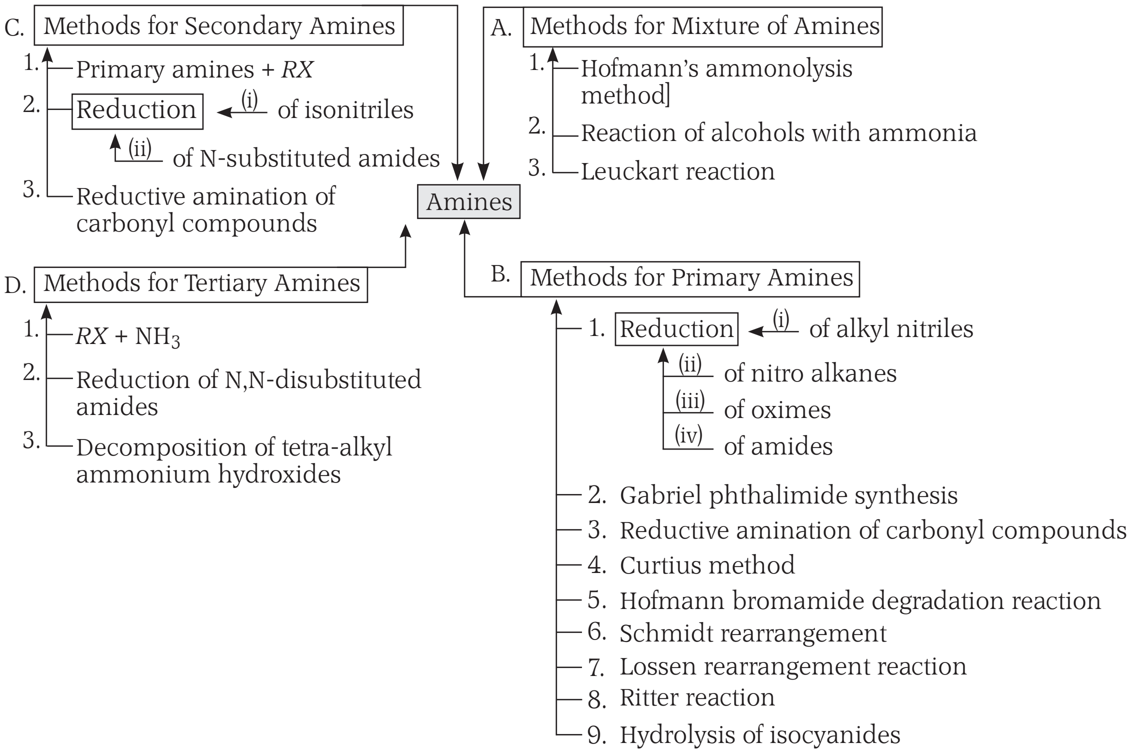
(c) Decomposition of Tetra-alkyl Ammonium Hydroxides

This reaction is called **Hofmann's elimination reaction.** In this reaction, the quaternary ammonium salts when heated, undergo cleavage to form a tertiary amine and an alkene (less substituted).

$$R_4N^+OH^- \xrightarrow{\Delta} R_3N + H_2O + CH_2{=}CH_2 \text{ (Decomposition)}$$

In this reaction, the OH^- abstracts a H^+ from the β-C atom to form water, a molecule of 3° amine and alkene.

The outline of the methods of preparation of amines looks like



12.3 Properties of Aliphatic Amines

Various physical and chemical properties exhibit by amines are dicussed below

Physical Properties

These include

1. Lower amines are gases or low-boiling liquids, with a characteristic ammonia like smell.
2. Their boiling point are higher in comparison to non-polar compounds of same molecular weight (due to intermolecular H-bonding). However, tertiary amines are exceptions of this due to absence of H-bonding.
3. These are miscible with water (due to intermolecular H–bonding with H_2O molecules also).

Chemical Properties

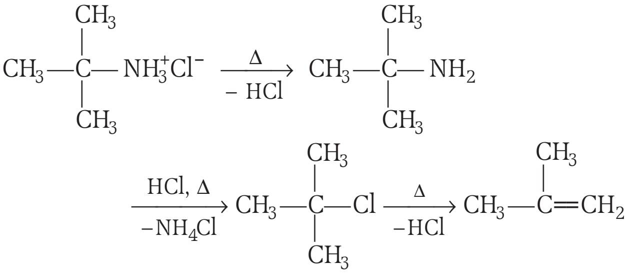
The main reactions exhibited by amines are as follows

(a) With Mineral Acids

Amines being basic in nature, react with acids to form salt.

$$RNH_2 + \underset{\text{hydrochloric acid}}{HCl} \longrightarrow \underset{\text{salt}}{R\overset{+}{N}H_3Cl^-}$$

If a tertiary-alkyl group is present, this is eliminated as an alkene.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-NH_3^+Cl^- \xrightarrow[-\text{ HCl}]{\Delta} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-NH_2 \xrightarrow[-NH_4Cl]{HCl,\ \Delta} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Cl \xrightarrow[-HCl]{\Delta} CH_3-\overset{CH_3}{C}=CH_2$$

(b) Nature of Aqueous Solution

Amines react with water to give alkyl ammonium hydroxides which ionises into hydroxide ions in solution, *i.e.*, the aqueous solutions of amines are basic in nature.

$$\underset{1^\circ\text{ amine}}{RNH_2} + HOH \rightleftharpoons RNH_3OH^- \rightleftharpoons [RNH_3]^+ + OH^-$$

$$\underset{2^\circ\text{ amine}}{R_2NH} + HOH \rightleftharpoons R_2\overset{+}{N}H_2OH^- \rightleftharpoons [R_2NH_2]^+ + OH^-$$

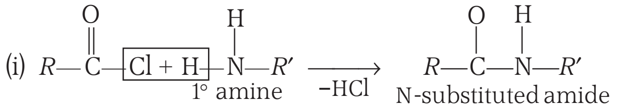
$$\underset{3^\circ\text{ amine}}{R_3N} + HOH \rightleftharpoons R_3\overset{+}{N}HOH \rightleftharpoons [R_3NH]^+ + OH^-$$

The aqueous solutions of amines behave like NH_4OH and give ferric hydroxide precipitate with ferric chloride and blue solution with copper sulphate.

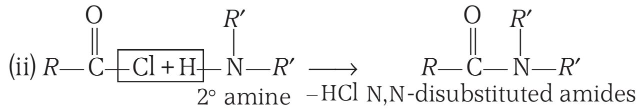
$$3\,RNH_3OH + FeCl_3 \longrightarrow \underset{\text{brown ppt.}}{Fe(OH)_3} \downarrow + 3\,RNH_3Cl$$

(c) Acylation

In this reaction, 1° amines give N-substituted amide while 2° amines give N,N-disubstituted amides.

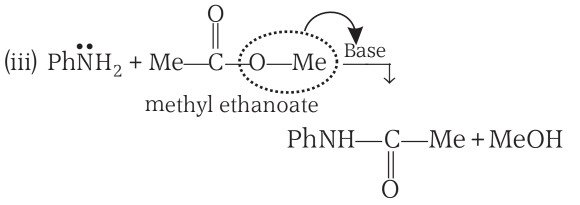


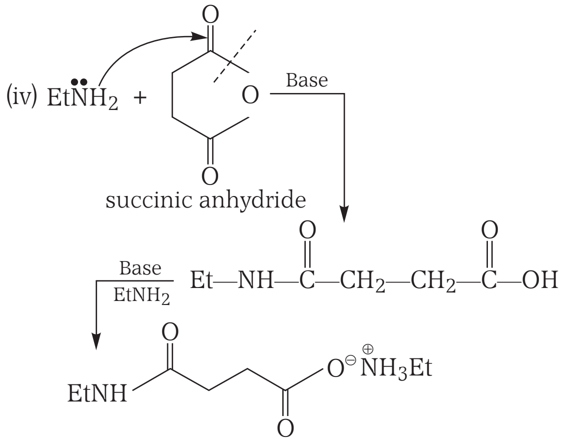
$$\text{(i)}\ R-\overset{\overset{\displaystyle O}{\|}}{C}-\boxed{Cl + H}-\overset{\overset{\displaystyle H}{|}}{\underset{1^\circ\text{ amine}}{N}}-R' \xrightarrow[-HCl]{} \underset{\text{N-substituted amide}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-R'}$$

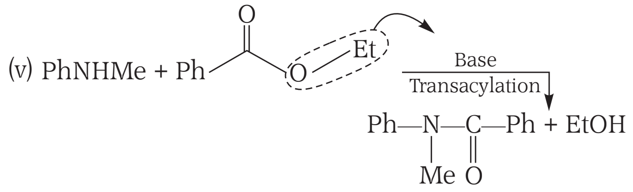


$$\text{(ii)}\ R-\overset{\overset{\displaystyle O}{\|}}{C}-\boxed{Cl + H}-\overset{\overset{\displaystyle R'}{|}}{\underset{2^\circ\text{ amine}}{N}}-R' \xrightarrow[-HCl]{} \underset{\text{N,N-disubstituted amides}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle R'}{|}}{N}-R'}$$

There is no active H at 3° amines hence, there is no reaction with them. For acylation, $RCOCl$ or $(RCO)_2O$ can be used. The reaction is carried out in the presence of a base stronger than amine, such as pyridine, which removes HCl so formed and shifts the equilibrium to the right hand side.

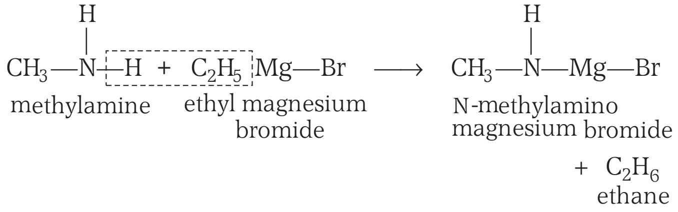




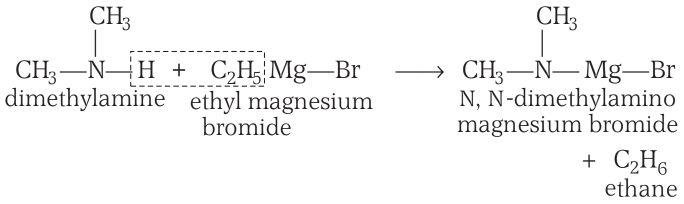


(d) Reaction with Grignard's Reagents

Both primary and secondary amines give alkanes with Grignard's reagents *e.g.*,



$$\underset{\text{methylamine}}{CH_3-\overset{\overset{\displaystyle H}{|}}{N}}-\boxed{H + C_2H_5}\underset{\text{ethyl magnesium bromide}}{Mg-Br} \longrightarrow \underset{\text{N-methylamino magnesium bromide}}{CH_3-\overset{\overset{\displaystyle H}{|}}{N}-Mg-Br} + \underset{\text{ethane}}{C_2H_6}$$



$$\underset{\text{dimethylamine}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{N}}-\boxed{H + C_2H_5}\underset{\text{ethyl magnesium bromide}}{Mg-Br} \longrightarrow \underset{\text{N, N-dimethylamino magnesium bromide}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{N}-Mg-Br} + \underset{\text{ethane}}{C_2H_6}$$

Tertiary amines do not react with Grignard's reagent, because of the absence of H attached directly with N.

(e) Reaction with Transition Metal Ions

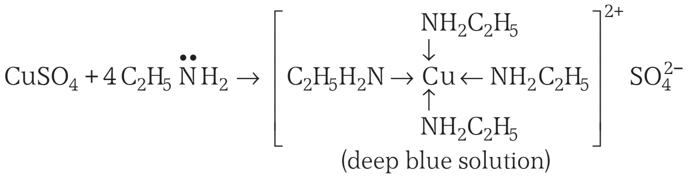
Amines form coordination compounds with transition metal ions such as Ag^+ or Cu^{2+} ions by donating the electron pair present on the nitrogen atom.

Ethylamine dissolves white precipitate of silver chloride to form a complex as

$$\underset{\text{(white precipitate)}}{AgCl} + \underset{\text{ethylamine}}{2C_2H_5\ddot{N}H_2} \longrightarrow$$

$$\underset{\text{(soluble complex)}}{[C_2H_5-H_2N \longrightarrow Ag \longleftarrow H_2N-C_2H_5]^+Cl^-}$$

Similarly, copper sulphate also reacts with amine to give a deep blue solution.

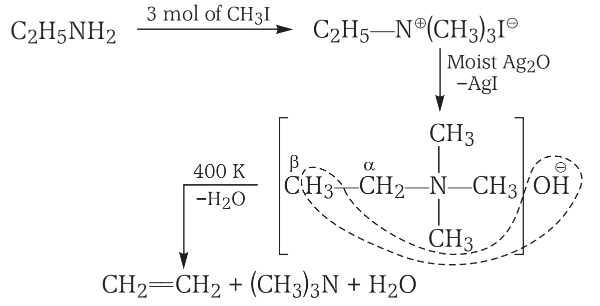


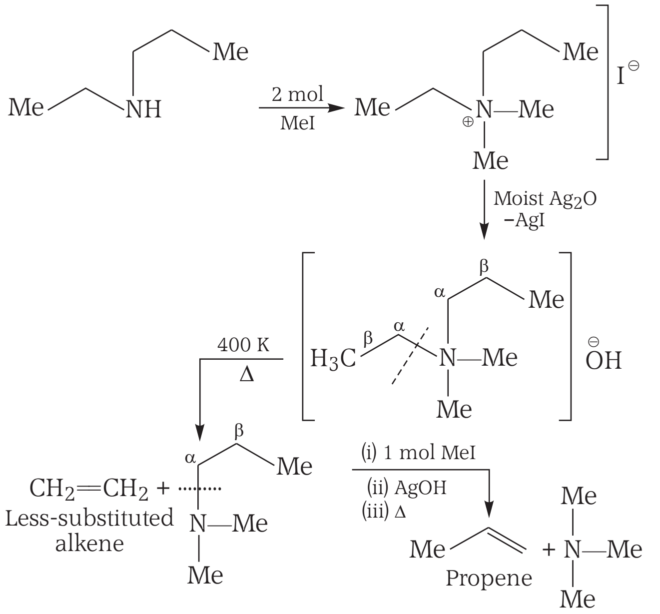
$$CuSO_4 + 4\,C_2H_5\ddot{N}H_2 \rightarrow \left[\begin{array}{c} NH_2C_2H_5 \\ \downarrow \\ C_2H_5H_2N \rightarrow Cu \leftarrow NH_2C_2H_5 \\ \uparrow \\ NH_2C_2H_5 \end{array}\right]^{2+} SO_4^{2-}$$

(deep blue solution)

(f) Hofmann's Exhaustive Methylation and Elimination

The process of converting an amine (1°, 2° or 3°) into quaternary ammonium salt by treating it with excess of CH_3I is called **Hofmann's exhaustive methylation**. This quaternary salt when treated with moist Ag_2O gives silver halide as precipitate and quanternary ammonium hydroxide, which on heating at 400 K or above undergoes an elimination reaction to produce an alkene, trimethylamine and water. This is called **Hofmann's elimination reaction**. In the pyrolysis, less-substituted alkene is formed first, *e. g.*,





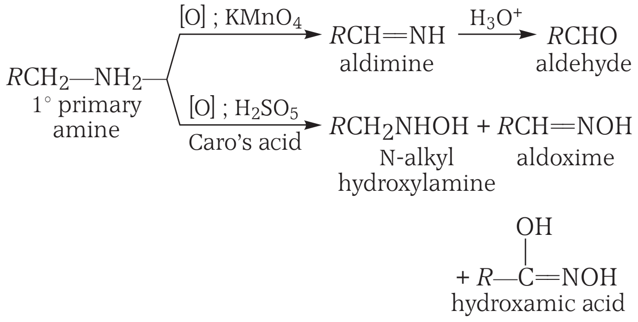
The reaction is E_2 and in last step, the leaving group is NMe_3. $RCH_2CH_2NH_2$ does not undergo E2 elimination as $\overset{\ominus}{N}H_2$ is a poor leaving group.

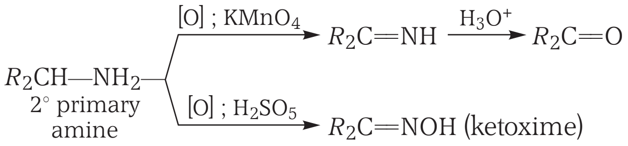
Caution Point *A novel aspect of the Hofmann elimination is its regioselectivity. Elimination in alkyl-trimethyl ammonium hydroxide proceeds in the direction that gives the less substituted alkene, and is opposite to the Saytzeff rule that prefers the formation of more substituted alkene. It is less sterically hindred β-hydrogen that is removed by the base in Hofmann elimination reactions. Methyl* ($—CH_3$) *groups are deprotonated in preference to methylene* ($—CH_2—$) *groups, and methylene groups are deprotonated in preference to methines* ($—\overset{|}{\underset{|}{C}}H$).

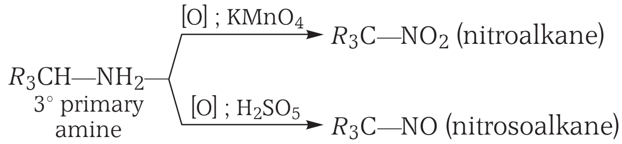
(g) Oxidation of Amines

Oxidative products depend upon the type of amine taken and also on the nature of oxidant used.

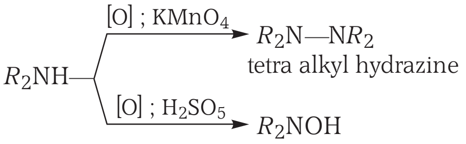
(i) **Oxidation of primary amines**



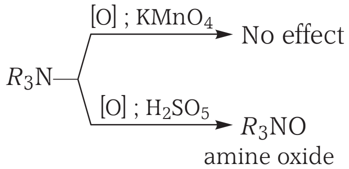




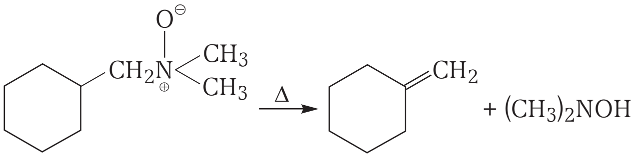
(ii) **Oxidation of secondary amines**



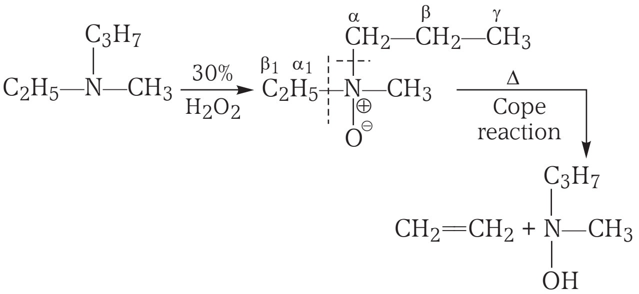
(iii) **Oxidation of tertiary amines**



Cope elimination The tertiary amine oxide containing a β-H atom, on heating forms an alkene. The reaction is called cope elimination, *e. g.*,



In Cope reaction, the alkene formed will be less substituted (not Saytzeff product but Hofmann elimination product). Cope reaction is similar to Hofmann exhaustive methylation and elimination reaction. *e. g.*,

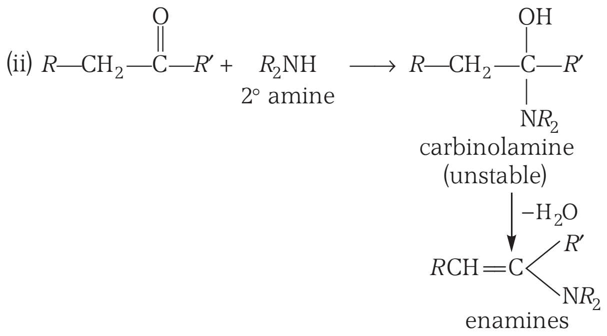


Cope reaction is an E2 reaction in which leaving groups are H and $R_2N—O^{\ominus}$, which form $R_3N—OH$.

(h) With Carbonyl Compounds

Amines form Schiff's base and examine with carbonyl compounds.

(i) $\underset{\text{1° amine}}{R—N\boxed{H_2 + O}}═C\langle \longrightarrow \underset{\text{Schiff's base}}{R—C═N\langle}$



$$R{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}R' + \underset{2^\circ\text{ amine}}{R_2NH} \longrightarrow \underset{\substack{\text{carbinolamine}\\ \text{(unstable)}}}{R{-}CH_2{-}\overset{OH}{\overset{|}{\underset{\underset{NR_2}{|}}{C}}}{-}R'}$$

(iii) $R_3N + \rangle C{=}O \longrightarrow$ No reaction

Identification of 1°, 2° and 3° Amines

Several reactions can be used to identify 1°, 2° *and* 3° *amines. Some important of these are*

(a) With Nitrous Acid

This reaction is used as the basis of test to distinguish between primary, secondary and tertiary amines *i.e.*,

(i) Primary amine ⟶ N_2 gas bubbled out

$$\underset{1^\circ\text{ amine}}{R{-}NH_2} + HONO \longrightarrow \underset{\text{alcohol}}{ROH} + N_2 + H_2O$$

The reaction takes place through the formation of unstable diazonium salt (diazotisation) which changes to carbocation as one of the intermediates. This carbocation gives variety of products.

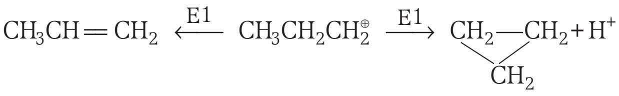
$$CH_3CH_2CH_2NH_2 \xrightarrow[(NaNO_2+HCl)]{HNO_2} \underset{\substack{n\text{-propyl diazonium}\\ \text{chloride}}}{CH_3CH_2CH_2N_2^+Cl^-}$$

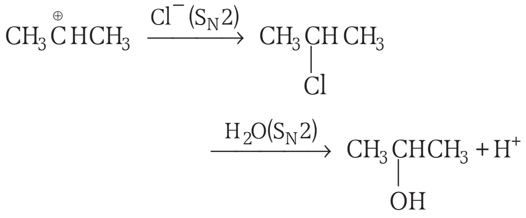
$$CH_3CH_2CH_2N_2^+Cl^- \longrightarrow \underset{1^\circ\text{ carbocation}}{CH_3CH_2CH_2^{\oplus}} + N_2 + \underset{\substack{\text{leaving}\\ \text{group}}}{Cl^-}$$

$$CH_3CH_2\overset{\oplus}{C}H_2 \xrightarrow{\text{1,2-hydride shift}} \underset{\substack{2^\circ\text{ carbocation}\\ \text{(more stable than } 1^\circ)}}{CH_3\overset{\oplus}{C}HCH_3}$$

$$CH_3CH_2\overset{\oplus}{C}H_2 \xrightarrow{Cl\,(S_N2)} CH_3CH_2CH_2Cl$$

$$\xrightarrow{H_2O,\,(S_N2)} CH_3CH_2CH_2OH + H^+$$



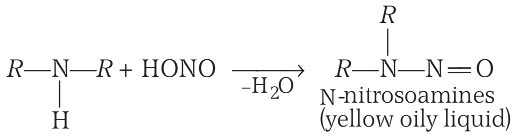


$$CH_3\overset{\oplus}{C}HCH_3 \xrightarrow{Cl^-\,(S_N2)} CH_3\underset{\underset{Cl}{|}}{C}HCH_3$$

$$\xrightarrow{H_2O(S_N2)} CH_3\underset{\underset{OH}{|}}{C}HCH_3 + H^+$$

All these side-products have been isolated. Since, nitrogen-free products result from the formation and decomposition of diazonium ions, these reactions are also called **deamination reactions.**

(ii) Secondary amine ⟶ Yellow oily layer



$$R{-}\underset{\underset{H}{|}}{N}{-}R + HONO \xrightarrow[-H_2O]{} \underset{\substack{\text{N-nitrosoamines}\\ \text{(yellow oily liquid)}}}{R{-}\overset{R}{\overset{|}{N}}{-}N{=}O}$$

The N-nitrosoamines on warming with a crystal of phenol and a few drops of conc. H_2SO_4 form a green solution which when made alkaline with *aq.* NaOH turns deep blue and then red on dilution. This reaction is called **Liebermann's nitroso reaction** and used as a test for secondary amines.

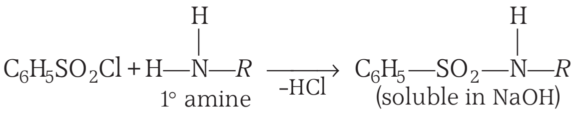
(iii) Tertiary amine ⟶ Trialkyl ammonium nitrite

$$R_3N + HONO \longrightarrow \underset{\text{soluble in water}}{R_3\overset{+}{N}HNO_2^-}$$

(b) With Benzene Sulphonyl Chloride, *i.e.*, Hinsberg Reagent

Hinsberg reagent is also used to distinguish between 1°, 2° and 3° amines.

(i) Primary amines + $C_6H_5SO_2Cl \longrightarrow$ Sulphonamide (soluble in NaOH)



$$C_6H_5SO_2Cl + \underset{1^\circ\text{ amine}}{H{-}\overset{H}{\overset{|}{N}}{-}R} \xrightarrow[-HCl]{} \underset{\text{(soluble in NaOH)}}{C_6H_5{-}SO_2{-}\overset{H}{\overset{|}{N}}{-}R}$$

The solubility of sulphonamide of primary amine is due to the presence of replaceable acidic H present in them, which is eliminated by $—OH^-$ of base.

(ii) Secondary amine + $C_6H_5SO_2Cl \longrightarrow$ Sulphonamide (insoluble in NaOH)

$$C_6H_5SO_2Cl + H{-}NR_2 \xrightarrow[-HCl]{} \underset{\text{(insoluble in NaOH)}}{C_6H_5{-}SO_2{-}NR_2}$$

(iii) Tertiary amine + $C_6H_5SO_2Cl \longrightarrow$ No reaction

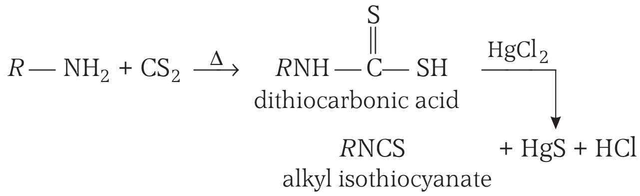
(c) Carbylamine Reaction

This reaction is given by only primary amines (both aliphatic and aromatic). Primary amines when warmed with chloroform and alcoholic KOH, give extremely bad smelling compounds called **carbylamines** or **isocyanides.**

$$RNH_2 + CHCl_3 + 3KOH(alc) \longrightarrow \underset{\substack{\text{phenyl}\\ \text{carbylamine}}}{RN \overset{\rightarrow}{=} C} + 3KCl + 3H_2O$$

(d) Hofmann Mustard Oil Reaction

1° amines on warming with CS_2 from a dithiocarbamic acid. This is decomposed by $HgCl_2$ to give alkyl isothiocyanate and black precipate of HgS. This is called **Hofmann mustard oil reaction** (a test for 1° amines.)



$$R-NH_2 + CS_2 \xrightarrow{\Delta} \underset{\text{dithiocarbonic acid}}{RNH-\overset{\overset{\large S}{\|}}{C}-SH} \xrightarrow{HgCl_2} \underset{\text{alkyl isothiocyanate}}{RNCS} + HgS + HCl$$

Sample Problem 9 *Methylamine reacts with* HNO_2 *to form* **[NCERT Exemplar]**

(a) $CH_3-O-N=O$

(b) CH_3-O-CH_3

(c) CH_3OH

(d) CH_3CHO

Interpret (a,b,c)

$$CH_3NH_2 + HONO \xrightarrow[\text{ice cold}]{HCl} \underset{\text{unstable}}{CH_3N_2^+Cl^-} + 2H_2O$$

$$\downarrow$$

$$CH_3^+ + N_2 + Cl^-$$

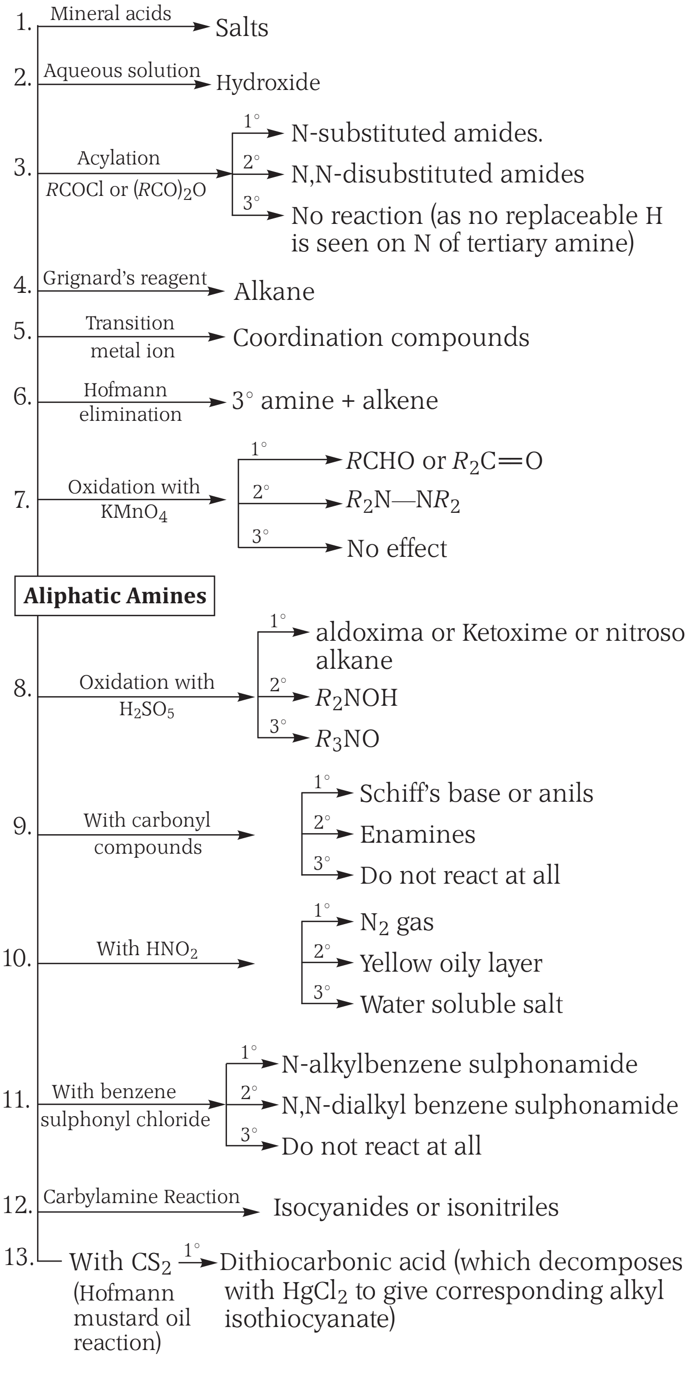
$$\downarrow HONO$$

$$CH_3-O-CH_3 + CH_3ONO + H^+ + CH_3OH$$

Check Point 1

1. Tertiary amine has the lowest boiling point in a group of isomeric amines. Explain, why?
2. Why is silver chloride soluble in methylamine?
3. The sulphonamide of 1° amine is soluble in water while that of 2° amines is not. Explain with appropriate reason.
4. Why amines are more basic than amides?
5. In gas phase, $(CH_3)_3N$ is more basic than $(CH_3)_2NH$ but in aqueous solution, reverse is true. Explain, why?

The outline of chemical properties of amines looks like



Separation of 1°, 2° and 3° Amines

Separation of 1°, 2° *and* 3° *amines can be done through following methods*

(a) Fractional Distillation

Easy to apply as their boiling points are quite different.

(b) Hinsberg Method

In this method, mixture is treated with $C_6H_5SO_2Cl$ and the solution is made alkaline with aqueous NaOH. On distillation, this alkaline solution gives **tertiary amine** and remaining mixture is filtered. The filtrate on acidification gives sulphonamide of **primary amine,** while the solid residue is **sulphonamide of secondary amine.** The two sulphonamides thus isolated, are hydrolysed with conc. HCl and distilled over NaOH to yield the respective amines.

(c) Hofmann Method

Here, mixture is treated with diethyl oxalate

(i) **Primary amines** form a solid compound called dialkyloxamide $\left(\begin{array}{l}\text{CONH}R\\ |\\ \text{CONH}R\end{array}\right)$.

(ii) **Secondary amines** form on oily liquid called dialkyloxamic ester $\left(\begin{array}{l}\text{CO—N}R_2\\ |\\ \text{COOC}_2\text{H}_5\end{array}\right)$.

(iii) Tertiary amines do not react at all.

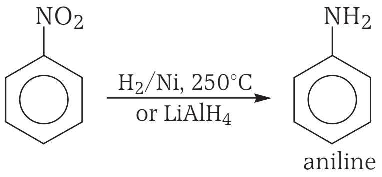
Now, the mixture is fractionally distilled. Unreacted tertiary amines come out as first fraction, followed by oily oxamic ester as second fraction, oxamide (solid) remains in the distillation flask. Oxamic ester and oxamide gave respective amines back on treatment with KOH.

12.4 Methods of Preparation of Aromatic Amines

Aromatic amines can be prepared the following methods.

1. Reduction of Nitro Compounds

The reaction looks like



Infact, reduction of nitro compounds gives different products as

$$R\text{—NO}_2 \xrightarrow[-H_2O]{+2H} \underset{\text{nitroso compounds}}{R\text{—N=O}} \xrightarrow{+2H} R\text{—}\underset{\mathrm{H}}{\underset{|}{\mathrm{N}}}\text{—OH} \xrightarrow[-H_2O]{+2H} R\text{—NH}_2$$

The final product of reduction depends upon pH of the reaction medium and nature of reducing agent, *i.e.*.

(i) Both aromatic as well as aliphatic nitro compounds can be reduced to corresponding primary amine by metal/acid reducing agent combination.

(ii) **Hydroxylamines** are produced in neutral medium (Zn dust and NH_4Cl solution) by both aliphatic and aromatic nitrocompounds.

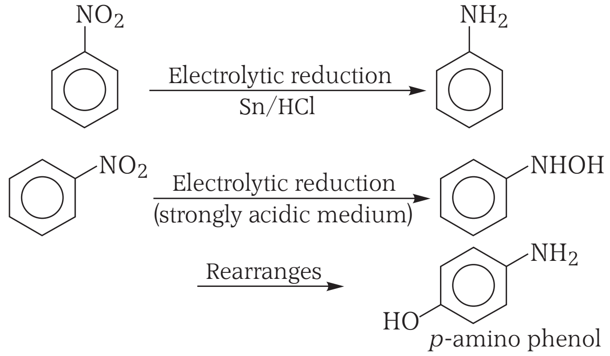
(iii) In alkaline medium, different products are produced under different conditions as

I. Azoxybenzene $\left(C_6H_5\text{—}\overset{\overset{\displaystyle O}{\uparrow}}{N}\text{=N—}C_6H_5\right)$ with Na_3AsO_3 / NaOH

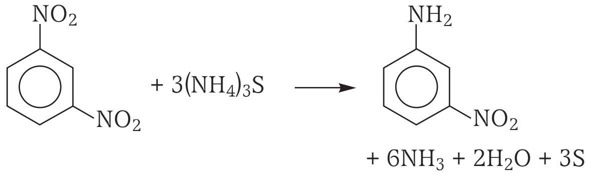
II. Azobenzene $(C_6H_5N{=}NC_6H_5)$ with Zn/NaOH in CH_3OH.

III. Hydrazobenzene $\left(C_6H_5\ \underset{\mathrm{H}}{\underset{|}{\mathrm{N}}}\text{—}\underset{\mathrm{H}}{\underset{|}{\mathrm{N}}}\text{—}C_6H_5\right)$ with Zn/NaOH, in C_2H_5OH (cold conc. HCl).

(iv) Electrolytic reduction of nitrobenzene in weakly acidic medium gives **aniline** while electrolytic reduction in strongly acidic medium produces ***p*-amino phenol** as

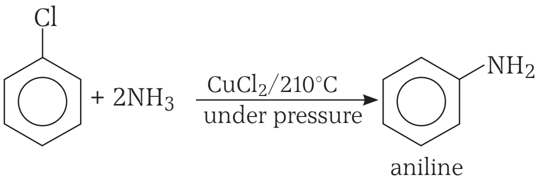


(v) If two or more nitro groups are present on benzene ring, it is possible to reduce one of them without affecting the other **(selective reduction)** as



This reduction with sulphides and polysulphides is called **Zinin reduction.**

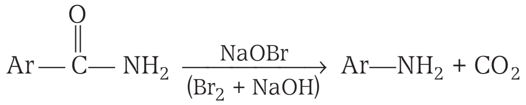
2. Ammonolysis of Aryl Chlorides



The method can be carried out conveniently under ordinary conditions if a strong electron withdrawing group (*e. g.*, —NO_2) is present at *ortho* or *para*-position to —Cl.

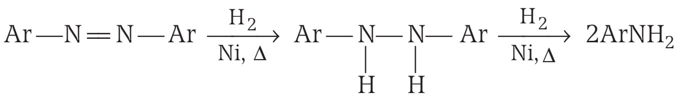
3. Hofmann's Bromamide Degradation Reaction

This reaction involves intramolecular phenyl migration, the rate of which is increased by the presence of electron releasing substituents.



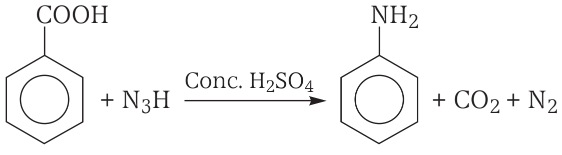
$$Ar—\overset{\overset{\large O}{\|}}{C}—NH_2 \xrightarrow[(Br_2 + NaOH)]{NaOBr} Ar—NH_2 + CO_2$$

4. Reduction of Azo Compounds



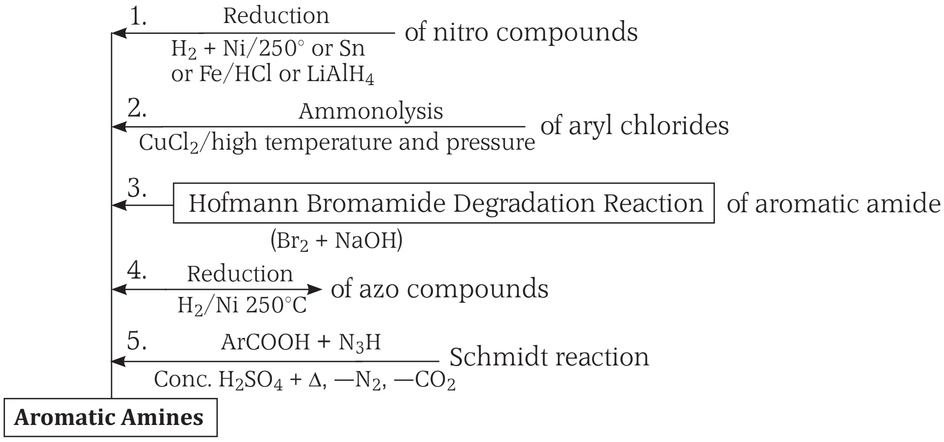
$$Ar—N{=}N—Ar \xrightarrow[Ni,\,\Delta]{H_2} Ar—\underset{\underset{H}{|}}{N}—\underset{\underset{H}{|}}{N}—Ar \xrightarrow[Ni,\,\Delta]{H_2} 2ArNH_2$$

5. Schmidt Reaction



Some other methods are very similar to those used for aliphatic amines

The outline of methods of preparation of aromatic amines looks like



12.5 Properties of Aromatic Amines

Various physical and chemical properties of aromatic amines are discussed below

Physical Properties

1. These are colourless liquids or solids having characteristic odour.
2. They turn brown in air due to oxidation.
3. They have high boiling point (due to intermolecular H-bonding) and are sparingly soluble in water but more soluble in organic solvents, steam volatile, toxic substances and carcinogenic in nature.
4. They are less basic as compared to aliphatic amines. Generally, the presence of electron releasing groups like —CH_3, —OCH_3 etc., increases the basic strength of aromatic amines while presence of electron withdrawing groups like —NO_2, —*X*, —CN etc., decreases the same. (The electron releasing or withdrawing groups are more effective at *para* position or their effect is more pronounced at *para* position).

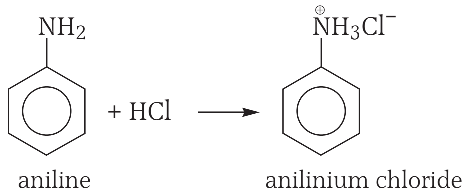
Between diphenyl amine and aniline, aniline is more basic because of the presence of two electron withdrawing phenyl groups in diphenylamine (Here, lone pair of N-atom is used up by two benzene nucleus).

Chemical Properties

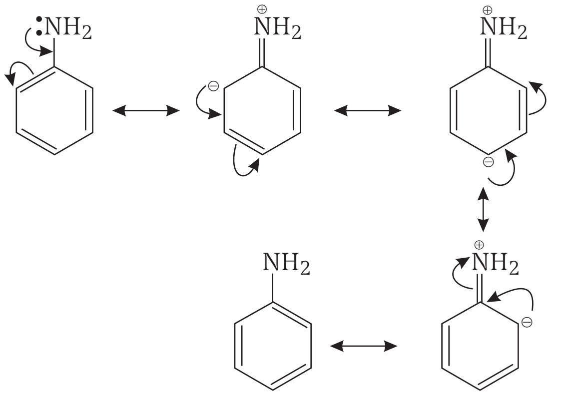
Important reactions exhibited by aromatic amines are as follows

(a) **Salt Formation**

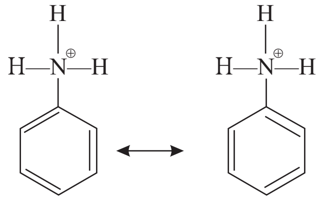
Like aliphatic amines, aromatic amines also form salt with acids, this shows their basic nature. However, these are less basic as compared to aliphatic amines due to delocalisation of electrons. The reaction looks as



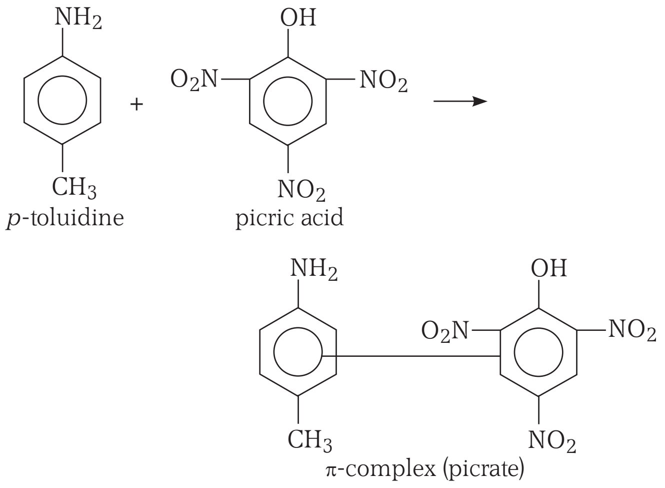
Anilinium ion is less resonance stabilised as compared to aniline, *i.e.*, the following resonating structures are possible for aniline and anilinium ion.



(Resonance structures of aniline)

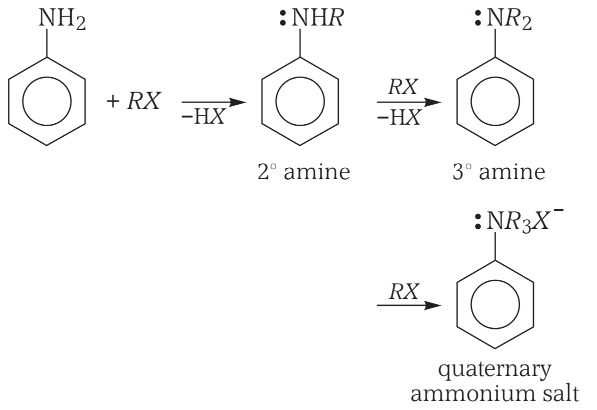


(Resonance structures of anilinium ion)



(b) **Alkylation**

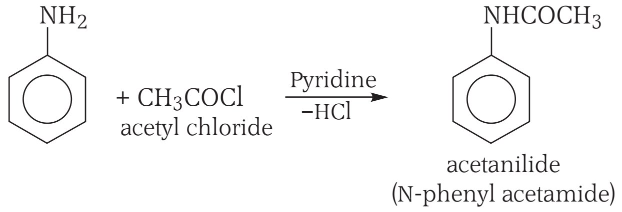
Like primary aliphatic amines, aromatic amines also react with alkyl halides to give respective secondary and tertiary amines. The reaction looks as

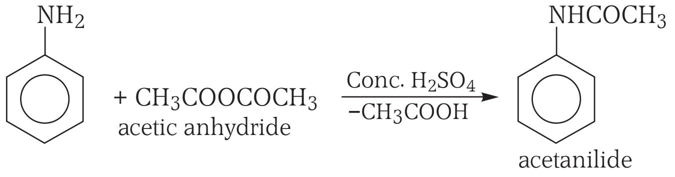


The process of conversion of a 1° amines into quarternary ammonium salt is called **Hofmann exhaustive alkylation.**

(c) **With Acids and Acid Derivatives**

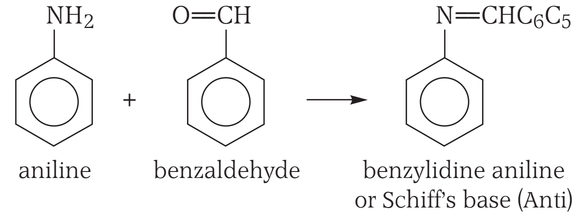
N-aryl amide are formed in this reaction. The reaction looks like





(d) **With Aldehydes**

The reaction is as

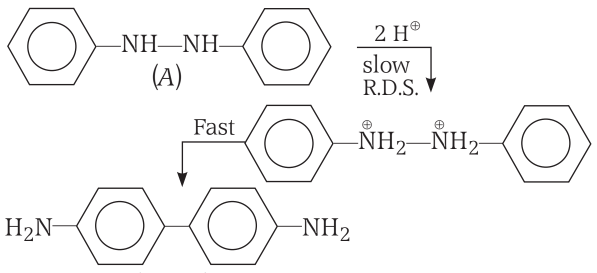


On catalytic hydrogenation, Schiff's base gives secondary amines

$$C_6H_5N{=}CHC_6H_5 + H_2 \xrightarrow{Ni} \underset{\text{N-phenyl benzylamine}}{C_6H_5CH_2NHC_6H_5}$$

(e) Benzidine Rearrangement Reaction

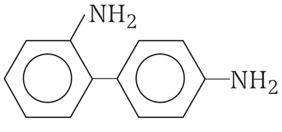
In stronglty acidic solution, hydrazobenzene (PhNHNHPh) intramolecular rearranges to benzidine.



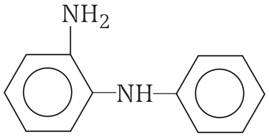
benzidine
(major) (70%)

$$\text{Rate} = k[A][H^+]^2$$

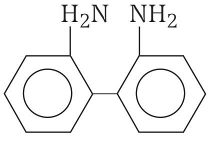
The other products formed are



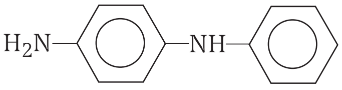
diphenyline
(~30%)



o-semidine
(minor)

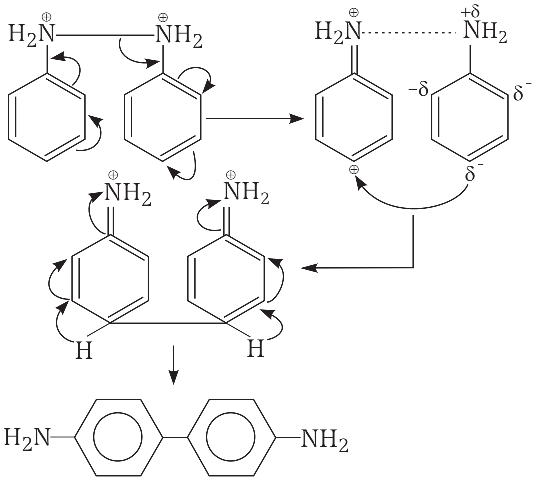


o-benzidine
(minor)



p-semidine
(minor)

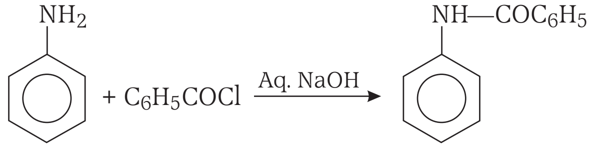
Mechanism The two independent mechanisms can operate in this reaction, a one-proton and a two-proton mechanism. The latter is described here



This mechanism leads to a C—C linking and can give rise to 4, 4′-product (benzidine) and/or to 2, 4′-product (diphenyline). Aromatic nuclei lie in approximately parallel planes.

(f) Benzoylation or Schotten Baumann Reaction

The reaction looks like

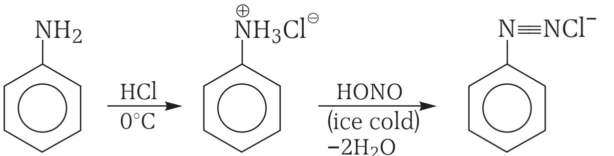


benzanilide
or N-phenyl benzamide

(g) With HNO_2

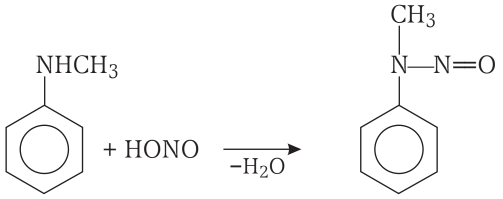
1°, 2° and 3° aromatic amines react differently with HNO_2.

(i) Primary aromatic amines, like aniline when react with HNO_2 (nitrous acid) under ice cold conditions form benzene diazonium chloride. The reaction is called **diazotisation reaction.**



aniline
aniline
hydrogen chloride
benzene
diazonium chloride

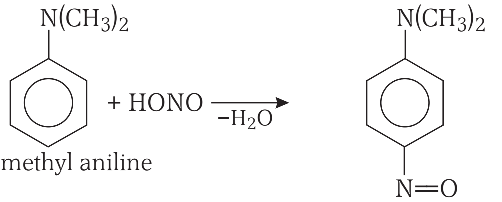
(ii) Secondary aromatic amines, like aliphatic 2° amines, form a yellow oily layer of nitroso derivatives.



2° amine

N-nitroso-N-methylaniline
(yellow oily liquid)

(iii) Tertiary aromatic amines, on the other hand, form a coloured nitroso derivative (*p*-product). The reaction is called **nitrosation.**



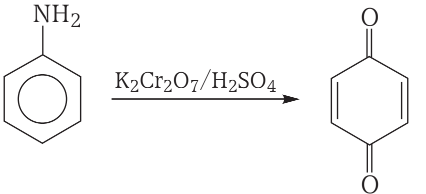
dimethyl aniline

p-nitroso-N, N-dimethylaniline

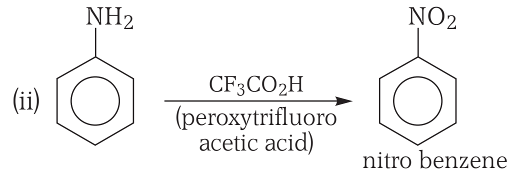
(h) Oxidation

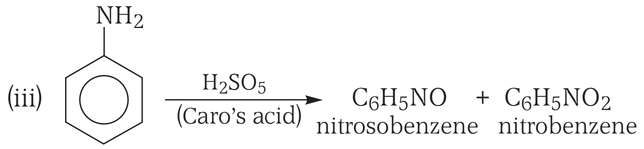
Aniline is quite sensitive to oxidation and gives different products with different oxidising agents. *e.g.,*

(i)



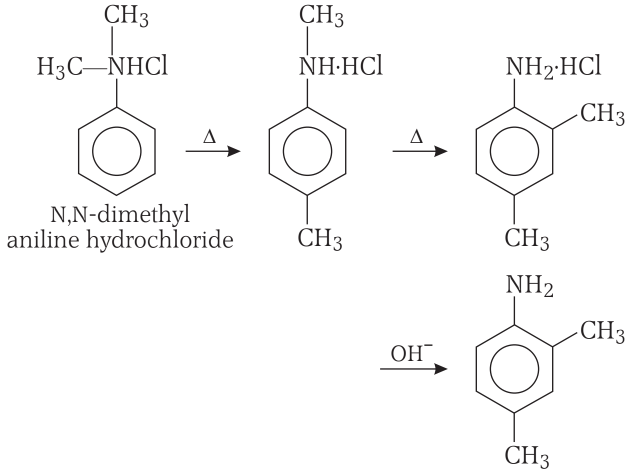
p-benzoquinone





(i) Hofmann Martius Rearrangement

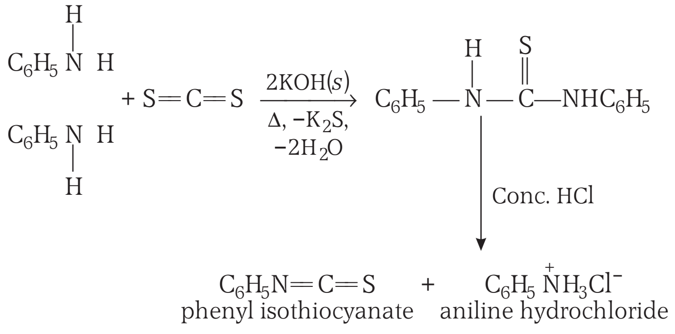
By this reaction, a 2° aromatic amine (in the form of salt) rearrange itself to give a 1° aromatic amine.



(Here, the alkyl group preferentially migrates to *p*-position and if it is occupied then to *o*-position).

(j) Hofmann Mustard Oil Reaction

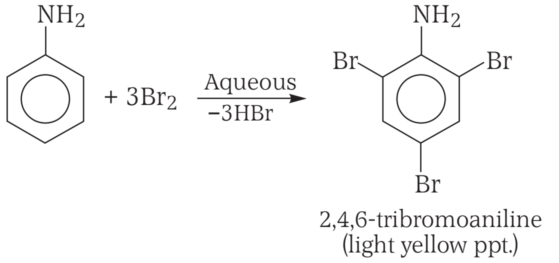
Primary aromatic amines, like aniline when heated with ethanolic solution of CS_2 and solid KOH, give N,N-diphenylthiourea which reacts with conc. HCl to give phenyl isothiocyanate (having a smell of mustard oil).



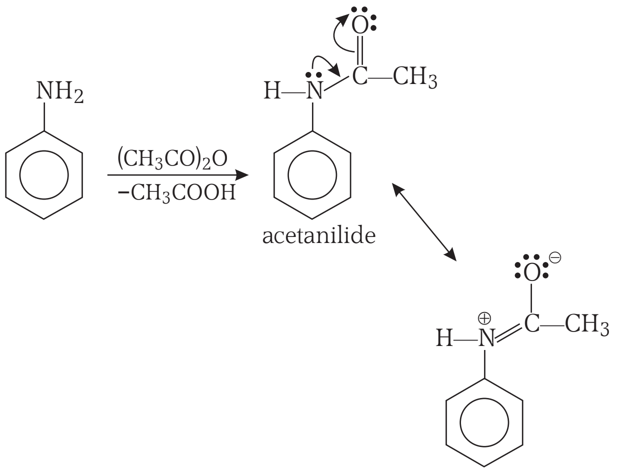
(k) Electrophilic Substitution Reactions

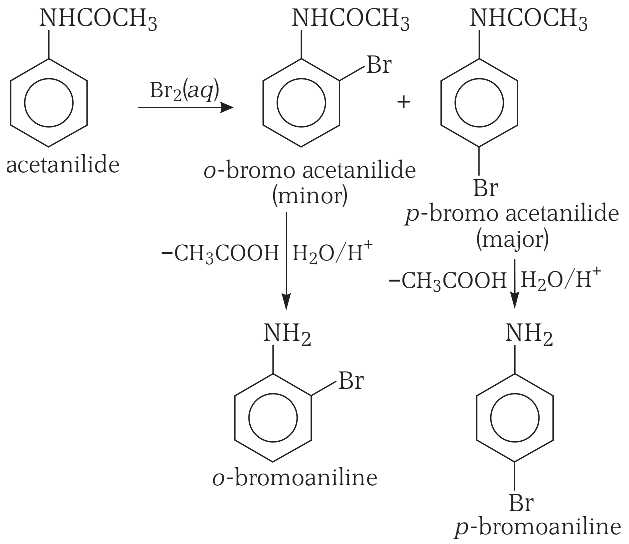
—NH_2 is an *ortho/para* directing group and activates the ring strongly so that the substitution takes place readily even under mild conditions.

(i) On halogenation, in aqueous medium, aniline gives a trisubstituted product.

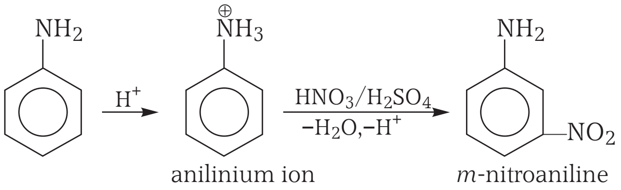


However, in order to prepare monohalo aniline derivative, the —NH_2 group of aniline is first protected by reacting it with acetyl chloride or acetic anhydride and after that it is subjected to halogenation.

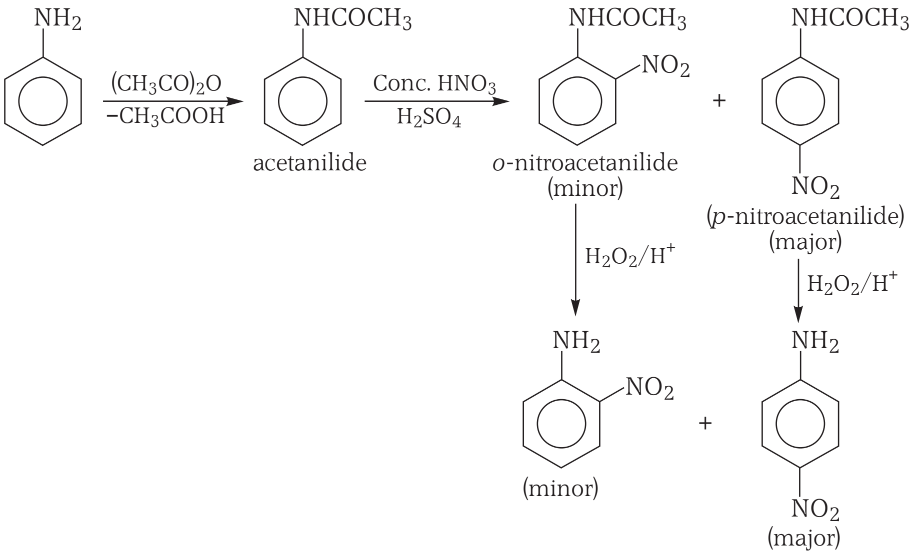




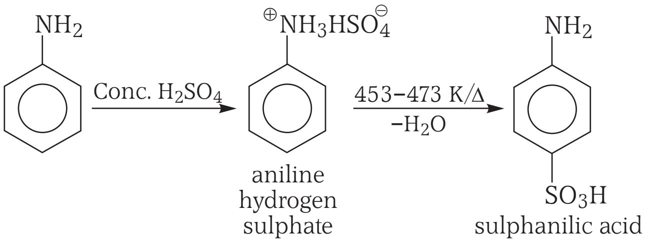
(ii) On nitration (with nitrating mixture, *i.e.,* Conc. HNO_3 / Conc. H_2SO_4), aniline, gets converted into black tarry mass and a itro product is obtained in very poor yield. However, in the presence of strongly acidic medium, aniline gets converted into anilinium ion which being electron deficient, deactivates the *o/p* position and thus, a *meta*-nitro derivative is obtained.



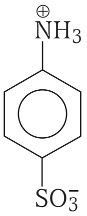
Hence, to obtain *o/p* products, first aniline is deactivated by treating it with acetic anhydride (or acetyl chloride) and then subjected to nitration. The obtained *o/p*-nitro acetanilide upon hydrolysis give *o/p*-nitro aniline.



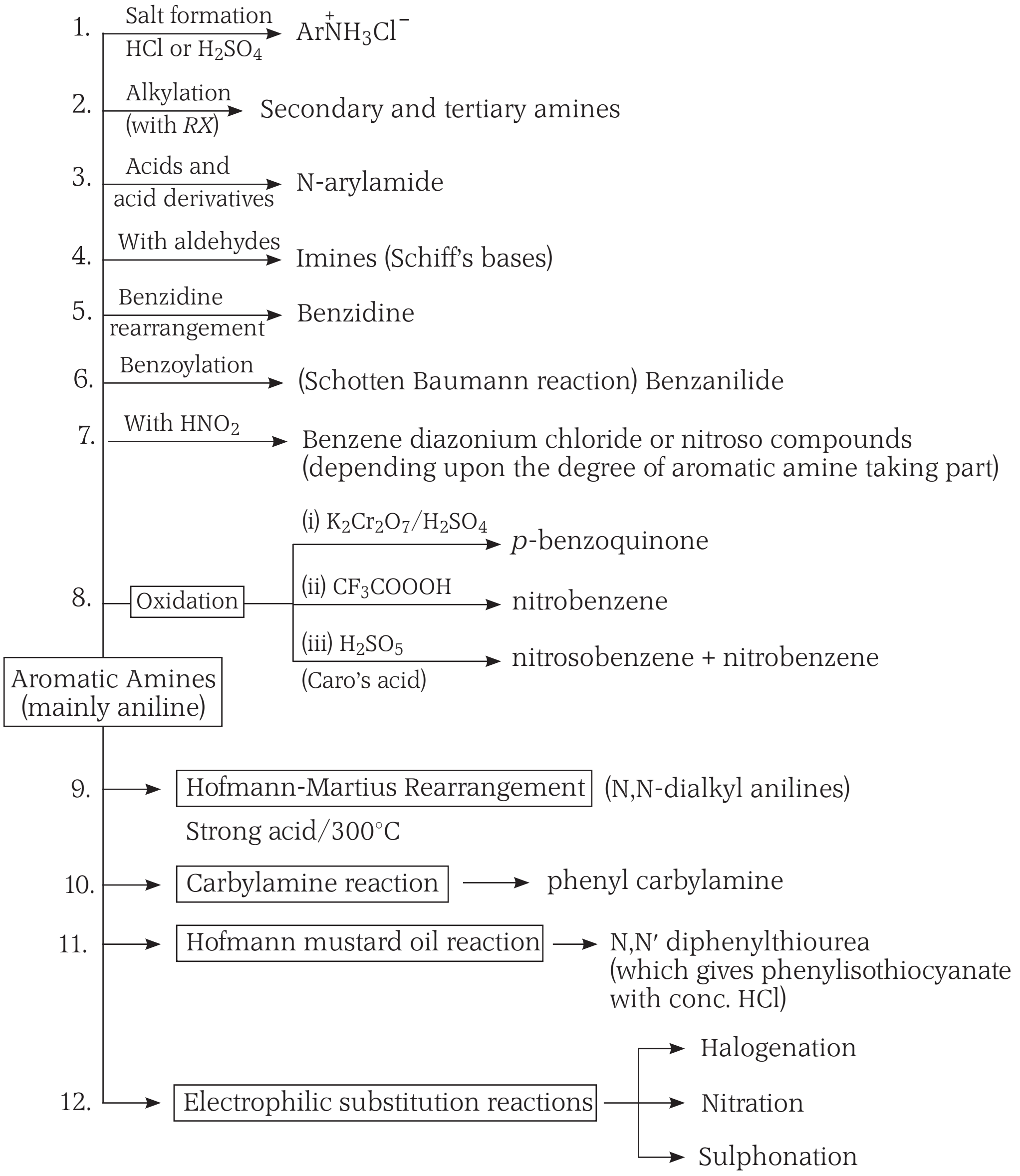
(iii) Aniline, when subjected to sulphonation (*i.e.,* treated with conc. H_2SO_4), form anilinium hydrogen sulphate, a salt, which on heating at 453–473 K gives *p*-aminobenzene sulphonic acid (also called sulphanilic acid).



Sulphanilic acid, usually, exists in the form of a dipolar ion, called **Zwitter ion** as



The outline of the chemical properties of aromatic amines looks like



12.6 Use of Amines

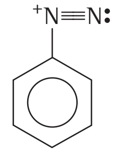
1. Amines are the important consituents of proteins, enzymes, many harmones. Thus, these play an important role in human life.
2. Lower members of the aliphatic amines such as ethylamine, diethylamine etc., are used as reagents in the synthesis of organic compounds and also as solvents both in the laboratory and industry.
3. Quaternary ammonium salts derived from long chain tertiary amines are used as detergents.
4. Aniline and other aromatic amines used in the manufacture of dyes and drugs.
5. Aniline is used to synthesise diazonium salts which are of synthetic importance.

Hot Spot 2

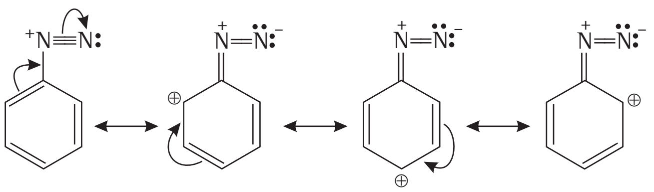
BENZENE Diazonium Salts

It is the most important topic of this chapter for JEE Main examination. The questions are generally based on its synthetic reactions and in the type of sequence reactions. The level of questions vary from easy to average.

All benzene diazonium salts contain benzene diazonium ion, which has the following structure.



This ion is stabilised by resonance (involved between the benzene nucleus and N atom) as

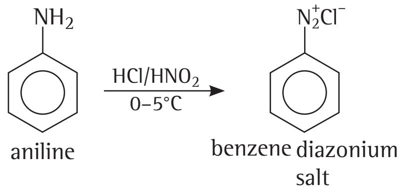


(Resonance structures of benzene diazonium ion)

Presence of electron releasing group like —NR_2, — OR etc., at *ortho/para* position in the benzene ring stabilises the benzene diazonium ion (or salts).

Method of Preparation

Primary aromatic amines when reacts with HNO_2 form diazonium salts at low temperatures (0–5°C). The reaction is called **diazotisation.**



Physical Properties

1. Diazonium salts are colourless crystalline solids but get colour when exposed to air.
2. Due to their ionic nature, they are water soluble.
3. In aqueous solution, these are good conductors of electricity.

Chemical Properties

Due to better leaving ability of diazonium group, it is substituted by other groups such as $Cl^{\ominus}$, $Br^{\ominus}$, $I^{\ominus}$, $CN^{\ominus}$ and $OH^{\ominus}$, which displaces nitrogen from the aromatic ring. The nitrogen formed escaped from the reaction mixture as a gas.

Moreover, benzene diazonium salts being weak electrophiles, react with strongly activated ring (like phenol, naphthols, aromatic amines) to form coupling products. Thus, these reactions are called coupling reactions.

The conditions for coupling reactions are

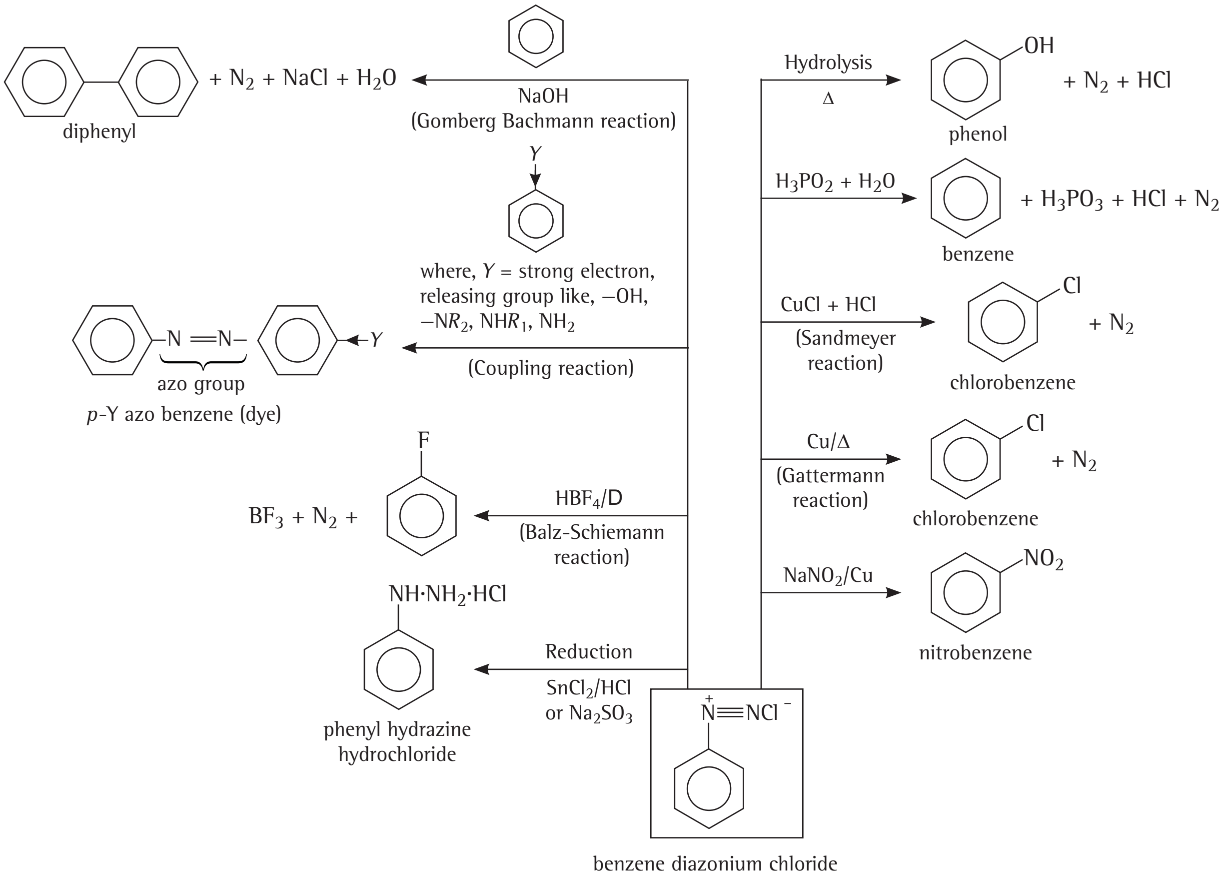
1. The solution must be so alkaline that the concentration of diazonium ion is too low.
2. It must not be so acidic that the concentration of free amine or phenoxide ion is too low.

That is why amines couple fastest in mild acidic solution and phenols couple fastest in mild alkaline solution.

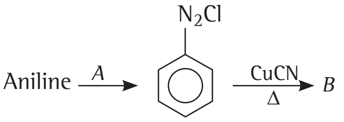
Coupling is better in the following cases.

1. The more electron withdrawing group in diazonium ion, the faster the coupling is.
2. The more electron donating group in coupling compound, the faster the coupling is.
3. $ArN_2^{\oplus}$ is weak alectrophile which undergoes diazo coupling only with the ring activated by (— OH), (—NH_2), (—NHR), or (—NR_2) groups.

Diazonium salt have very wide synthetic activities that are summarised as



Sample Problem 9



A and B respectively are

(a) HNO_2/H^+ and methylcyanide

(b) $NaNO_2$/HCl and benzonitrile

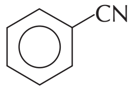
(c) HNO_3 and benzonitrile

(d) Phenol and methyl nitrile

Interpret (b) $NaNO_2$/HCl (or HNO_2) causes diazotisation of aniline and results in the formation of diazonium salt which when react with CaCN gives benzonitrile.

Thus, $A = HNO_2$ or $NaNO_2/HCl$

$B =$



Check Point 2

1. Why is it necessary to convert aniline into acetanilide before subjected to halogenation or nitroation to get monoderivative?
2. Diphenyl amine is less basic while N-methyl aniline is more basic as compared to aniline. Explain.
3. Why does diazonium salt give coupling reaction?
4. $CH_3C_6H_4CONH_2$ undergoes Hofmann bromamide reaction readily as compared to $C_6H_5CONH_2$. Explain.

WORKED **OUT**
Examples

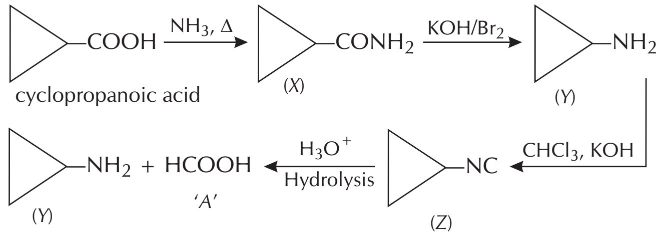
Example 1 *Cyclopropanoic acid* $\xrightarrow{NH_3,\ heat} X \xrightarrow{KOH/Br_2} Y$

$\xrightarrow{CHCl_3/KOH} Z \xrightarrow{H_3O^+} \underset{(A)}{\text{Carboxylic acid}}$

The final products of the above sequence of steps are

(a) *X and Z*
(b) HCOOH *and Y*
(c) CH_3NH_2 *and A*
(d) *A and X*

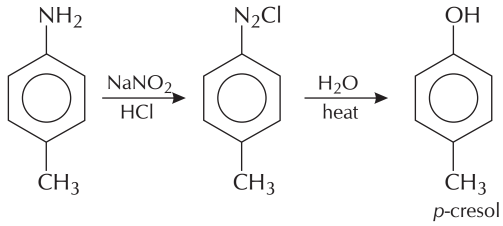
Solution (*b*) The chemical reactions involved in the above sequence of steps are as follows



Example 2 *p-toluidine is treated with an ice cold solution of sodium nitrite and hydrochloric acid. The crystalline precipitate so formed is boiled with water. The resulting product is*

(a) *toluic acid*
(b) *phenol*
(c) *p-cresol*
(d) *p-nitro toluene*

Solution (*c*)



Example 3 *An aliphatic amine with molar mass 73 g mol*$^{-1}$ *on heating with excess of* CH_3I *gave a quaternary salt. The amine can be*

I. N,N-diethyl ethanamine
II. N-methyl propanamine
III. 2-butanamine
IV. Neo-pentylamine

(a) *II and III*
(b) *II only*
(c) *I and III*
(d) *IV only*

Solution (*a*) Let the amine be $C_nH_{2n+3}N$.

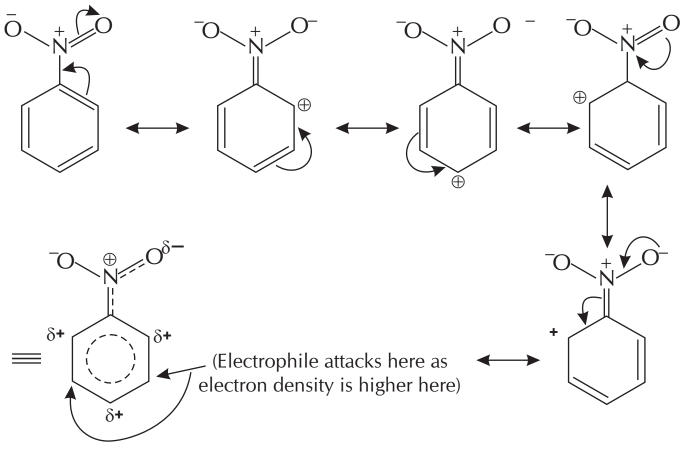
$$\text{The molar mass} = (14n + 17)$$
$$14n + 17 = 73 \quad \text{or} \quad n = 4$$

Among the given amines only II and III correspond to the given data and also have four carbons.

Example 4 *When nitrobenzene is treated with* Br_2 *in the presence of* $FeBr_3$*, the major product formed is m-bromo nitrobenzene. Which of the following statements is/are related to the process?*

(a) *Electron density on m-carbon is more than that on ortho or para carbons*
(b) *Loss of aromaticity occurs, when* Br^+ *attacks at the ortho or para positions and not at meta position*
(c) *Intermediate carbocation formed after initial attack of* Br^+ *at the meta position is least stabilised*
(d) *Easier loss of* H^+ *to regain aromaticity from meta position than from ortho and para position*

Solution (*a*) Nitrobenzene has the following resonating structures



Example 5 *Benzylamine may be alkylated as shown in the following equation*

$$C_6H_5CH_2NH_2 + R\text{—}X \longrightarrow C_6H_5CH_2NHR$$

(pyridine is used to scavage HX *produced here)*

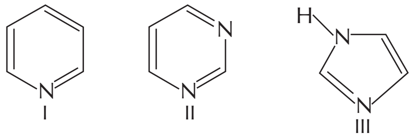
Which of the following alkyl halides is best suited for this reaction?

(a) $(CH_3)_3CCH_2Br$
(b) C_6H_5Br
(c) $C_6H_5CH_2Br$
(d) $(CH_3)_3CCl$

Solution (*c*) The given reaction proceeds through S_N2 mechanism, thus, 1° alkyl halide is the most preferred site.

Example 6 *Three heterocyclic amines are shown below :*

I. *Pyridine*, II. *Pyrimidine* III. *Imidazole.*



What is the order of increasing basicity?

(*weaker base* < *stronger base*)

(*a*) II < I < III (*b*) II < III < I

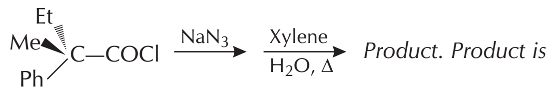
(*c*) I < II < III (*d*) III < II < I

Solution (*a*) Among the given, imidazole is most basic as it is non-aromatic and has one nitrogen atom in sp^3 hybrid state.

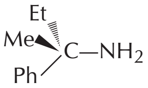
Between pyridine and pyrimidine, pyridine is more basic as in it, the lone pair of electrons is relatively more free for donation. Thus, the order of basic character is

$$II < I < III$$

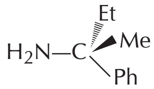
Example 7 *Consider the following reaction*



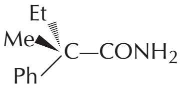
(*a*)



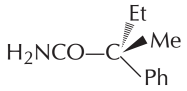
(*b*)



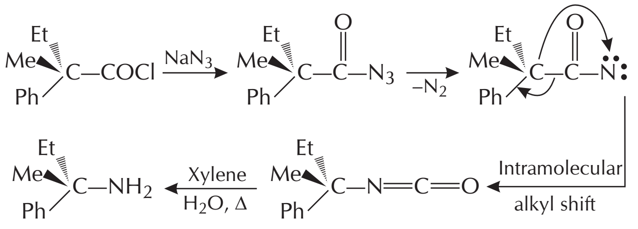
(*c*)



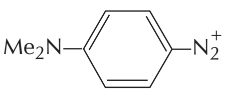
(*d*)



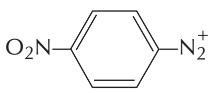
Solution (*a*) Curtius rearrangement involves retention of configuration of the migratory group. Thus,



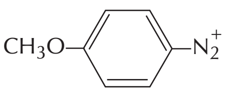
Example 8 *Consider the following diazonium ions*



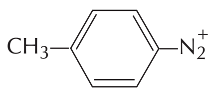
(I)



(II)



(III)



(IV)

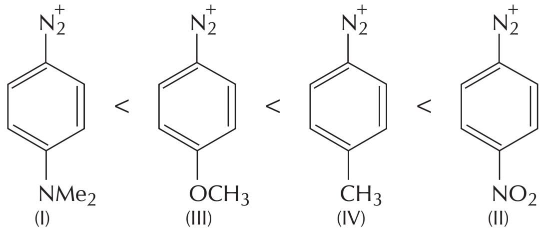
The order of reactivity towards diazo-coupling with phenol in the presence of dil. NaOH *is*

(*a*) I < IV < II < III (*b*) I < III < IV < II

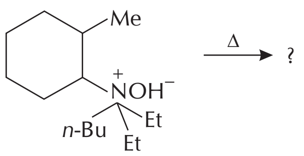
(*c*) III < I < II < IV (*d*) III < I < IV < II

Solution (*b*) Diazonium ion acts as an electrophile in coupling reactions. Greater the electron withdrawing power, higher the electrophilicity.

Thus, the order of reactivity towards diazo-coupling with phenol in the presence of dilute NaOH is

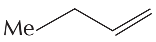


Example 9



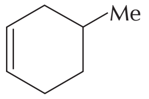
The alkene formed as a major product in this elimination reaction is

(*a*)

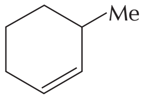


(*b*) $CH_2{=}CH_2$

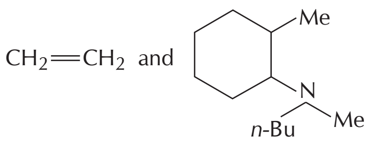
(*c*)



(*d*)



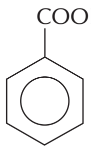
Solution (*b*) The heating involves Hofmann elimination giving least substituted alkene along with 3° amine. The products are



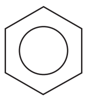
Example 10 $C_6H_6 \xrightarrow[\text{(ii) Zn/HCl }\Delta]{\text{(i) HNO}_3/\text{H}_2\text{SO}_4} X \xrightarrow[\text{HCl}]{\text{NaNO}_2} Y \xrightarrow[\text{H}_2\text{O}]{\text{H}_3\text{PO}_2} Z$

Z in the following sequence of reactions is

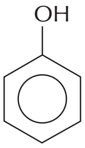
(*a*)



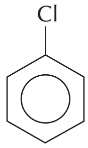
(*b*)



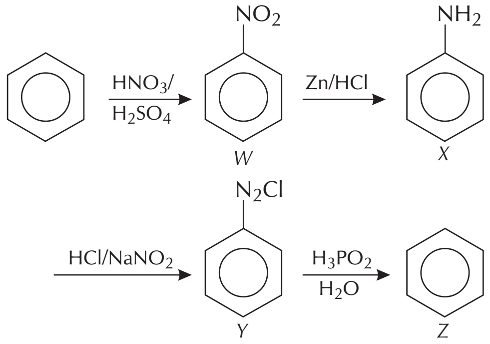
(*c*)



(*d*)



Solution (*b*)

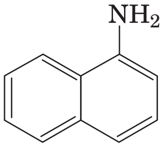


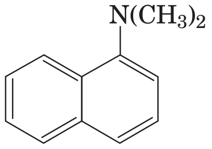
Start Practice for JEE Main

Round I (Topically Divided Problems)

General Introduction

1. How many of these are primary amines? **[NCERT]**





$(C_2H_5)_2CHNH_2$ $(C_2H_5)_2NH$

(a) 1 (b) 2
(c) 3 (d) 4

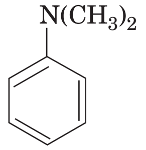
2. How many isomeric amines corresponds to the molecular formual $C_4H_{11}N$? **[NCERT]**

(a) 4 (b) 6
(c) 8 (d) 10

3. What is the structure and IUPAC name of the compound, allyl amine? **[NCERT Exemplar]**

(a) Propanamine (b) 2-methyl propanamine
(c) Prop-1-ene-1-amine (d) Prop-2-ene-1-amine

4. Write down the IUPAC name of **[NCERT Exemplar]**



(a) N-methyl-N-benzyl methanamine
(b) dimethyl phenyl amine
(c) N-phenyl-N-methyl methanamine
(d) N, N-dimethyl benzenamine

5. IUPAC name of the compound $(C_2H_5)_2NCH_3$ is **[NCERT]**

(a) 2,2-diethyl methanamine
(b) N,N-diethyl methanamine
(c) N-ethyl-N-methyl ethanamine
(d) N-methyl butanamine

6. *Iso*-propyl amine is a

(a) primary amine (b) secondary amine
(c) tertiary amine (d) quaternary amine

Methods of Preparation of Amines

7. Production of amines by ammonia and alkyl halides is called

(a) Frankland reaction
(b) Hofmann's ammonolysis
(c) Hofmann's mustard oil reaction
(d) Hofmann's bromamide reaction

8. Which of the following cannot be used for the following conversion?

$$CH_3CN \longrightarrow CH_3CH_2NH_2$$

(a) Pt/H_2 (b) $LiAlH_4$
(c) Na/C_2H_5OH (d) $SnCl_2/HCl$

9. $>C=O$ compounds reacts with NH_3 or amines followed by H_2 / Ni. The reaction is called

(a) Mendius reaction
(b) Hofmann bromamide
(c) Reductive amination
(d) Gabriel's phthalimide

10. The source of nitrogen in Gabriel synthesis of amines is **[NCERT Exemplar]**

(a) sodium azide, NaN_3
(b) sodium nitrite, $NaNO_2$
(c) potassium cyanide, KCN
(d) potassium phthalimide, $C_6H_4(CO)_2N^-K^+$

11. Best method for preparing primary amines from alkyl halides without changing the number of carbon atoms in the chain is **[NCERT Exemplar]**

(a) Hofmann bromamide reaction
(b) Gabriel phthalimide synthesis
(c) Sandmeyer reaction
(d) reaction with NH_3

12. Hofmann bromamide degradation reaction is shown by **[NCERT Exemplar]**

(a) $ArNH_2$ (b) $ArCONH_2$

(c) $ArNO_2$ (d) $ArCH_2NH_2$

13. Which of the following methods of preparation of amines will give same number of carbon atoms in the chain of amines as in the reactant? **[NCERT Exemplar]**

(a) Reaction of nitrite with $LiAlH_4$

(b) Reaction of amide with $LiAlH_4$ followed by treatment with water

(c) Heating alkylhalide with potassium salt of phthalimide followed by hydrolysis

(d) Treatment of amide with bromine in aqueous solution of sodium hydroxide

14. Which of the following reagents would not be a good choice for reducing an aryl nitro compound to an amine? **[NCERT Exemplar]**

(a) H_2 (excess)/Pt (b) $LiAlH_4$ in ether

(c) Fe and HCl (d) Sn and HCl

15. In the reaction,

$RCONH_2 + X \longrightarrow RNH_2$, the reagent X is

(a) soda lime (b) PCl_5

(c) NaOBr (d) All of these

16. Nitrobenzene is reduced by Zn and alcoholic potash mixture to get

(a) $C_6H_5—NH_2$

(b) $C_6H_5—NH—NH—C_6H_5$

(c) $C_6H_5—N—N=C_6H_5$

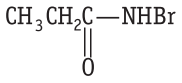
(d) $C_6H_5—NH—CO—C_6H_5$

17. Given the following sequence of reactions,

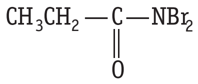
$$CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{Partial hydrolysis}]{OH^-} B \xrightarrow{Br_2/NaOH} C$$

The major product 'C' is

(a) $CH_3CH_2NH_2$

(b) 
$CH_3CH_2\underset{\underset{O}{\|}}{C}—NHBr$

(c) $CH_3CH_2—COONH_4$

(d) 
$CH_3CH_2—\underset{\underset{O}{\|}}{C}—NBr_2$

18. $A \xrightarrow{H_2NOH} B \xrightarrow{\text{Reduction}} C \xrightarrow{NOCl} CH_3CH_2Cl$

In the above sequence A and C are

(a) methanal, methyl amine

(b) acetone, ethaneamine

(c) ethanal, dimethyl amine

(d) acetaldehyde, ethyl amine

19. Amine is not formed in the reaction

I. hydrolysis of RCN

II. reduction of $RCH=NOH$

III. hydrolysis of RNC

IV. hydrolysis of $RCONH_2$

The correct answer is

(a) I, II, IV (b) I, IV

(c) II, III (d) I, II, III

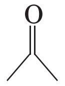
20. Ethyl isocyanide on hydrolysis in acidic medium generates

(a) ethyl amine salt and methanoic acid

(b) propanoic acid and ammonium salt

(c) ethanoic acid and ammonium salt

(d) methyl amine salt and ethanoic acid

21. 
$\xrightarrow{NH_2OH} X \xrightarrow{LiAlH_4} Y$. In the above sequence, Y is

(a) tertiary amine (b) secondary amine

(c) primary amine (d) 2-nitropropane

22. Reduction of aromatic nitro compounds using Fe and HCl gives **[NCERT Exemplar]**

(a) aromatic oxime

(b) aromatic hydrocarbon

(c) aromatic primary amine

(d) aromatic amide

23. In order to prepare a 1° amine from an alkyl halide with simultaneous addition of one CH_2 group in the carbon chain, the reagent used as source of nitrogen is **[NCERT Exemplar]**

(a) sodium amide, $NaNH_2$

(b) sodium azide, NaN_3

(c) potassium cyanide, KCN

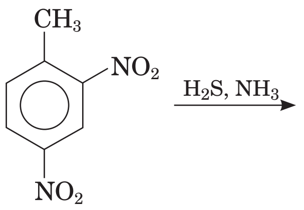
(d) potassium phthalimide, $C_6H_4(CO)_2N^-K^+$

24. The best reagent for converting, 2-phenylpropanamide into 1- phenylethanamine is **[NCERT Exemplar]**

(a) excess H_2/Pt (b) $NaOH/Br_2$

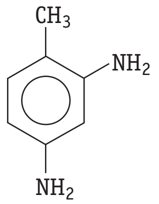
(c) $NaBH_4$/methanol (d) $LiAlH_4$/ether

25. The product obtained in the reduction

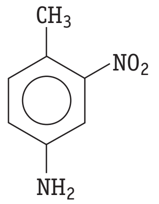


is

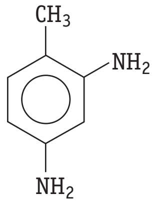
(a)



(b)



(c)



(d) The compound is not reduced

26. Match the following.

	Reactions		Name
A.	$(CH_3)_3C-OH + HCN \xrightarrow{H^+} (CH_3)_3C-NH_2$	1.	Grignard
B.	$CH_3CONH_2 + Br_2 + KOH \longrightarrow RNH_2$	2.	Mendius
C.	$CH_3CN + 4H \xrightarrow[alc.]{Na} CH_3CH_2NH_2$	3.	Hofmann bromamide
D.	$CH_3MgBr + ClNH_2 \longrightarrow CH_3NH_2$	4.	Ritter

Codes

	A	B	C	D		A	B	C	D
(a)	1	2	3	4	(b)	4	3	2	1
(c)	2	3	4	1	(d)	4	2	3	1

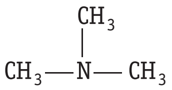
27. In which reaction, nitrene is not the intermediate?
(a) Schmidt
(b) Curtius
(c) Hofmann bromamide
(d) Gabriel's phthalimide

Basicity and Physical Properties of Amines

28. Which of the following statements are correct?
(a) Aniline is a stronger base than ethyl amine
(b) Aniline is a stronger base than *p*-methoxyaniline
(c) Aniline must be acetylated before nitration with an acid mixture
(d) Aniline is soluble in an ammonium hydroxide solution

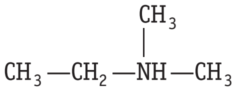
29. Choose the incorrect statement.
(a) In the case of primary, secondary and tertiary amines, the basic strength depends on the extent of hydrogen bonding in the protonated amines
(b) The presence of groups like $-OCH_3$ and $-CH_3$ increases the basic strength of amines
(c) The presence of groups like $-NO_2$, $-CN$ and halogens reduces the basic strength of amines
(d) The basic strength of amines depends on their concentration

30. Which of the following is the most basic in aqueous medium?
(a) $CH_3CH_2CH_2CH_2NH_2$
(b) $CH_3-CH_2-CH_2-NH_2$
(c)



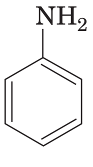
$CH_3-\underset{}{\overset{CH_3}{\overset{|}{N}}}-CH_3$

(d)

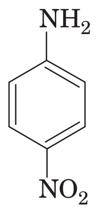


$CH_3-CH_2-\overset{CH_3}{\overset{|}{N}H}-CH_3$

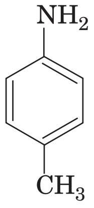
31. The correct increasing order of basic strength for the following compounds is **[NCERT Exemplar]**



(I)



(II)

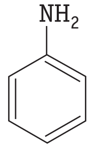


(III)

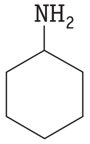
(a) II < III < I
(b) III < I < II
(c) III < II < I
(d) II < I < III

32. Which of the following compounds is the weakest Bronsted base? **[NCERT Exemplar]**

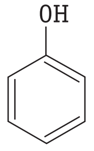
(a)



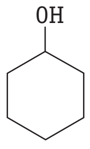
(b)



(c)



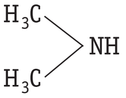
(d)



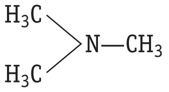
33. The most reactive amine towards dilute hydrochloric acid is **[NCERT Exemplar]**

(a) CH_3-NH_2

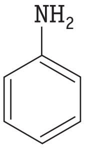
(b)



(c)



(d)

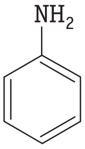


34. Arrange the following in the decreasing order of pK_b values

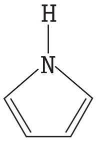
I. $C_2H_5NH_2$, II. $C_6H_5NHCH_3$,
III. $(C_2H_5)_2NH$ IV. $C_6H_5NH_2$ **[NCERT]**

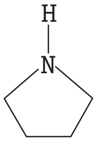
(a) IV > II > I > III
(b) IV > II > III > I
(c) I > III > IV > II
(d) I > III > II > IV

35. Among the following amines, the strongest Bronsted base is

(a) 

(b) NH_3

(c) 

(d) 

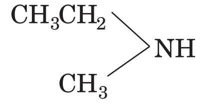
36. Among the following, the weakest base is
(a) $C_6H_5CH_2NH_2$ (b) $C_6H_5CH_2NHCH_3$
(c) $O_2NCH_2NH_2$ (d) CH_3NHCHO

37. Correct order of basic nature of $CH_3NH_2(A)$, CH_3CN (B) and $CH_3N{=}CHCH_3$ (C) is
(a) $A > B > C$ (b) $B > C > A$
(c) $A > C > B$ (d) $C > A > B$

38. The compound, N-ethyl-N-methylpropanamine forms non-superimposable mirror images but does not show optical activity. This is due to
(a) absence of a chiral N-atom
(b) presence of a chiral N-atom
(c) presence of lone pair on N-atom
(d) rapid flipping of one form into another

39. Which of the following should be most volatile? **[NCERT Exemplar]**

I. $CH_3CH_2CH_2NH_2$ II. $(CH_3)_2N$

III. 
$(CH_3CH_2)(CH_3)NH$

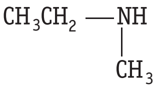
IV. $CH_3CH_2CH_3$

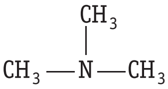
(a) II (b) IV (c) I (d) III

40. In pyridine, the state of hybridisation of the nitrogen atom is
(a) sp^2 (b) sp^3
(c) sp (d) None of these

41. Which of the following amines form maximum hydrogen bonds within themselves?
(a) CH_3NH_2 (b) $(CH_3)_2NH$
(c) $(CH_3)_3N$ (d) None of these

42. Which among the following has the highest boiling point?
(a) $CH_3CH_2CH_2NH_2$

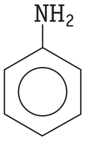
(b) 
$CH_3CH_2{-}NH{-}CH_3$

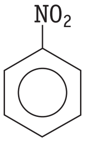
(c) 
$CH_3{-}N(CH_3){-}CH_3$

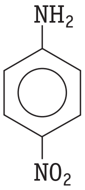
(d) CH_3NH_2

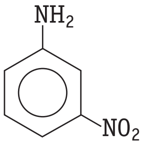
43. Which of the following statements is not correct?
(a) Primary amines show intermolecular hydrogen bonding
(b) Secondary amines show intermolecular hydrogen bonding
(c) Tertiary amines show intermolecular hydrogen bonding
(d) Amines have lower boiling points as compared to those of alcohols and carboxylic acids of comparable molar masses

44. Which of the following will have larger dipole moment?

(a) 

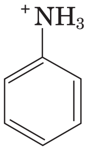
(b) 

(c) 

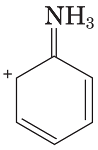
(d) 

45. The basicity of aniline is less than that of cyclohexylamine. This is due to
(a) $+R$-effect of $-NH_2$ group
(b) $-I$-effect of $-NH_2$ group
(c) $-R$-effect of $-NH_2$ group
(d) hyperconjugation effect

46. Examine the following two structures for the anilinium ion and choose the correct statement from the ones given below



(I)



(II)

(a) II is not acceptable as canonical structure because carbonium ions are less stable than ammonium ions
(b) II is not an acceptable canonical structure because it is non-aromatic
(c) II, is not an acceptable canonical structure because in it, N has 10 valence electrons
(d) II is an acceptable canonical structure

Chemical Properties of Amines

47. The compound that will react most readily with NaOH to form methanol is
(a) $(CH_3)_4N^+I^-$ (b) CH_3OCH_3
(c) $(CH_3)_3S^+I^-$ (d) $(CH_3)_3CCl$

48. Acid anhydrides on reaction with primary amines give **[NCERT Exemplar]**
(a) amide (b) imide
(c) secondary amine (d) imine

49. What is the role of pyridine in the acylation reaction of amines? **[NCERT Exemplar]**
(a) Pyridine dissolves the product formed
(b) Pyridine makes CH_3COCl more reactive
(c) Pyridine removes side product
(d) None of the above

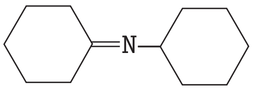
50. 1 mole of ethyl amine on reaction with HNO_2 gives at NTP
(a) 11.2 L of N_2 (b) 5.6 L of N_2
(c) 22.4 L of N_2 (d) 1 L of N_2

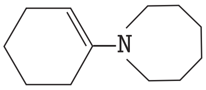
51. The gas evolved when methylamine reacts with nitrous acid is **[NCERT Exemplar]**
(a) NH_3 (b) N_2
(c) H_2 (d) C_2H_6

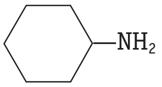
52. Which of the following reactions is given by only primary amines?
(a) Reaction with HONO
(b) Reaction with chloroform and alcoholic KOH
(c) Reaction with acetyl chloride
(d) Reaction with Grignard reagent

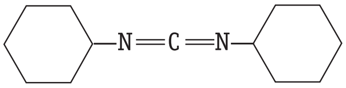
53. Isopropylamine $\xrightarrow{KMnO_4} X \xrightarrow{H_3O^+} Y$.
In the above sequence, X and Y are respectively
(a) acetaldimine, ethanal
(b) ethanal, ketimine
(c) ketimine, acetone
(d) acetone, propan-2-ol

54. Which of the following is an enamine?

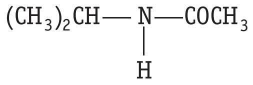
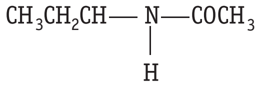
(a) 

(b) 

(c) 

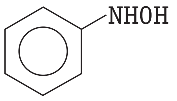
(d) 

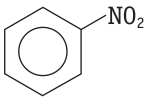
55. A positive carbylamine test is given by
(a) N,N-dimethylaniline
(b) 2,4-dimethylaniline
(c) N-methyl-*o*-methylaniline
(d) N-methylbenzylamine

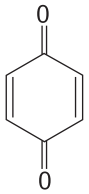
56. *Iso*-propyl amine, with excess of acetyl chloride will give
(a) $(CH_3CO)_2N—C—(CH_3)_3$
(b) 
$(CH_3)_2CH—\underset{H}{\underset{|}{N}}—COCH_3$
(c) $(CH_3)_2CHN(COCH_3)_2$
(d) 
$CH_3CH_2CH—\underset{H}{\underset{|}{N}}—COCH_3$

57. Which of the following compounds will undergo carbylamine reaction?
(a) $(CH_3CH_2)_2NH$ (b) $(CH_3)_2NH$
(c) $C_6H_5NH_2$ (d) $(CH_3)_3N$

58. The oxidation of aniline with per acetic acid in the presence of acetic acid by refluxing gives

(a) 

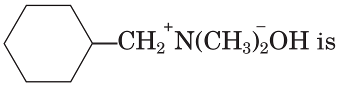
(b) 

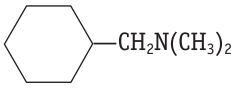
(c) 

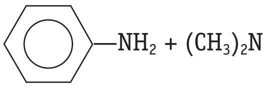
(d) None of these

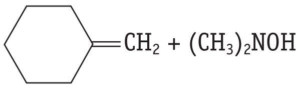
59. Amine oxide, when heated forms alkene. The reaction is known as
(a) Curtius
(b) Cope elimination
(c) Mannich
(d) Hofmann elimination

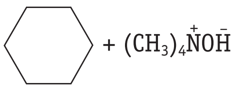
60. The product of Hofmann elimination of



(a) 

(b) 

(c) 

(d) 

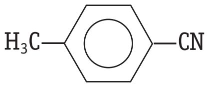
61. Reaction of benzaldehyde with methylamine gives
(a) C_6H_5COOH (b) $C_6H_5N{=}NCl$
(c) $C_6H_5—CH{=}N—CH_3$ (d) $C_6H_5NH_2$

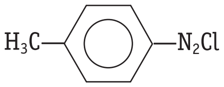
62. The end product in the below reaction is

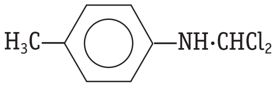
$$C_2H_5NH_2 \xrightarrow{HNO_2} A \xrightarrow{PCl_5} B \xrightarrow{NH_3} C$$

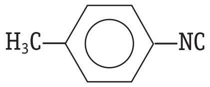
(a) ethyl cyanide (b) ethyl amine
(c) methyl amine (d) acetamide

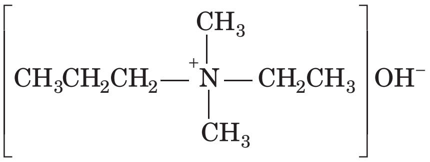
63. The reaction of chloroform with alcoholic KOH and *p*-toluidine form

(a) 

(b) 

(c) 

(d) 

64. When 
$\left[CH_3CH_2CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{\overset{+}{N}}}-CH_2CH_3\right]OH^-$
is heated, then

(a) propene is the major product
(b) ethene and $C_3H_7N(CH_3)_2$ are the only product
(c) ethene and propene are obtained while ethene as the major product
(d) equimolar amounts of ethene and propene are obtained

65. $Y \underset{Z}{\overset{\text{Reduction}}{\rightleftharpoons}} [R_2C{=}NH] \xrightarrow{H_3O^+} X$

In the above sequence of reactions *X*, *Y*, *Z* are respectively

(a) aldehyde, ketone, NH_3
(b) ketone, 1° amine, $KMnO_4$
(c) ketone, 2° amine, $KMnO_4$
(d) ketimine, 1° amine, H_2SO_5

66. In the following reaction, *X* is

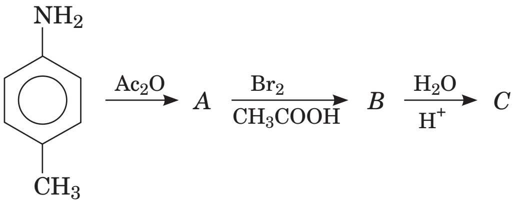
$X \xrightarrow{\text{Bromination}} Y \xrightarrow[+\,HCl]{NaNO_2} Z \xrightarrow[C_2H_5OH]{\text{Boiling}}$ Tribromo benzene

(a) benzoic acid
(b) salicylic acid
(c) phenol
(d) aniline

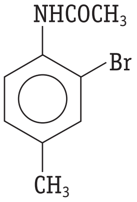
67. $C_6H_5NH_2 \xrightarrow[180°C]{H_2SO_4} H_2NC_6H_4(SO_3H)$ (*para*)

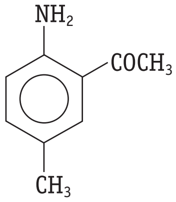
The true statement about the product is

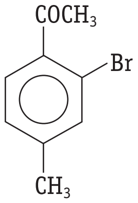
(a) It does not exist as Zwitter ion
(b) $—NH_2$ displays a powerful basic character
(c) It does not act as inner salt
(d) $—SO_3$ dimminishes the basic character of $—NH_2$

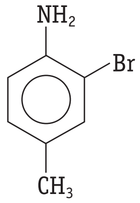
68. 

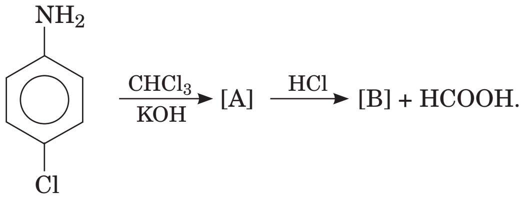
The final product '*C*' in the above reaction is

(a) 

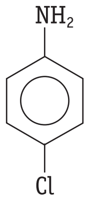
(b) 

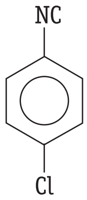
(c) 

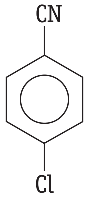
(d) 

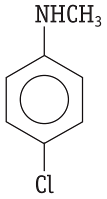
69. 

What is [*B*]?

(a) 

(b) 

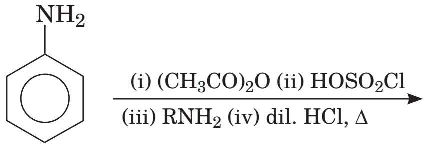
(c) 

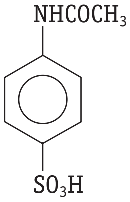
(d) 

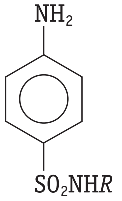
70. Identify the product Z in the following reaction scheme

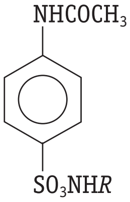
$$C_6H_5NH_2 \xrightarrow{Ac_2O} X \xrightarrow{Br_2/CCl_4} Y \xrightarrow{HOH} Z$$

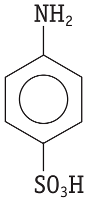
(a) *p*-bromoaniline
(b) *p*-bromoacetophenone
(c) *p*-bromoacetanilide
(d) *o*-bromoacetophenone

71.  $[X]$; here X is

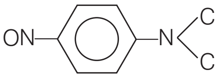
(a) 

(b) 

(c) 

(d) 

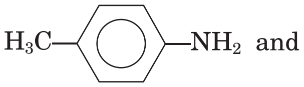
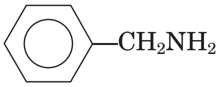
72. Match the following.

	Column I		Column II
A.	$RNH_2 \xrightarrow{NaNO_2 + HCl}$	1.	R_2NNO
B.	$\phi NH_2 \xrightarrow{NaNO_2 + HCl}$	2.	$ROH + N_2$
C.	$\phi N(CH_3)_2 \xrightarrow{NaNO_2 + HCl}$	3.	$\phi NNCl$
D.	$R_2NH \xrightarrow{NaNO_2 + HCl}$	4.	

Codes

	A	B	C	D		A	B	C	D
(a)	2	3	4	1	(b)	1	3	4	2
(c)	2	4	3	1	(d)	1	2	3	4

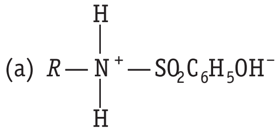
73. Which of the following reagents will be useful as the basic for a simple chemical test to distinguish between?

 and 

(a) $C_6H_5SO_2Cl$ and OH^- in H_2O
(b) HONO, then β-naphthol
(c) Dilute HCl
(d) $AgNO_3$ in H_2O

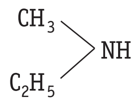
74. Name of method use to separate primary, secondary and tertiary amines is
(a) Hofmann method
(b) Lucas method
(c) Victor Meyer method
(d) Kolbe method

75. RNH_2 reacts with $C_6H_5SO_2Cl$ in aqueous KOH to give a clear solution. On acidification, a precipitate is obtained which is due to the formation of

(a) 
$R-\overset{H}{\underset{H}{N^+}}-SO_2C_6H_5OH^-$

(b) $R-N^-SO_2C_6H_5K^+$
(c) $C_6H_5SO_2NH_2$
(d) $R-NH-SO_2-C_6H_5$

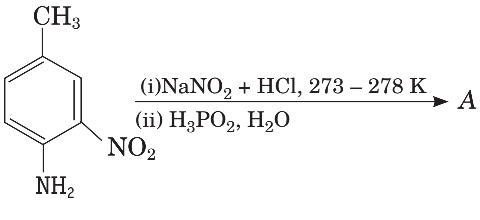
76. A compound of molecular formula C_3H_9N when reacts with benzene sulphonyl chloride gives a product soluble in dilute NaOH solution. The compound should be

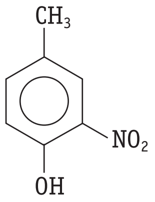
(a) $(CH_3)_3N$
(b) $(CH_3)_2CH-NH_2$
(c) 
$\begin{matrix} CH_3 \\ C_2H_5 \end{matrix}\!\!>NH$
(d) All of these

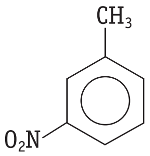
77. A compound Z with molecular formula C_3H_9N reacts with $C_6H_5SO_2Cl$ to give a solid, insoluble in alkali. Identify Z. **[NCERT Exemplar]**
(a) propylamine
(b) N-methylethanamine
(c) 2-amino propane
(d) N,N-dimethyl methanamine

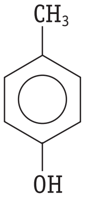
78. When aniline reacts with benzoyl chloride, the product obtained is **[NCERT]**
(a) acetanilie
(b) benzanilide
(c) phenyl amine
(d) N-methyl benzamide

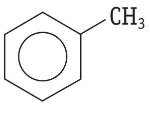
79. Give the structure of 'A' in the following reaction. **[NCERT Exemplar]**

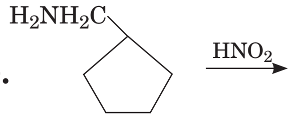


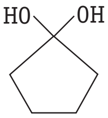
(a) 

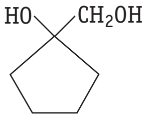
(b) 

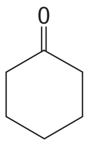
(c) 

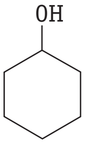
(d) 

80.  ? Product is

(a) 

(b) 

(c) 

(d) 

81. The reagents used (incorrect sequence) to convert benzene into N,N-dimethyl aniline is **[NCERT]**

(a) HNO_3/H_2SO_4, Sn/HCl, C_2H_5I
(b) HNO_3/H_2SO_4, Sn/HCl, CH_3I (2 mol)
(c) Sn / HCl, HNO_3 /H_2SO_4, CH_3I (2 mol)
(d) None of the above

82. An organic amino compound reacts with aqueous nitrous acid at low temperature to produce an oily nitroso amine. The compound is

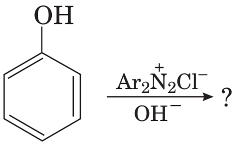
(a) CH_3NH_2 (b) $CH_3CH_2NH_2$
(c) $(CH_3CH_2)_3N$ (d) $CH_3CH_2—NHCH_2CH_3$

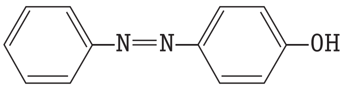
83. Although amino group is *o*/p directing in aromatic electrophilic substitution, aniline on nitration gives a substantial amount of *m*-nitroalinine. This is because **[NCERT]**

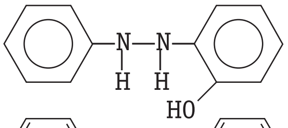
(a) electron density becomes lower at *m*-position
(b) *m*-directing anilinium ion is formed
(c) aniline becomes deactivated in acidic medium
(d) All of the above

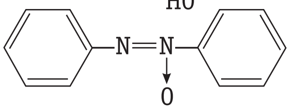
Benzene Diazonium Salts

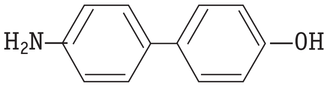
84. Complete the following reaction. **[NCERT Exemplar]**



(a) 

(b) 

(c) 

(d) 

85. The reaction $\mathrm{Ar}\overset{+}{\mathrm{N}}_2\,\mathrm{Cl}^- \xrightarrow{\mathrm{Cu/HCl}} \mathrm{ArCl} + \mathrm{N}_2 + \mathrm{CuCl}$ is named as **[NCERT Exemplar]**

(a) Sandmeyer reaction (b) Gattermann reaction
(c) Claisen reaction (d) Carbylamine reaction

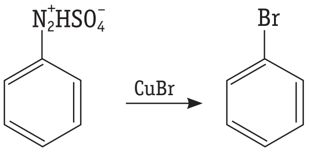
86. Which of the following compound will not undergo azo coupling reaction with benzene diazonium chloride? **[NCERT Exemplar]**

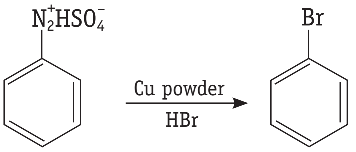
(a) Aniline (b) Phenol
(c) Anisole (d) Nitrobenzene

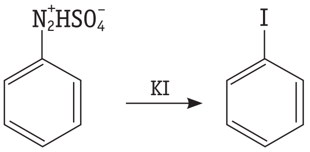
87. Which one of the following is not the correct reaction of aryl diazonium salts?

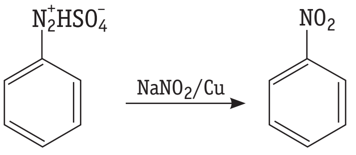
(a) $C_6H_5N_2^+Cl^- + Cu_2Cl_2 \longrightarrow C_6H_5Cl$
(b) $C_6H_5N_2^+Cl^- + HBF_4 \xrightarrow{\text{Heat}} C_6H_5F$
(c) $C_6H_5N_2^+Cl^- + H_3PO_2 \longrightarrow C_6H_5PO_4$
(d) $C_6H_5N_2^+Cl^- + SnCl_2/HCl \longrightarrow C_6H_5NHNH_2$

88. Which of the following reactions is an example of Sandmeyer reaction?

(a) 

(b) 

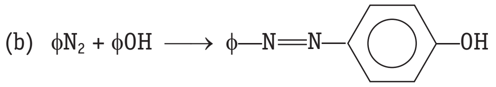
(c) 

(d) 

89. Benzene diazonium chloride on reaction with phenol in weakly basic medium gives
(a) diphenyl ether
(b) *p*-hydroxyazobenzene
(c) chlorobenzene
(d) benzene

90. During coupling reaction of benzene diazonium chloride and aniline, the pH of reaction medium should be approximately
(a) 1–2
(b) 9–10
(c) 4–5
(d) 7–8

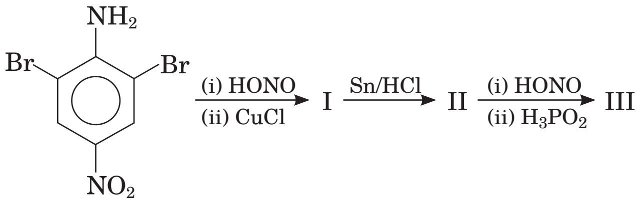
91. During diazotisation of benzenamine with sodium nitrite and hydrochloric acid, the excess of hydrochloric acid is used primarily to
(a) check the hydrolysis of φ —OH
(b) ensure a stoichiometric amount of nitrous acid
(c) check the concentration of free aniline
(d) neutralise any base formed during reaction

92. Which of the following reaction will not occur?
(a) $\phi N_2^+ + CuBr \xrightarrow{HBr} \phi - Br$
(b) 
(c) $\phi N_2^+ \xrightarrow[HOH]{H_3PO_2} \phi H$
(d) $\phi N_2^+ + I^- \longrightarrow \phi - I$

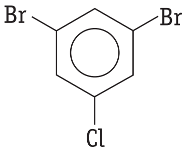
93. $C_6H_5NH_2 \xrightarrow[HCl]{NaNO_2} X \xrightarrow{Cu_2(CN)_2} Y \xrightarrow{H_2O/H^+} Z$

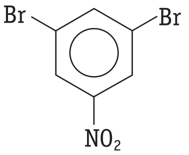
Z is identified as
(a) $C_6H_5-NH-CH_3$
(b) C_6H_5-COOH
(c) $C_6H_5-CH_2-NH_2$
(d) $C_6H_5-CH_2COOH$

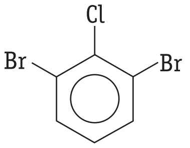
94. The final product (III) obtained in the reaction sequence



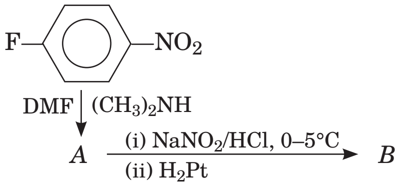
is

(a) 

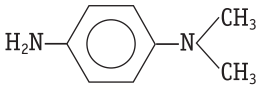
(b) 

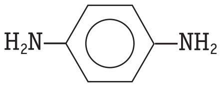
(c) 

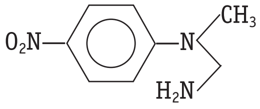
(d) None of these

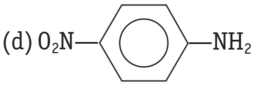
95. 

In the above sequence, *B* is

(a) 

(b) 

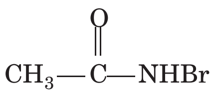
(c) 

(d) 

Round II (Mixed Bag)

Only One Correct Option

1. CH_3CONH_2, Br_2 and KOH give CH_3NH_2 as the product. The intermediates of the reaction are

I. 
$CH_3-\overset{\overset{O}{\|}}{C}-NHBr$

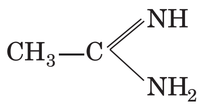
II. $CH_3-Nz{=}C{=}O$

III. CH_3NHBr

IV. CH_3CONBr_2

The correct answer is
(a) I, II
(b) I, III
(c) III, IV
(d) II, IV

2. The correct order of basicities of the following compounds is



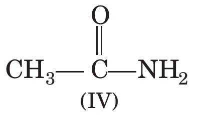
(I)

$CH_3CH_2NH_2$

(II)

$(CH_3)_2NH$

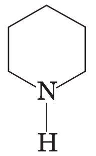
(III)

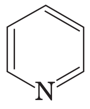

$CH_3-\overset{\overset{O}{\|}}{C}-NH_2$

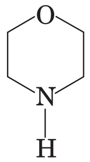
(IV)

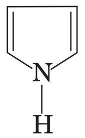
(a) II > I > III > IV
(b) I > III > II > IV
(c) III > I > II > IV
(d) I > II > III > IV

3. Arrange the following compounds in the increasing order of basic strength


(I)

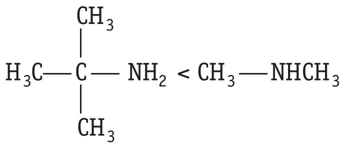

(II)


(III)


(IV)

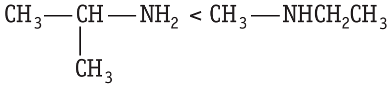
(a) IV > I > III > II (b) III > I > IV > II
(c) II > I > III > IV (d) I > III > II > IV

4. Choose the incorrect comparision(s).

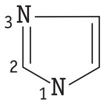
(a) 
$H_3C-C(CH_3)_2-NH_2 < CH_3-NHCH_3$

(basicity in the aqueous medium)

(b) $CH_3CH_2CH_2NH_2 > (CH_3)_3N$
(basicity in the aqueous medium)

(c) 
$CH_3-CH(CH_3)-NH_2 < CH_3-NHCH_2CH_3$

(basicity in the gaseous state)

(d) 
N(1) > N(3)
(basicity in the aqueous medium)

5. $(CH_3)_3N \xrightarrow[\text{(ii) } H_2O, \Delta]{\text{(i) BrCN}} [X]$, here $[X]$ is

(a) CH_3NH_2 (b) $(CH_3)_2NH$
(c) $(CH_3)_3NO$ (d) $(CH_3)_2NNO$

6. In the reaction of (S) 2-phenylpropanamide with NaOBr/H_2O to give 1-phenylethylamine

(a) there is retention of configuration
(b) there is inversion of configuration
(c) a mixture of two products is obtained
(d) there is no reaction

7. I. $C_2H_5NH_2 \xrightarrow[\text{(ii) } AgNO_2]{\text{(i) NOCl}} [W]$

II. $(CH_3)_2CHNH_2 \xrightarrow[\text{(ii) } AgNO_2]{\text{(i) NOCl}} [X]$

III. $(CH_3)_3CNH_2 \xrightarrow[\text{(ii) } AgNO_2]{\text{(i) NOCl}} [Y]$

IV. $CH_3CH(NH_2)C_2H_5 \xrightarrow[\text{(ii) } AgNO_2]{\text{(i) NOCl}} [Z]$

Which product will not show tautomerism?

(a) W (b) X
(c) Y (d) Z

8. Match the following column.

	Column I		Column II
A.	$RNH_2 \xrightarrow{KMnO_4}$	1.	$R_3N \rightarrow O$
B.	$R_2NH \xrightarrow{H_2SO_5}$	2.	R_3CNO_2
C.	$R_3N \xrightarrow{H_2SO_5}$	3.	R_3CHO
D.	$R_3CNH_2 \xrightarrow{H_2SO_5}$	4.	R_2NOH

Codes

	A	B	C	D
(a)	3	1	4	2
(b)	2	3	4	1
(c)	3	2	1	4
(d)	1	2	3	4

9. Benzaldehyde condenses with N,N-dimethylaniline in the presence of anhydrous $ZnCl_2$ to give

(a) azo dye
(b) malachite green
(c) michler's ketone
(d) buffer yellow

10. N_2 gas is liberated when [HCl + $NaNO_2$] react with the following compounds

I. $CH_3CH_2NH_2$ II. urea
III. CH_3CONH_2 IV. $C_6H_5NH_2$

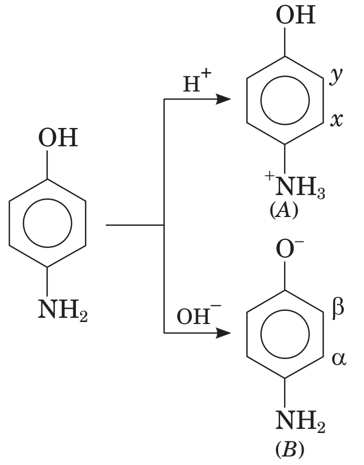
The answer is

(a) I, II, III (b) II, III, IV
(c) I, III, IV (d) I, II, IV

11. Dichlorocarbene does not form as an intermediate in this reaction

(a) phenol + $CHCl_3$ + 4KOH
(b) ethyl amine + $CHCl_3$ + KOH
(c) phenol + CCl_4 + 4KOH
(d) $CHCl_3$ + KOH

12. Consider *p*-aminophenol



Which positions are activated for coupling reaction in acidic and basic media respectively?

(a) x in A and β in B (b) x in A and α in B

(c) y in A and α in B (d) y in A and β in B

13. The correct set of the products obtained in the following reactions is

I. $R\text{CN} \xrightarrow{\text{Reduction}}$ II. $R\text{CN} \xrightarrow[\text{(ii) } H_2O]{\text{(i) } CH_3MgBr}$

III. $R\text{NC} \xrightarrow{\text{Hydrolysis}}$ IV. $R\text{NH}_2 \xrightarrow{HNO_2}$

	I.	II.	III.	IV
(a)	2° amine	methyl ketone	1° amine	alcohol
(b)	1° amine	methyl ketone	1° amine	alcohol
(c)	2° amine	methyl ketone	2° amine	acid
(d)	2° amine	methyl ketone	2° amine	aldehyde

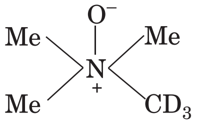
14. m-fluoronitrobenzene is best synthesised by using the reaction

(a) nitrobenzene $\xrightarrow[H_2SO_4\text{, heat}]{\text{Fuming } HNO_3} [\quad] \xrightarrow[H_2S]{NH_3} [\quad] \xrightarrow[\text{(ii) } HBF_4,\ \Delta]{\text{(i) HONO}}$

(b) aniline $\xrightarrow[\text{heat}]{F_2}$

(c) fluorobenzene $\xrightarrow[H_2SO_4\text{, heat}]{HNO_3}$

(d) $m\text{-}C_6H_4(NH_2)_2 \xrightarrow[\text{(ii) } CuNO_2,\ \text{(iii) } HBF_4]{\text{(i) HONO}}$

15. Pyrolysis of  would give

(a) mixture of $CH_2{=}CH{-}CD_3$ and $CH_3{-}CH{=}CD_2$

(b) $CH_3{-}CH{=}CD_2$

(c) $Me_2N^+{=}C(CD_3)(CH_3)$

(d) $CH_2{=}CH{-}CD_3$

16. Aromatic diazonium group can be replaced by various groups/atoms. In this context, match. Column I with Column II and select the correct answer using the codes given below the columns.

	Column I (Reaction/reaction type)		Column II (Replacement)
A.	H_3PO_2	1.	Hydrogen
B.	Sandmeyer reaction	2.	Hydroxyl group
C.	Boiling with water	3.	Aryl group
D.	Gomberg reaction	4.	Chlorine

Codes

	A	B	C	D
(a)	4	3	2	1
(b)	1	4	2	3
(c)	1	2	3	4
(d)	2	3	4	1

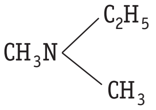
17. An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br_2 and KOH forms a compound 'C' of molecular formula C_6H_7N. Compound A is

(a) benzoic acid (b) benzamide

(c) aniline (d) benzene

18. A hydrocarbon 'A' (C_4H_8) on reaction with HCl gives a compound 'B' (C_4H_9Cl), which on reaction with 1 moles of a NH_3 gives a compound 'C' ($C_4H_{11}N$). On reacting with $NaNO_2$ and HCl followed by the treatment with water, compound 'C' yields an optically active alcohol, 'D'. Ozonolysis of 'A' gives 2 moles of acetaldehyde. **[NCERT Exemplar]**

The structure of compound C is

(a) $CH_3CH_2CH_2CH_2NH_2$ (b) 

$CH_3N\begin{smallmatrix}C_2H_5\\ CH_3\end{smallmatrix}$

(c) $(C_2H_5)_2NH$ (d) $C_2H_5CH(NH_2)CH_3$

19. The best method to synthesise m-dibromobenzene is by using the reaction

(a) Benzene $\xrightarrow{Br_2/FeBr_3/\text{heat}}$

(b) Aniline $\xrightarrow{Br_2,\ H_2O} [\quad] \xrightarrow[\text{(ii) CuBr}]{\text{(i) HONO}}$

(c) Nitrobenzene

$\xrightarrow[H_2SO_4,\ \Delta]{\text{Fuming } HNO_3} [\quad] \xrightarrow[C_2H_5OH\text{, heat}]{Fe/HCl} [\quad] \xrightarrow[\text{(ii) CuBr}]{\text{(i) HONO}}$

(d) Bromobenzene

$\xrightarrow[H_2SO_4]{HNO_3} [\quad] \xrightarrow[C_2H_5OH\text{, heat}]{Fe/HCl} [\quad] \xrightarrow[\text{(ii) CuBr}]{\text{(i) HONO}}$

20. In the following reactions, reactants A, B and C are

$$C_2H_5NH_2 + A \longrightarrow C_2H_5N{=}CH{-}C_6H_5 + H_2O$$
$$\text{urea} + B \longrightarrow H_2N{-}NHCONH_2 + NH_3$$
$$C_2H_5NH_2 + C \longrightarrow C_2H_5Cl + H_2O + N_2$$

(a) CH_3CHO, $NH_2{-}NH_2$ and PCl_5

(b) C_6H_5CHO, $NH_2{-}NH_2$ and $SOCl_2$

(c) C_6H_5CHO, $NH_2{-}NH_2$ and NOCl

(d) CH_3CHO, $NH_2{-}NH_2$ and PCl_3

21. Aniline is reacted with Br_2 water and the resulting product is treated with an aqueous solution of sodium nitrite in the presence of dilute HCl. The compound so formed is converted into tetrafluoroborate which is subsequently heated dry. The end product is

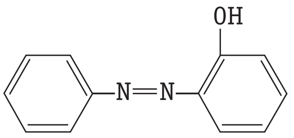
(a) p-bromofluorobenzene

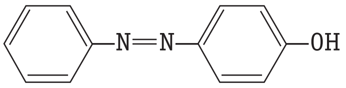
(b) p-bromoaniline

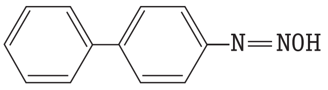
(c) 2,4,6-tribromofluoro benzene

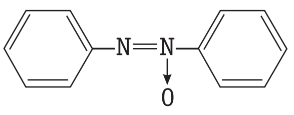
(d) 1,3,5-tribromobenzene

22. A colourless substance '*A*' (C_6H_7N) is sparingly soluble in water and gives a water soluble compound '*B*' on treating with mineral acid. On reacting with $CHCl_3$ and alcoholic potash, '*A*' produces an obnoxious smell due to the formation of compound '*C*'. Reaction of '*A*' with benzene sulphonyl chloride gives compound '*D*' which is soluble in alkali. With $NaNO_2$ and HCl, '*A*' forms compound '*E*' which reacts with phenol in alkaline medium to give an orange dye '*F*'. Compound *F* is [**NCERT** Exemplar]

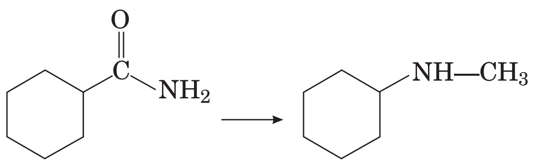
(a) 

(b) 

(c) 

(d) 

23. Suggest a route by which the following conversion can be accomplished? [**NCERT** Exemplar]



(a) (i) Br_2 / KOH (ii) $CHCl_3$ / KOH (iii) H_2 / Pd

(b) (i) $LiAlH_4$ (ii) AgCN, (iii) H_2 / Pd

(c) (i) $LiAlH_4$ (ii) KCN (iii) H_2 / Pd

(d) (i) Br_2 /KOH (ii) AgCN (iii) H_2/Pd

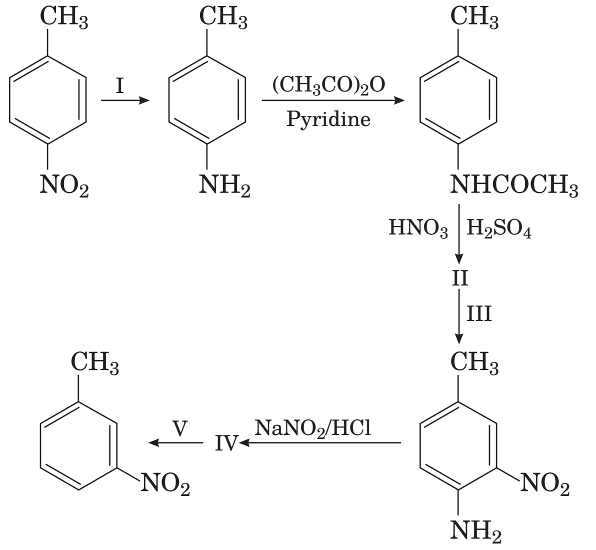
24. Match the following.

	Column I		Column II
A.	$\phi NO_2 \xrightarrow{Zn/NH_4Cl}$	1.	$\phi-N=N-\phi$
B.	$\phi NO_2 \xrightarrow[NaOH]{Zn/alc.}$	2.	$\phi-NH_2$
C.	$\phi NO_2 \xrightarrow{LAH}$	3.	$\phi NHOH$
D.	$\phi NO_2 \xrightarrow{Na_3AsO_3/NaOH}$	4.	$\phi-N=\overset{\overset{O}{\uparrow}}{N}-\phi$

Codes

	A	B	C	D		A	B	C	D
(a)	1	2	3	4	(b)	2	3	1	4
(c)	3	1	2	4	(d)	2	4	3	1

25. Consider the following reaction sequence. [**NCERT** Exemplar]



Reagent I and V are respectively

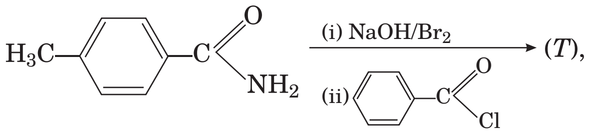
(a) H_2O / H^+, H_3PO_2 / H_2O

(b) Zn/ HCl, H_2O / H^+

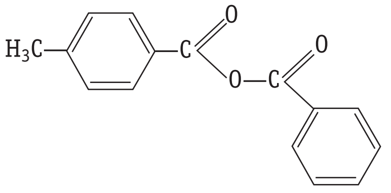
(c) Sn/ HCl, H_3PO_2 / H_2O

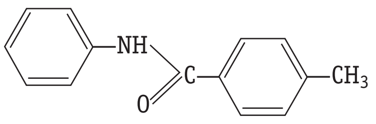
(d) None of the above is correct

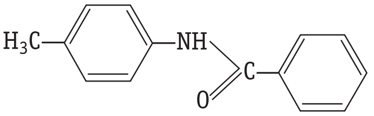
26. In the reaction,

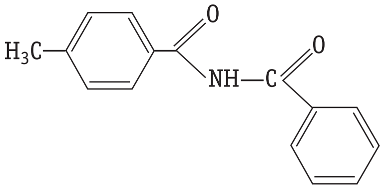


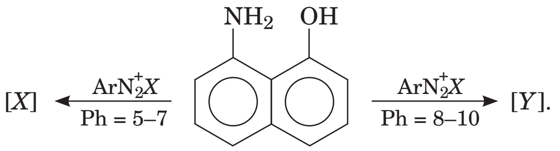
the structure of the product (*T*) is

(a) 

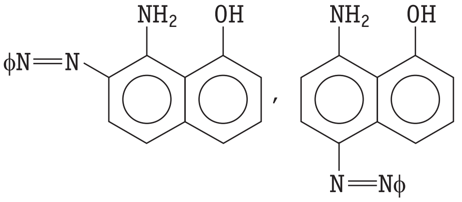
(b) 

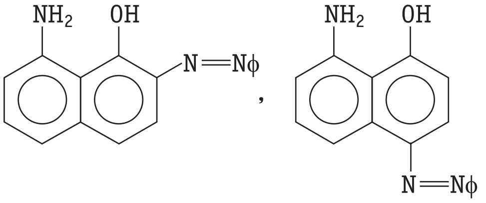
(c) 

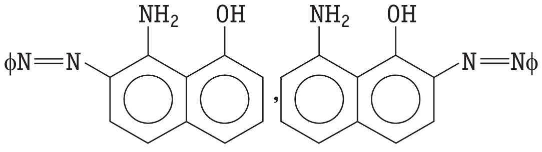
(d) 

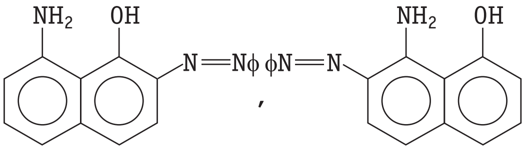
27. 

[X] and [Y] are

(a) 

(b) 

(c) 

(d) 

28. Match the following columns.

	Column I		Column II
A.	Aniline	1.	Sulpha drug
B.	TNT	2.	Solvent in Friedel-Craft
C.	Sulphanilamide	3.	Explosive
D.	Nitrobenzene	4.	Used in azo dyes

Codes

	A	B	C	D
(a)	1	2	3	4
(b)	4	3	2	1
(c)	2	3	4	1
(d)	4	3	1	2

More than One Correct Option

29. $(A) \xrightarrow[\text{[H]}]{\text{Reduction}}$ Primary amine

The compound (A) may be

(a) alkyl isocyanide
(b) alkyl cyanide
(c) acidamide
(d) 1° nitroalkane

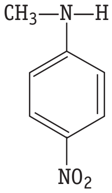
30. Under which of the following reaction conditions, aniline gives p-nitro derivative as the major product? **[NCERT Exemplar]**

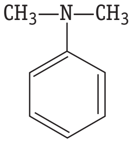
(a) Acetyl chloride/pyridine followed by reaction with conc. H_2SO_4 + conc. HNO_3
(b) Acetic anhydride/pyridine followed by conc. H_2SO_4 + conc. HNO_3
(c) Dil. HCl followed by reaction with conc. H_2SO_4 + conc. HNO_3
(d) Reaction with conc. HNO_3 + conc. H_2SO_4

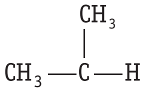
31. Which of the following reactions belong to electrophilic aromatic substitution? **[NCERT Exemplar]**

(a) Bromination of acetanilide
(b) Coupling reaction of aryldiazonium salts
(c) Diazotisation of aniline
(d) Acylation of aniline

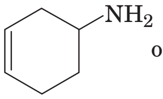
32. Which of the following amines will show positive Liebermann's nitroso test?

(a) 

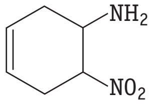
(b) 

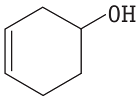
(c) 
$CH_3-\overset{CH_3}{\overset{|}{C}}-H$

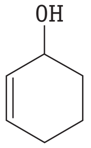
(d) None of these

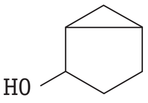
33. 

on reaction with HNO_2 forms

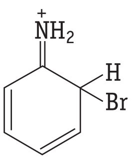
(a) 

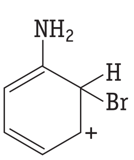
(b) 

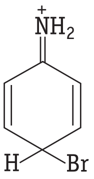
(c) 

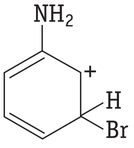
(d) 

34. Arenium ion involved in the bromination of aniline is **[NCERT Exemplar]**

(a) 

(b) 

(c) 

(d) 

35. Which of the following cannot be prepared by Sandmeyer's reaction? [**NCERT** Exemplar]

(a) Chlorobenzene (b) Bromobenzene
(c) Iodobenzene (d) Fluorobenzene

Assertion and Reason

Directions (Q. Nos. 36 to 40) *Each of these questions contains two statements : Statement* I *(Assertion) and Statement* II *(Reason). Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes* (*a*), (*b*), (*c*), (*d*) *given below :*

(a) Statement I is true; Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true; Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

36. **Statement I** Only a small amount of HCl is required in the reduction of nitro compounds with iron scrap and HCl in the presence of steam.

Statement II $FeCl_3$ formed gets hydrolysed to release HCl during the reaction. [**NCERT** Exemplar]

37. **Statement I** Hofmann degradation and Curtius degradation methods are used to prepare 1° amines.

Statement II Both involves intermolecular alkyl shift.

38. **Statement I** Tertiary amine is less basic than secondary amine in aqueous solution.

Statement II Over crowding due to I^+ effect of three alkyl groups increases strain.

39. **Statement I** Hofmann's bromamide reaction is given by primary amines.

Statement II Primary amines are more basic than secondary amines. [**NCERT** Exemplar]

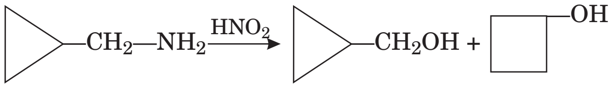
40. **Statement I** Acylation of amines gives a monosubstituted product whereas alkylation of amines gives polysubstituted product.

Statement II Acyl group sterically hinders the approach of further acyl groups. [**NCERT** Exemplar]

Comprehension Based Questions

Directions (Q. Nos. 41 to 43) Nitrous acid reacts with all classes of amines. The products obtained from their reactions depend on whether the amine is primary, secondary or tertiary and whether the amine is aliphatic or aromatic.

Aliphatic primary amines reacts with nitrous acid ($NaNO_2$ + HCl) to form alcohol as a major product. In addition to alcohol, alkene and alkyl halides are also formed as minor products. Certain cyclic primary amines can undergo either ring expansion or ring contraction reactions on treatment with nitrous acid. The reaction is called Demjanor ring expansion or contraction.

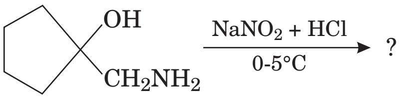


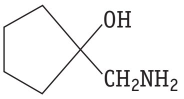
Answer the following questions.

41. What will be the major product when 2-amino propane is treated with nitrous acid?

(a) 1-propanol
(b) 2-propanol
(c) Propene
(d) Cyclopropane

42. The product(s) obtained in the following reaction will be



(a)


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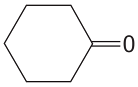

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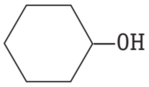
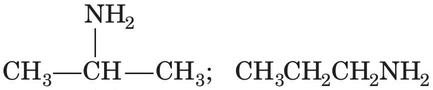


(d) All of these

43. Two compounds (*A*) and (*B*) are treated with nitrous acid,



$CH_3—\underset{}{\overset{NH_2}{\overset{|}{C}H}}—CH_3$; $CH_3CH_2CH_2NH_2$

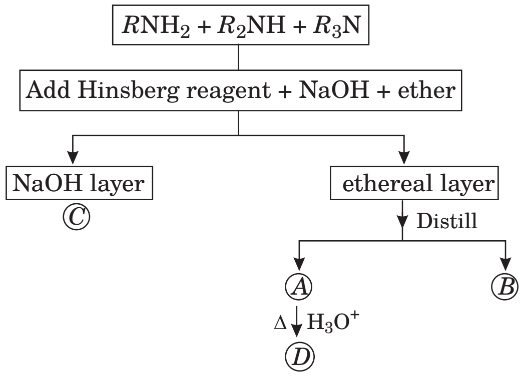
(*A*) (*B*)

The corresponding stable carbocation intermediates are

	(From *A*)	(From *B*)
(a)	$CH_3—CH_2—\overset{+}{C}H_2$	$CH_3—CH_2—\overset{+}{C}H_2$
(b)	$CH_3—\overset{+}{C}H—CH_3$	$CH_3—\overset{+}{C}H—CH_3$
(c)	$CH_3—\overset{+}{C}H—CH_3$	$CH_3—CH_2—\overset{+}{C}H_2$

(d) None of the above

Directions (Q. Nos. 44 to 46) When alkyl halide and ammonia react, there is always formation of 1°, 2° and 3° amines even under controlled conditions. Given outline describes the technique to separate the mixture. Go through it and properties of the amines to answer the questions at the end.



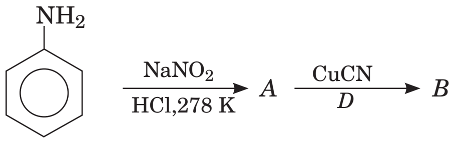
44. NaOH layer (C) contains
(a) sodium salt of 1° amine N-alkyl benzene sulphonamide
(b) sodium salt of 2° amine N,N-dialkyl benzene sulphonamide
(c) Both (a) and (b)
(d) None of the above

45. Distillation of ethereal layer gives
(a) A (N,N-dialkyl benzene sulphonamide) and B (3° amine)
(b) A (sodium salt of N-alkyl benzene sulphonamide) and B (3° amine)
(c) A (2° amine) and B (3° amine)
(d) None of the above

46. D is
(a) 1° amine
(b) 2° amine
(c) 3° amine
(d) mixture of 1° and 2° amine

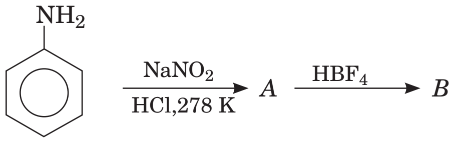
Previous Years' Questions

47. In the chemical reactions



Compounds A and B respectively are **[AIEEE 2011]**
(a) fluorobenzene and phenol
(b) benzene diazonium chloride and benzonitrile
(c) nitrobenzene and chlorobenzene
(d) phenol and bromobenzene

48. In the chemical reactions,



Compounds A and B respectively are **[AIEEE 2011]**
(a) nitrobenzene and fluorobenzene
(b) phenol and benzene
(c) benzene diazonium chloride and fluorobenzene
(d) nitrobenzene and chlorobenzene

49. Toluene is nitrated and the resulting product is reduced with tin and hydrochloric acid. The product so obtained is diazotised and then heated with cuprous bromide. The reaction mixture so formed contains **[AIEEE 2008]**
(a) mixture of *o*-and *p*-bromotoluenes
(b) mixture of *o*-and *p*-dibromobenzenes
(c) mixture of *o*-and *p*-bromoanilines
(d) mixture of *o*-and *m*-bromotoluenes

50. Which one of the following is the strongest base in aqueous solution? **[AIEEE 2007]**
(a) Trimethylamine (b) Aniline
(c) Dimethylamine (d) Methylamine

51. In the chemical reaction,
$CH_3CH_2NH_2 + CHCl_3 + 3KOH \longrightarrow (A) + (B) + 3H_2O$
The compounds (A) and (B) are respectively. **[AIEEE 2007]**
(a) C_2H_5CN and 3KCl
(b) $CH_3CH_2CONH_2$ and 3KCl
(c) C_2H_5NC and K_2CO_3
(d) C_2H_5NC and 3KCl

52. Fluorobenzene (C_6H_5F) can be synthesized in the laboratory **[AIEEE 2006]**
(a) by heating phenol with HF and KF
(b) from aniline by diazotisation followed by heating the diazonium salt with HBF_4
(c) by direct fluorination of benzene with F_2 gas
(d) by reacting bromobenzene with NaF solution

53. Which one of the following methods is neither meant for the synthesis nor for the separation of amines? **[AIEEE 2005]**
(a) Curtius reaction (b) Wurtz reaction
(c) Hofmann method (d) Hinsberg method

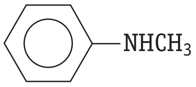
54. Amongst the following, the most basic compound is **[AIEEE 2005]**
(a) *p*-nitroaniline
(b) acetanilide
(c) aniline
(d) benzylamine

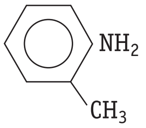
55. Reaction of cyclohexanone with dimethylamine in the presence of catalytic amount of an acid forms a compound. Water during the reaction is continuously removed. The compound formed is generally known as **[AIEEE 2005]**

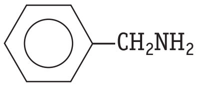
(a) an amine (b) an imine
(c) an enamine (d) a Schiff 's base

56. Which of the following is the strongest base? **[AIEEE 2004]**

(a) 

(b) 

(c) 

(d) 

57. The correct order of increasing basic nature for the bases NH_3, CH_3NH_2 and $(CH_3)_2NH$ is **[AIEEE 2003]**

(a) $CH_3NH_2 < NH_3 < (CH_3)_2NH$
(b) $(CH_3)_2NH < NH_3 < CH_3NH_2$
(c) $NH_3 < CH_3NH_2 < (CH_3)_2NH$
(d) $CH_3NH_2 < (CH_3)_2NH < NH_3$

Answers

Round I

1. (b)	**2.** (c)	**3.** (d)	**4.** (d)	**5.** (c)	**6.** (a)	**7.** (b)	**8.** (d)	**9.** (c)	**10.** (d)
11. (b)	**12.** (b)	**13.** (c)	**14.** (b)	**15.** (c)	**16.** (b)	**17.** (a)	**18.** (d)	**19.** (b)	**20.** (a)
21. (c)	**22.** (c)	**23.** (c)	**24.** (b)	**25.** (b)	**26.** (b)	**27.** (d)	**28.** (b)	**29.** (d)	**30.** (d)
31. (d)	**32.** (c)	**33.** (b)	**34.** (a)	**35.** (d)	**36.** (d)	**37.** (c)	**38.** (b)	**39.** (b)	**40.** (a)
41. (a)	**42.** (a)	**43.** (c)	**44.** (d)	**45.** (a)	**46.** (c)	**47.** (a)	**48.** (a)	**49.** (c)	**50.** (c)
51. (b)	**52.** (b)	**53.** (c)	**54.** (a)	**55.** (b)	**56.** (c)	**57.** (c)	**58.** (b)	**59.** (b)	**60.** (c)
61. (b)	**62.** (b)	**63.** (d)	**64.** (c)	**65.** (b)	**66.** (d)	**67.** (d)	**68.** (d)	**69.** (a)	**70.** (a)
71. (b)	**72.** (a)	**73.** (b)	**74.** (a)	**75.** (b)	**76.** (b)	**77.** (b)	**78.** (b)	**79.** (b)	**80.** (d)
81. (b)	**82.** (d)	**83.** (b)	**84.** (a)	**85.** (b)	**86.** (d)	**87.** (c)	**88.** (a)	**89.** (a)	**90.** (c)
91. (c)	**92.** (b)	**93.** (b)	**94.** (b)	**95.** (a)					

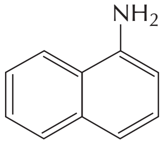
Round II

1. (a)	**2.** (b)	**3.** (d)	**4.** (d)	**5.** (b)	**6.** (a)	**7.** (c)	**8.** (a)	**9.** (b)	**10.** (a)
11. (c)	**12.** (b)	**13.** (b)	**14.** (a)	**15.** (a)	**16.** (b)	**17.** (a)	**18.** (d)	**19.** (c)	**20.** (c)
21. (c)	**22.** (b)	**23.** (a)	**24.** (c)	**25.** (c)	**26.** (c)	**27.** (c)	**28.** (d)	**29.** (b,c,d)	**30.** (a,b)
31. (a,b)	**32.** (a,c)	**33.** (b,c,d)	**34.** (a,b,c)	**35.** (c,d)	**36.** (a)	**37.** (a)	**38.** (a)	**39.** (c)	**40.** (c)
41. (b)	**42.** (b)	**43.** (c)	**44.** (a)	**45.** (b)	**46.** (b)	**47.** (b)	**48.** (c)	**49.** (a)	**50.** (c)
51. (d)	**52.** (b)	**53.** (b)	**54.** (d)	**55.** (c)	**56.** (d)	**57.** (c)			

the Guidance

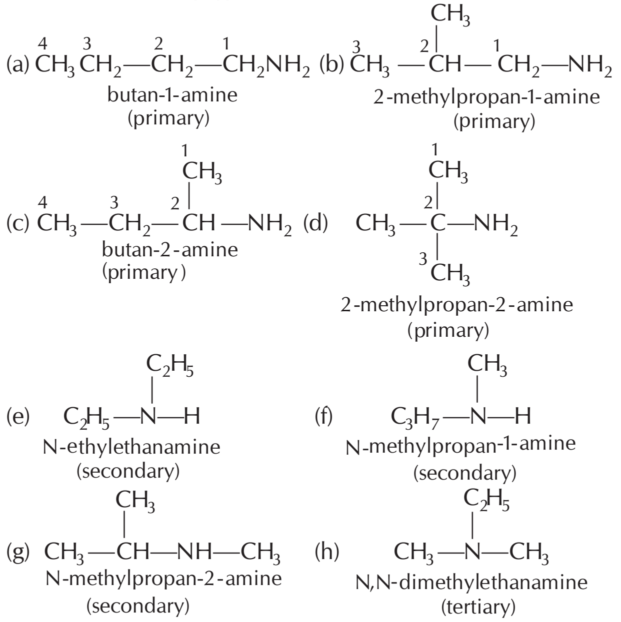
Round I

1. Primary amines have characteristic —NH_2 group, thus among the given, only



and $(C_2H_5)_2NH_2$ are primary amines.

2. Eight isomers of $C_4H_{11}N$ are



(a) $\overset{4}{C}H_3\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{1}{C}H_2NH_2$ butan-1-amine (primary)

(b) $\overset{3}{C}H_3-\overset{2}{C}H(CH_3)-\overset{1}{C}H_2-NH_2$ 2-methylpropan-1-amine (primary)

(c) $\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H(\overset{1}{C}H_3)-NH_2$ butan-2-amine (primary)

(d) $CH_3-\overset{2}{C}(\overset{1}{C}H_3)(\overset{3}{C}H_3)-NH_2$ 2-methylpropan-2-amine (primary)

(e) $C_2H_5-N(C_2H_5)-H$ N-ethylethanamine (secondary)

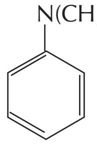
(f) $C_3H_7-N(CH_3)-H$ N-methylpropan-1-amine (secondary)

(g) $CH_3-CH(CH_3)-NH-CH_3$ N-methylpropan-2-amine (secondary)

(h) $CH_3-N(C_2H_5)-CH_3$ N,N-dimethylethanamine (tertiary)

3. $\overset{3}{C}H_2=\overset{2}{C}H-\overset{1}{C}H_2-NH_2$
prop-2-ene-1-amine

4.

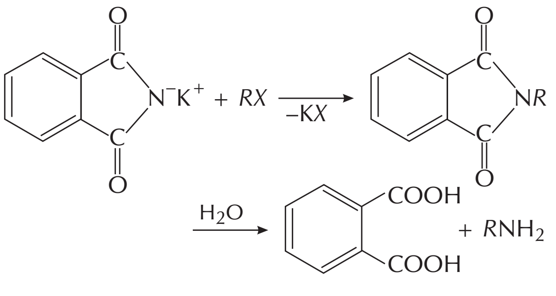


IUPAC name isN,N-dimethyl benzenamine.

5. $CH_3-CH_2-NCH_3-CH_3-CH_2$
IUPAC name is N-ethyl-N-methyl ethanamine (tertiary).

8. The mixture of $SnCl_2$ + HCl, reduces, —CN group partially.

10. The Gabriel synthesis reactions is



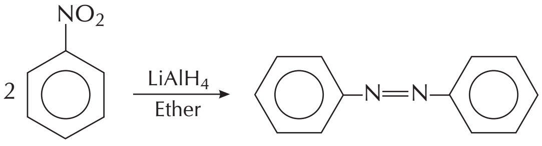
From the above reaction, it is clear that the N of amine comes from $C_6H_4(CO)_2N^-K^+$, so it is the source of nitrogen in this reaction.

11. Gabriel phthalimide synthesis is the best method for preparing primary amine from alkyl halides without changing the number of C atoms in the chain.

12. Hofmann bromamide degradation reaction is shown by only 1° amides like $RCONH_2$, $ArCONH_2$.

13. Gabriel phthalimide reaction, *i.e.*, heating of alkyl halide with potassium salt of phthalimide followed by hydrolysis is the best method for preparing amine with same number of C atom as that were in the parent alkyl halide.

14. $LiAlH_4$ in either is not a good reagent for reducing aryl intro compound into amine as it reduces aryl nitro compound to azo compound.



nitrobenzene azobenzene

other given reagents reduce aryl nitro compound to amine (aniline).

15. $RCONH_2 + \underset{'X'}{NaOBr} \longrightarrow RNH_2 + NaBr + Na_2CO_3 + 2H_2O$

16. Nitrobenzene is reduced by Zn and alcoholic KOH into hydrazobenzene.

$$2C_6H_5NO_2 + 10H \xrightarrow{Zn\ +\ alc.\ KOH} \underset{\text{hydrazobenzene}}{C_6H_5-NH-NH-C_6H_5} + H_2O$$

17. $CH_3CH_2I \xrightarrow{NaCN} CH_3CH_2CN \xrightarrow{OH^-} CH_3CH_2CONH_2 \xrightarrow{Br_2/NaOH} CH_3CH_2NH_2$

18. $\underset{\substack{\text{acetaldehyde}\\(A)}}{CH_3CHO} \xrightarrow{H_2NOH} \underset{(B)}{CH_3CH=OH} \xrightarrow{\text{Reduction}} \underset{\substack{\text{ethyl amine}\\(C)}}{CH_3CH_2NH_2} \xrightarrow[-N_2,\ -H_2O]{NOCl} \underset{\text{ethyl chloride}}{CH_3CH_2Cl}$

19.

$$RCN \xrightarrow{\text{Hydrolysis}} RCOOH + NH_3$$

$$RCH{=}NOH \xrightarrow{\text{Reduction}} RCH_2NH_2 + H_2O$$

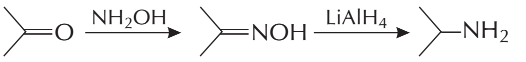
$$RNC + 2H_2O \xrightarrow{\Delta} RNH_2 + HCOOH$$

$$RCONH_2 \xrightarrow{\text{Hydrolysis}} RCOOH + NH_3$$

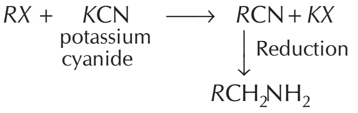
20. Ethyl isocyanide on hydrolysis in acidic medium gives methanoic acid and ethyl amine salt.

$$C_2H_5NC + H_2O \xrightarrow{H^+} \underset{\text{methanoic acid}}{HCOOH} + C_2H_5NH_2$$

$$\underset{\text{ethylamine}}{C_2H_5NH_2} + H^+ \longrightarrow \underset{\text{ethylamine salt}}{C_2H_5NH_3^+}$$

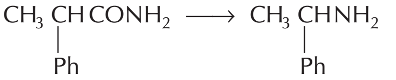
21. 

1° amine
2-aminopropane

23. 

$$RX + \underset{\text{potassium cyanide}}{KCN} \longrightarrow RCN + KX \xrightarrow{\text{Reduction}} RCH_2NH_2$$

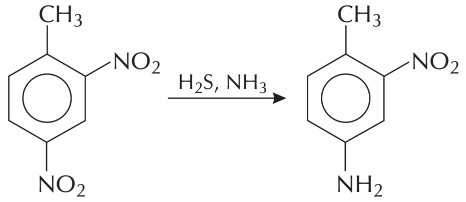
(having one more C atom as compared to parent halide)

24. 

$$\underset{\text{2-phenylpropanamide}}{CH_3\underset{|}{\underset{Ph}{C}}HCONH_2} \longrightarrow \underset{\text{1-phenylethanamine}}{CH_3\underset{|}{\underset{Ph}{C}}HNH_2}$$

Here —$CONH_2$ group is converted into —NH_2 group, so best reagent is $NaOH/Br_2$.

25. By using H_2S,NH_3 as reagents, selective reduction takes place.

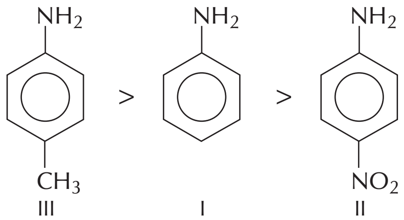


27. Nitrene is not the intermediate of Gabriel's phthalimide reaction.

29. Concentration does not affect the basic strength of amines.

30. The amines are basic in nature due to the presence of lone pair of electron on nitrogen. The 2° amines are most basic among 1°, 2° and 3° amines because of steric effect and hydration effect.

31. Presence of electron releasing group like —CH_3, —$COCH_3$ solvation increases electron density over N of —NH_2 group, and hence, makes it more basic. On the other hand electron withdrawing groups like —NO_2 reduces the basicity of aniline by decreasing electron density over N atom. Thus, the correct order of basic strength is



32. Phenol because of the resonance stabilisation of phenoxide ion, have higher tendency to give a proton instead of accepting it so, it is the weakest Bronsted base or strongest Bronsted acid.

33. Lone pair of —NH_2 group is responsible for the reaction of amine with dilute HCl. Thus, the amine with greater tendency of donating lone pair to proton of acid is more reactive towards dilute acid.

Among the given $(CH_3)_2NH$ is most reactive because of the presence of of two electron releasing group.

Note $(CH_3)_3N$ although have there electron releasing methyl groups but it is less reactive because of steric effect.

34. (a) Presence of electron donating methyl group increases the basicity of amines. However, 3° amines in aqueous solution are less basic due to steric hindrance.

(b) Aliphatic amines are more basic than aromatic amines because in later, lone pair takes part in delocalization, so less available for donation.

$$C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH.$$

35. In (a) and (c), lone pair involves in resonance so less available for protonation. In (d), lone pair is more available than NH_3 for protonation. So, (d) is the strongest Bronsted base.

36. Presence of electron withdrawing groups like —CN, —CHO, —NO_2 etc., decreases the electron density over N-atom of amines, and thus decreases their basic character as lone pair is less available for donation.

39. $CH_3CH_2CH_3$ have less boiling point than the corresponding amines because of the absence of H-bonding. That's why it is most volatile.

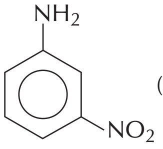
41. Primary amines have higher tendency of forming H-bonds.

42. As the molecular mass increases, boiling point increases. In case of isomeric amines, however, as the number of H-atoms attached directly to N-atom decreases, boiling point decreases because tendency to form H-bonds decreases. Hence, the order of boiling points of given amines is

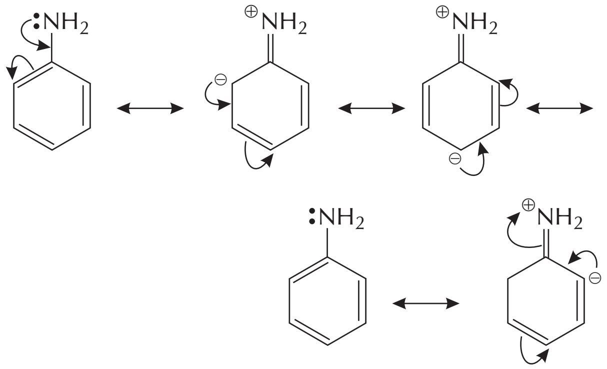
$$CH_3NH_2 < (CH_3)_3N < CH_3CH_2NH(CH_3) < CH_3CH_2CH_2NH_2$$

43. In tertiary amines, no H-atom is attached directly to the more electronegative N-atom. Hence, it has no tendency to form H-bond.

44. Usually symmetrical molecules have less dipole moment in comparision to unsymmetrical molecules.

Hence,  (*m*-nitroaniline) will show the highest dipole moment among the given.

45. —NH_2 has +*R* effect, it donates electrons to the benzene ring. As a result, the lone pair of electrons on the N-atom get delocalized over the benzene ring and thus less readily available for protonation. Hence, aniline is a weaker base than cyclohexylamine.



Resonance structure of aniline

48. $RNH_2 + \underset{\text{acid anhydride}}{O(OCR)_2} \xrightarrow[-RCOOH]{} \underset{2° \text{ amide}}{RNHCOR}$

49. Pyridine being a base, is used to remove the side product *i.e.*, HCl form reaction mixture.

50. $\underset{\substack{\text{ethyl amine}\\ \text{one mole}}}{CH_3CH_2NH_2} + HNO_2 \longrightarrow C_2H_5OH + H_2O + \underset{\substack{\text{one mole}\\ \text{22.4 L at NTP}}}{N_2}$

51. $CH_3NH_2 + HONO \longrightarrow CH_3OH + N_2\uparrow + H_2O$

52. In carbylamine reaction, when a primary amine reacts with chloroform in presence of alc. KOH, it gives iso-cyanide which has abnoxious odour. This reaction is given by primary amine.

$$\underset{\substack{\text{primary}\\ \text{amine}}}{RNH_2} + CHCl_3 + \underset{\text{(alc.)}}{3KOH} \xrightarrow{\Delta} \underset{\substack{\text{alkyl}\\ iso\text{-cyanide}}}{RNC} + 3KCl + 3H_2O$$

53. $\underset{iso\text{-propylamine}}{(CH_3)_2CHNH_2} \xrightarrow{KMnO_4[O]} \underset{\substack{'X'\\ \text{ketimine}}}{(CH_3)_2C{=}NH} \xrightarrow[-NH_3]{H_2O/H^+} \underset{\substack{'Y'\\ \text{acetone}}}{(CH_3)_2C{=}O}$

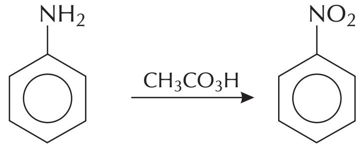
55. Only primary amines give positive carbylamine test.

56. $\underset{\substack{iso\text{-propyl amine}\\ \text{(primary amine)}}}{(CH_3)_2CH \cdot NH_2} + 2CH_3COCl \xrightarrow[-\,HCl]{} \underset{\text{tertiary-amine}}{(CH_3)_2CHN(COCH_3)_2}$

57. Carbylamine reaction is given by only primary amines (both aliphatic and aromatic). In this reation, a primary amine reacts with chloroform in basic medium, to form a very bad smelling compound, called carbylamine.

$$C_6H_5NH_2 + CHCl_3 + KOH \longrightarrow C_6H_5NC + KCl + H_2O$$

58. Aniline on oxidation with per acetic acid, CH_3CO_3H gives nitrobenzene.



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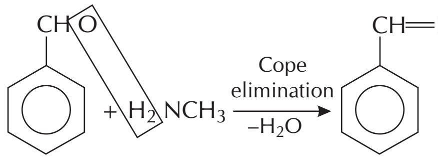

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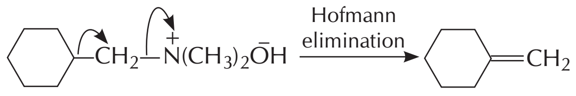
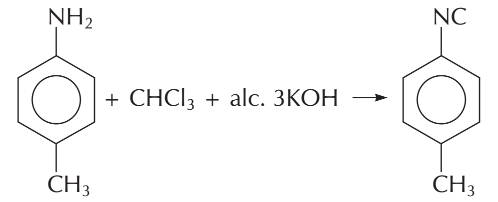


+ $(CH_3)_2NOH$

62. $\underset{\text{ethyl amine}}{C_2H_5NH_2} \xrightarrow{HNO_2} \underset{\substack{\text{ethyl alcohol}\\ (A)}}{C_2H_5OH} \xrightarrow{PCl_5} \underset{\substack{\text{ethyl chloride}\\ (B)}}{C_2H_5Cl} \xrightarrow{NH_3} \underset{\substack{\text{ethyl amine}\\ (C)}}{C_2H_5NH_2}$

63.

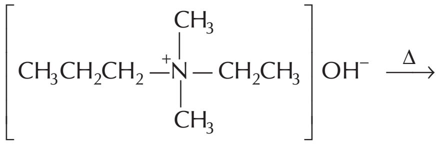


p-toluidine

+ 3KCl + $3H_2O$

It is a example of carbylamine reaction.

64. In Hofmann elimination reaction, less substituted alkene is the main product.

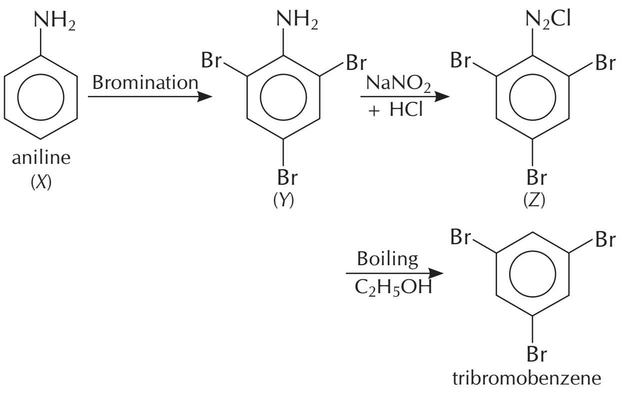


$$\left[CH_3CH_2CH_2-\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{\overset{+}{N}}}-CH_2CH_3\right]OH^- \xrightarrow{\Delta}$$

$$CH_3CH_2CH_2{-}N(CH_3)_2 + \underset{\text{(minor)}}{CH_3CH{=}CH_2} + \underset{\text{major}}{CH_2{=}CH_2}$$

65. $\underset{\substack{1° \text{ amine}\\ (Y)}}{R_2CHNH_2} \underset{}{\overset{[O]\ KMnO_4}{\rightleftharpoons}} [R_2C{=}NH] \xrightarrow{H_3O^+} \underset{\substack{\text{ketone}\\ (X)}}{R_2C{=}O}$

66.



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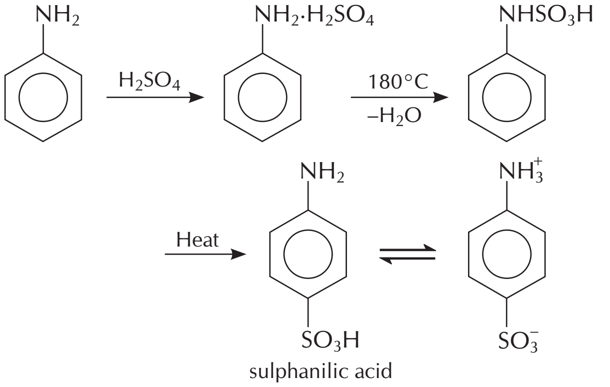
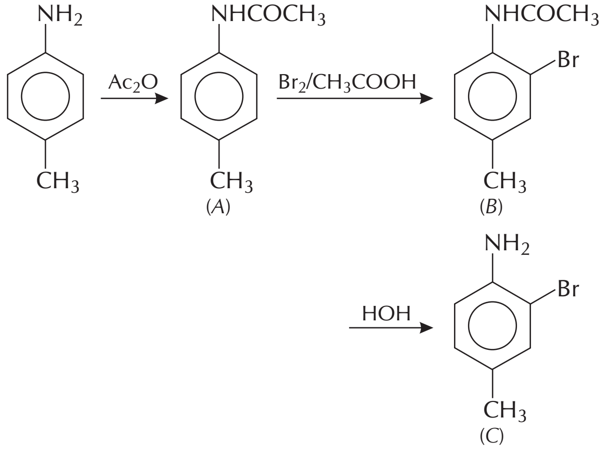


Sulphanilic acid exists as a dipolar ion which has acidic and basic groups in the same molecule. Such ions are called Zwitter ions or inner salts.

68.



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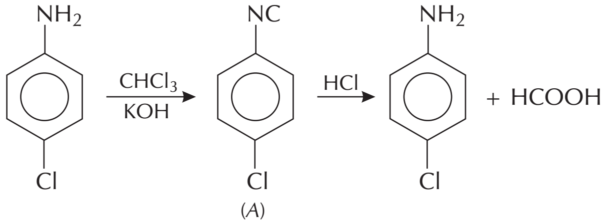

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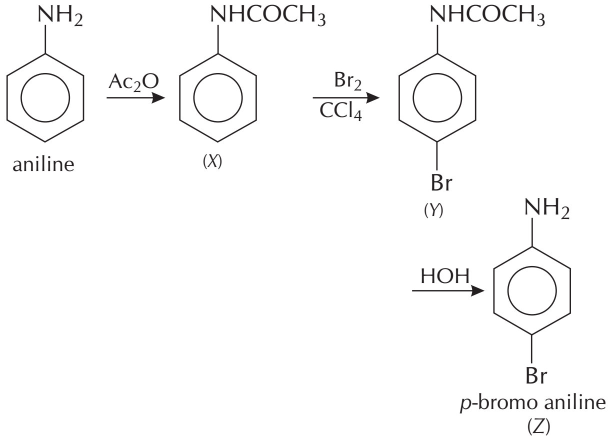

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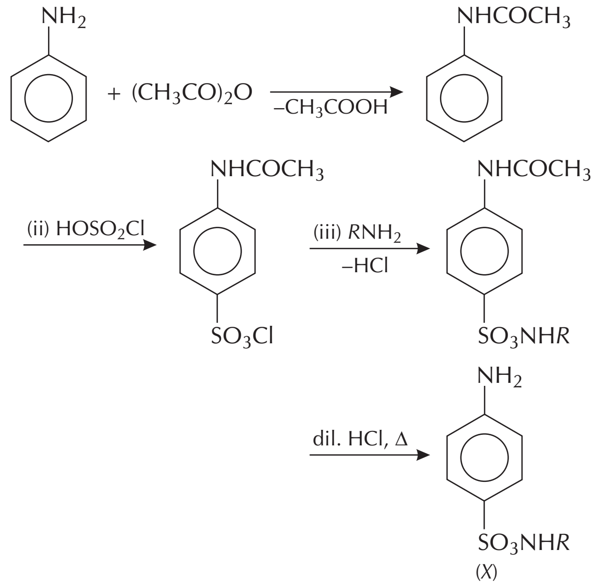
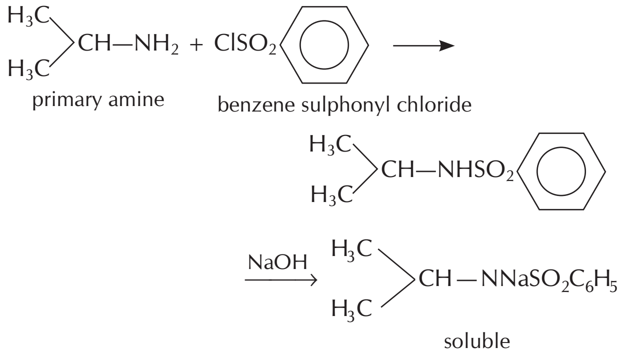


74. Hence, Hofmann method is used to separate a mixture of 1°, 2° and 3° amines.

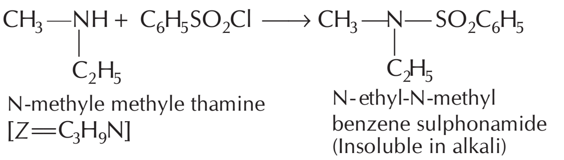
75.

$$\underset{\text{benzene sulphonyl chloride}}{C_6H_5SO_2Cl} + RNH_2 \longrightarrow \underset{\text{N-alkyl benzene sulphonamide}}{RNHSO_2C_6H_5} \xrightarrow{KOH} \underset{\text{soluble in KOH}}{R — NKSO_2C_6H_5}$$

76.

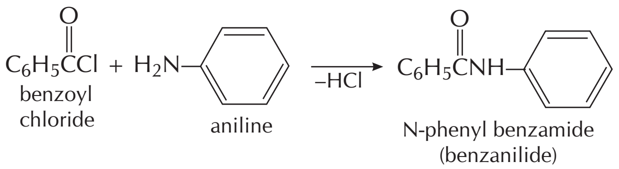


77. Z (C_3H_9N) is an aliphatic amine. On reaction with $C_6H_5SO_2Cl$ (Hinsberg's reagent), it gives a product insoluble in alkali. It means that the product does not have a replaceable H-atom attached to the N-atom. So, compound Z is a secondary amine (Ethyl methyl amine).



$$\underset{\substack{\text{N-methyle methyle thamine}\\ [Z{=}C_3H_9N]}}{CH_3—\underset{\substack{|\\ C_2H_5}}{NH}} + C_6H_5SO_2Cl \longrightarrow \underset{\substack{\text{N-ethyl-N-methyl}\\ \text{benzene sulphonamide}\\ \text{(Insoluble in alkali)}}}{CH_3—\underset{\substack{|\\ C_2H_5}}{N}—SO_2C_6H_5}$$

78.



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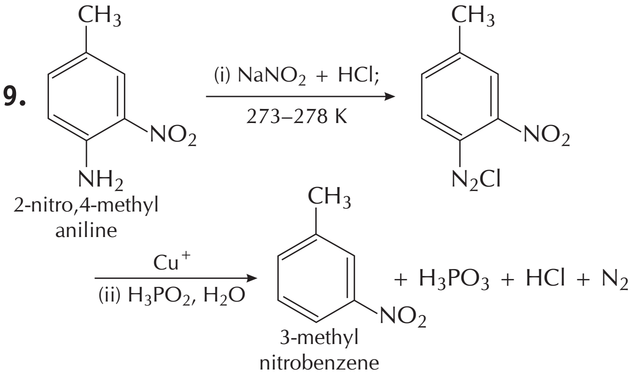

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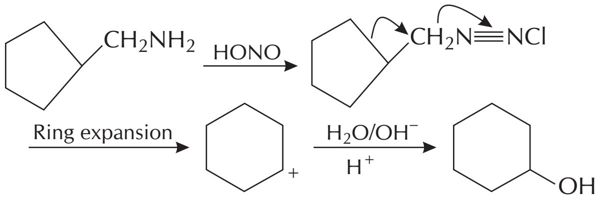
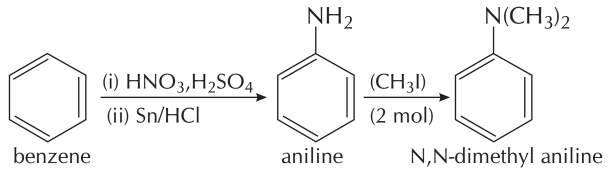


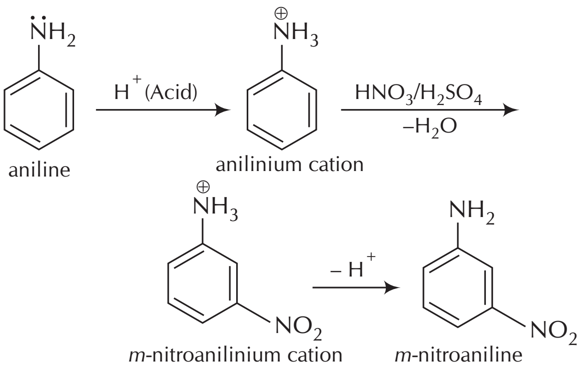
81. Benzene may be converted into N, N-dimethyl aniline as follows

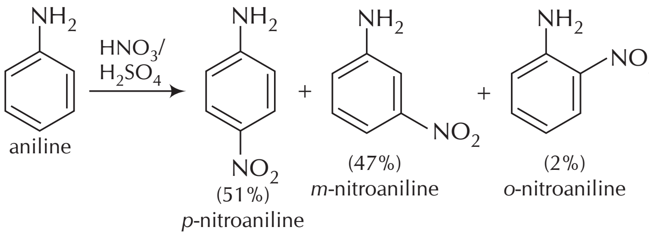


82. Secondary amines give oily nitrosoamine with nitrous acid.

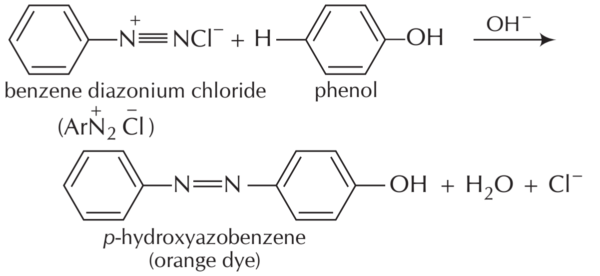
$$\underset{\text{secondary amine}}{(CH_3CH_2)_2NH} + \underset{\text{nitrous acid}}{HNO_2} \longrightarrow \underset{\text{oily nitrosoamine}}{(CH_3CH_2)_2N-NO} + H_2O$$

83. In the presence of conc. HNO_3 and conc. H_2SO_4, most of aniline gets protonated to form anilinium ion. Now aniline and anilinium ions both are present in the reaction mixture. In aniline, —NH_2 group is *o*- and *p*-directing but anilinium ion is *m*-directing. Because of more amount of anilinium ion, a lot of *m*-nitroaniline is formed.



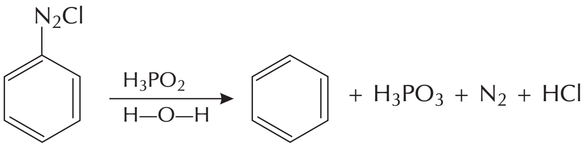


84. The reaction exhibits azo-coupling reaction of phenols. Benzene diazonium chloride reacts with phenol in such a manner that the *para* position of phenol is coupled with diazonium salt to form *p*-hydroxy azobenzene.

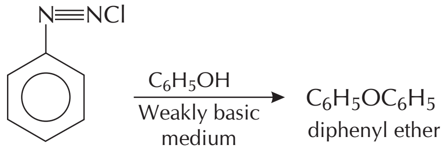


86. Only benzene derivative having electron releasing group are capable for undergoing coupling reaction. Nitrobenzene because of the presence of electron with drawing —NO_2 group is not capable to give coupling reaction.

87.

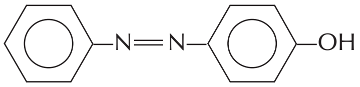


89.



92. $\phi N_2^+ + \phi OH \longrightarrow \phi N_2 \phi OH$

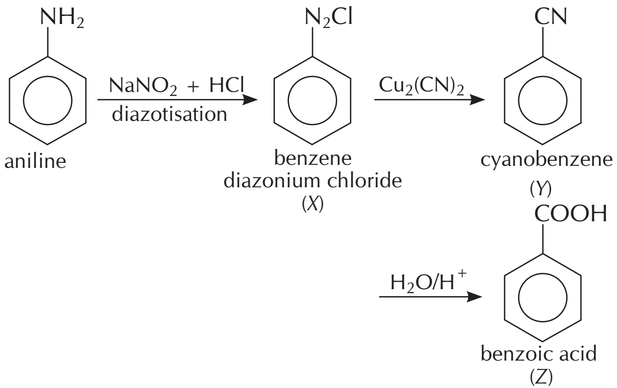
or



coupling product

Here reagent used is $\phi\ N_2^+$ instead of $\phi\ N_2$.

93.



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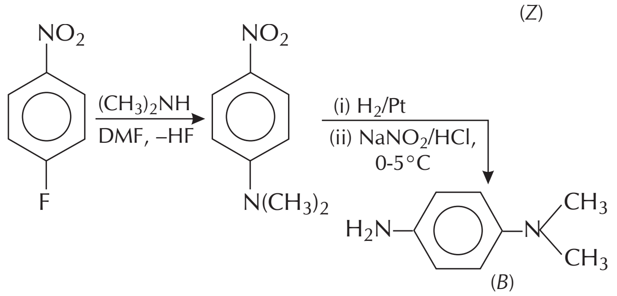
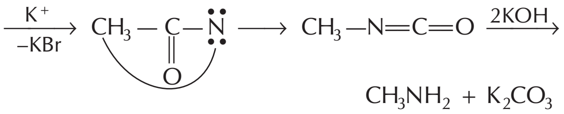


Round II

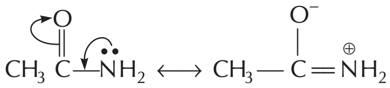
1. $CH_3CONH_2 \xrightarrow[-HBr]{Br} CH_3CONHBr \xrightarrow[-H_2O]{OH^-} CH_3CONBr^-$



$$\xrightarrow[-KBr]{K^+} CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-\ddot{\underset{\cdot\cdot}{N}} \longrightarrow CH_3-N{=}C{=}O \xrightarrow{2KOH}$$

$$CH_3NH_2 + K_2CO_3$$

2. In $CH_3C\begin{array}{l}\diagup NH\\ \diagdown NH_2\end{array}$, lone pair of —$NH_2$ remains more available for donation and its conjugate acid is resonance stabilised thus, its is most basic. Between $CH_3CH_2NH_2$ and $(CH_3)_2NH$, the later is more basic because of the presence of two alkyl group which facilitates the donation of lone pair easier. $CH_3\overset{\overset{\displaystyle O}{\|}}{C}—NH_2$ is least basic as in it lone pair of N involves in resonance.

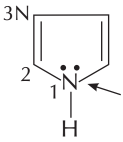


$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}—\ddot{N}H_2 \longleftrightarrow CH_3—\overset{\overset{\displaystyle O^-}{|}}{C}{=}\overset{\oplus}{N}H_2$$

Thus, the correct order of basicity is I > III > II > IV.

3. Piperidine and morpholine both are non-aromatic and N atom is sp^3 hybridised so these are more basic as compare to other two (which are aromatic and have sp^2 hybridised N atom). – *I* effect of O atom in morpholine makes it less basic as compared to piperidine. So, the order of basic character is

$$\underbrace{I > III}_{\text{Non-aromatic}} > \underset{\substack{\text{(lone pair does}\\ \text{not involves in}\\ \text{resonance but}\\ \text{N is } sp^2 \text{ hybridised)}}}{II} > \underset{\substack{\text{(least basic as}\\ \text{lone pair take}\\ \text{part in resonance)}}}{IV}$$

4. 

(less basic in aqueous medium as lone pair are delocalised)

5. $(CH_3)_3N \xrightarrow[\text{(ii) } H_2O, \Delta]{\text{(i) BrCN}} (CH_3)_2NH + CH_3Br + HCN$

6. Hofmann bromamide reaction proceeds with the retention of configuration.

7. Presence of α-H atom is the main condition for exhibiting tautomerism.

The reactant taken in reaction (*C*) does not contain any α-H atom, thus the product (*Y*) will also show the absence of α-H atom. Hence, *Y* will not show tautomerism.

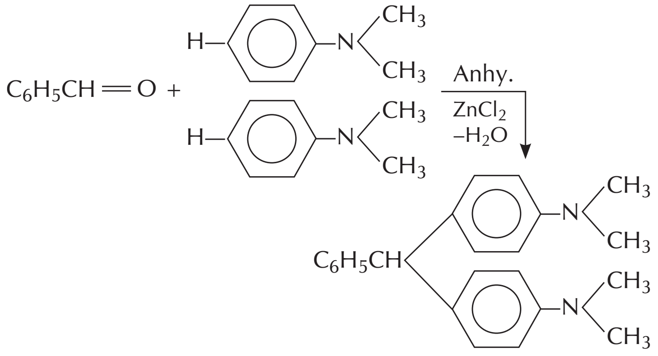
8. $RNH_2 \xrightarrow{KMnO_4} \underset{\text{aldimine}}{RCH{=}NH} \xrightarrow{H^+} RCHO$

$R_2NH \xrightarrow{H_2SO_5} R_2N—OH$

$R_3N \xrightarrow{H_2SO_5} R_3N \longrightarrow O$

$R_3C—NH_2 \xrightarrow{H_2SO_5} R_3C—NO_2$

9. Benzaldehyde condenses with N,N-dimethyl aniline in the presence of anhydrous $ZnCl_2$ to give malachite green.



malachite green

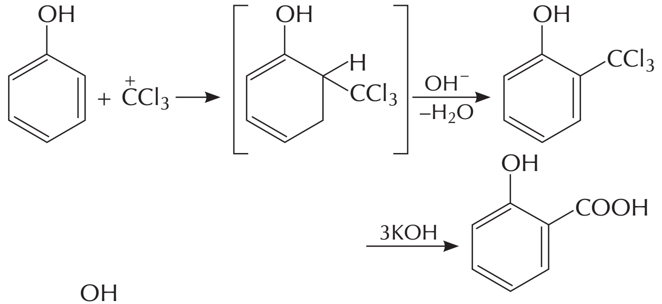
10. $\underset{\text{ethylamine}}{CH_3CH_2NH_2} \xrightarrow{NaNO_2 + HCl} CH_3CH_2OH + N_2 + H_2O + NaCl$

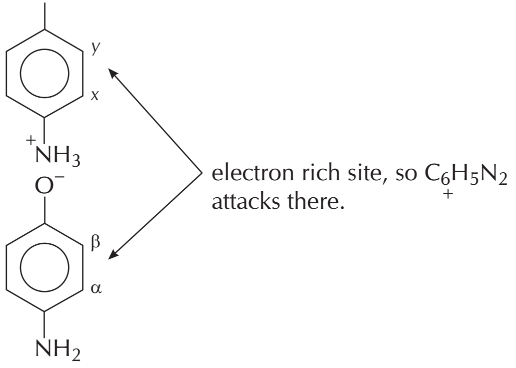
$\underset{\text{urea}}{NH_2CONH_2} \xrightarrow{NaNO_2 + HCl} 2N_2 + H_2O + CO_2 + NaCl$

$\underset{\text{acetamide}}{CH_3CONH_2} \xrightarrow{NaNO_2 + HCl} CH_3COOH + N_2 + H_2O + NaCl$

$\underset{\text{aniline}}{C_6H_5NH_2} \xrightarrow{NaNO_2 + HCl} C_6H_5N_2^+Cl^- + H_2O + NaCl$

11. $CCl_4 + K^+ \longrightarrow \underset{\substack{\text{trichloromethyl}\\ \text{carbonium ion}}}{\overset{+}{C}Cl_3} + KCl$

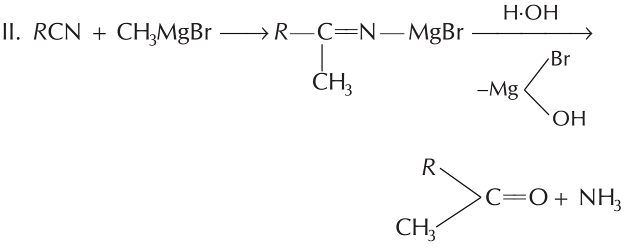


12. 

electron rich site, so $C_6H_5\overset{+}{N_2}$ attacks there.

13. I. $RCN \xrightarrow{\text{Reduction}} \underset{1^\circ\text{ amine}}{RCH_2NH_2}$

II. $RCN + CH_3MgBr \longrightarrow R—\underset{CH_3}{C}=N—MgBr \xrightarrow{H\cdot OH}$

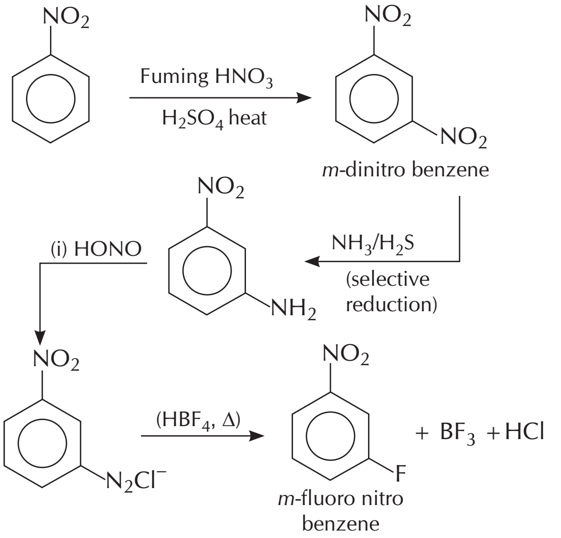


methyl ketone

III. $RNC \xrightarrow{\text{Hydrolysis}} HCOOH + \underset{1^\circ\text{ amine}}{RNH_2}$

IV. $RNH_2 \xrightarrow{HNO_2} ROH + N_2 + H_2O$

14.



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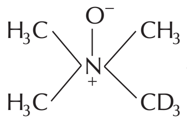


$\longrightarrow (CH_3)_2NO + CH_2=CH—CD_3$

$+ CH_3CH=CD_2$

16. (A) H_3PO_2 converts—$N_2^+\bar{C}l$ into –H.

(B) Sandmeyer reaction converts $-N_2^+Cl^-$ into $-Cl^-$

(C) Boiling with water introduces –OH group in place of $-N_2^+Cl^-$.

(D) Gomberg reaction introduces –Ar group in place of $-N_2^+Cl^-$.

17. (i) **To determine the structures of *B* and *C***

Compound '*B*' on heating with Br_2 and KOH forms compound '*C*'. So, '*B*' is amide and '*C*' is amine. Molecular formula C_6H_7N of '*C*' tells us that it is aniline ($C_6H_5NH_2$).

$$\underset{\substack{\text{benzamide}\\ [B]}}{C_6H_5CONH_2} \xrightarrow{Br_2/KOH} \underset{[C]\ C_6H_7N}{C_6H_5NH_2}$$

(ii) **To determine the structure of *A***

Compound '*A*' on treatment with aqueous ammonia forms '*B*' so '*A*' is benzoic acid.

$$\underset{\substack{\text{benzoic acid}\\ [A]}}{C_6H_5COOH} \xrightarrow[\text{Heat}]{\text{Aqueous } NH_3} \underset{\substack{\text{benzamide}\\ [B]}}{C_6H_5CONH_2}$$

18. (i) Addition of HCl to compound '*A*' shows that compound '*A*' is alkene. Compound '*B*' is C_4H_9Cl.

(ii) Compound '*B*' reacts with NH_2, it forms amine '*C*'.

$$\underset{[A]}{C_4H_8} \xrightarrow{HCl} \underset{[B]}{C_4H_9Cl} \xrightarrow{NH_3} \underset{[C]}{C_4H_{11}N \text{ or } C_4H_9NH_2}$$

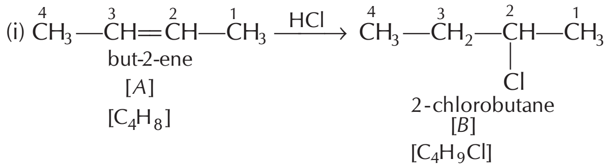
(iii) '*C*' gives diazonium salt with $NaNO_2$ / HCl, which yields an optically active alcohol. So, '*C*' is an aliphatic amine.

(iv) '*A*' on ozonolysis produces 2 moles of CH_3CHO.

So, '*A*' is $CH_3—CH=CH—CH_3$ (But-2-ene).

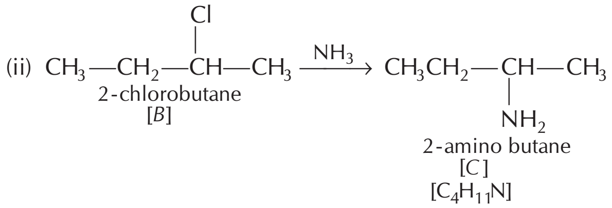
Reactions

(i)



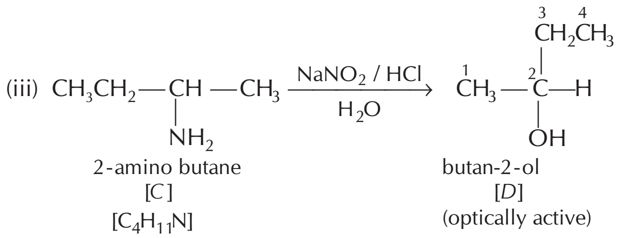
$$\underset{\substack{\text{but-2-ene}\\ [A]\\ [C_4H_8]}}{\overset{4}{C}H_3—\overset{3}{C}H=\overset{2}{C}H—\overset{1}{C}H_3} \xrightarrow{HCl} \underset{\substack{\text{2-chlorobutane}\\ [B]\\ [C_4H_9Cl]}}{\overset{4}{C}H_3—\overset{3}{C}H_2—\underset{Cl}{\overset{2}{C}H}—\overset{1}{C}H_3}$$

(ii)



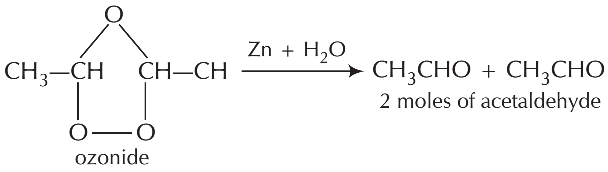
$$\underset{\substack{\text{2-chlorobutane}\\ [B]}}{CH_3—CH_2—\overset{Cl}{CH}—CH_3} \xrightarrow{NH_3} \underset{\substack{\text{2-amino butane}\\ [C]\\ [C_4H_{11}N]}}{CH_3CH_2—\underset{NH_2}{CH}—CH_3}$$

(iii)



$$\underset{\substack{\text{2-amino butane}\\ [C]\\ [C_4H_{11}N]}}{CH_3CH_2—\underset{NH_2}{CH}—CH_3} \xrightarrow[H_2O]{NaNO_2\ /\ HCl} \underset{\substack{\text{butan-2-ol}\\ [D]\\ \text{(optically active)}}}{\overset{1}{C}H_3—\underset{OH}{\overset{\overset{3\ \ 4}{CH_2CH_3}}{\overset{2}{C}}}—H}$$

(iv) $\underset{\substack{\text{but-2-ene}\\ [A]}}{CH_3–CH=CH–CH_3} + O_3 \longrightarrow$



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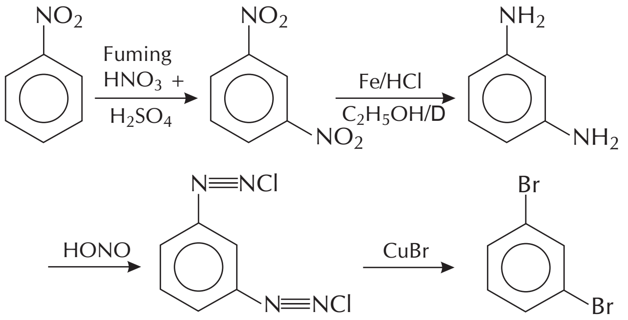
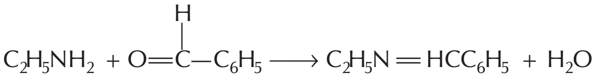


m-dibromobenzene

20.



$C_2H_5NH_2 + O{=}\overset{H}{C}{-}C_6H_5 \longrightarrow C_2H_5N{=}HCC_6H_5 + H_2O$

benzaldehyde
(*A*)

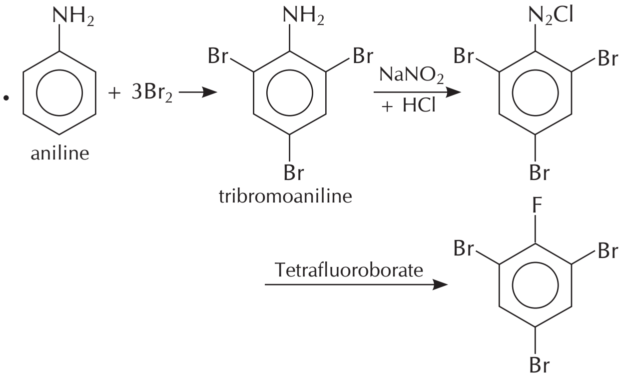
$NH_2\,CO\boxed{NH_2 + H}NH \cdot NH_2 \longrightarrow NH_2CONHNH_2 + NH_3$

urea hydrazine
(*B*)

$C_2H_5NH_2 + NOCl \longrightarrow C_2H_5Cl + H_2O + N_2$

(*C*)

21.

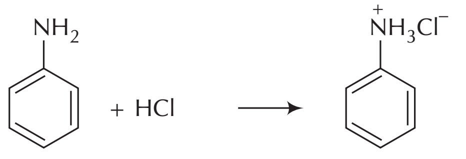


aniline

tribromoaniline

2,4,6-tribromo-fluoro benzene

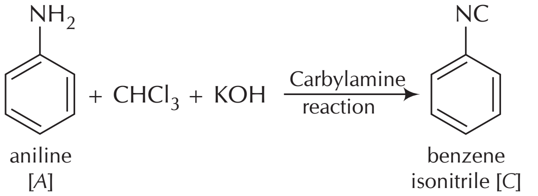
22. (i)



$[C_6H_7N]$
aniline [*A*]

anilinium chloride [*B*]

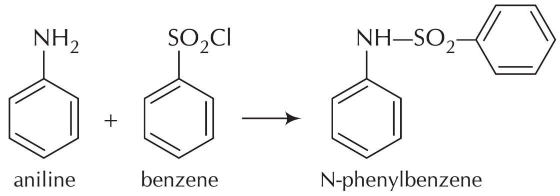
(ii)



aniline
[*A*]

benzene
isonitrile [*C*]
$+ 3KCl + 3H_2O$

(iii)

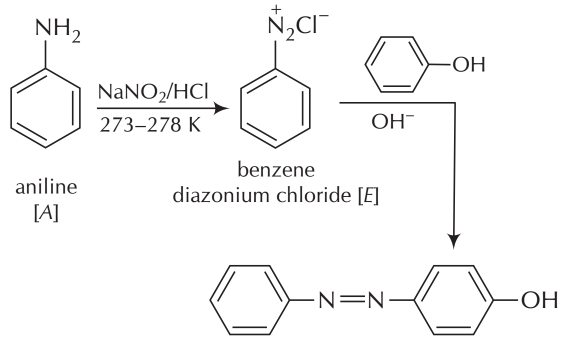


aniline
[*A*]

benzene
sulphonyl
chloride

N-phenylbenzene
sulphonamide [D]
(soluble in alkali)

(iv)

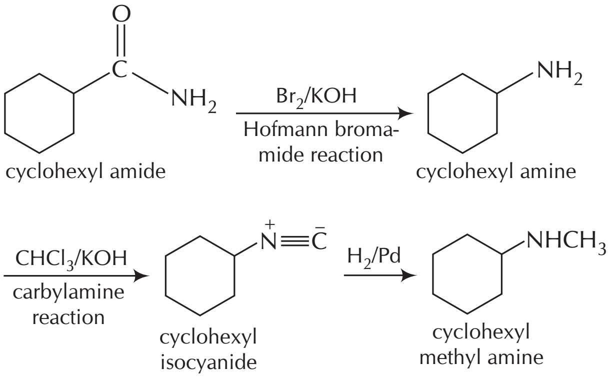


aniline
[*A*]

benzene
diazonium chloride [*E*]

p-hydroxy azobenzene
(orange dye)
[*F*]

23.



cyclohexyl amide

cyclohexyl amine

cyclohexyl
isocyanide

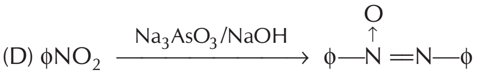
cyclohexyl
methyl amine

24. (A) $\phi NO_2 \xrightarrow{Zn/NH_4Cl} \phi NHOH$

(B) $\phi NO_2 \xrightarrow[NaOH]{Zn/al} \phi\ N{=}N\phi$ azobenzene

(C) $\phi NO_2 \xrightarrow{LAH} \phi NH_2$

(D)

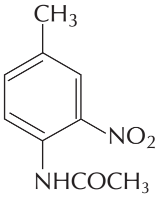


$\phi NO_2 \xrightarrow{Na_3AsO_3/NaOH} \phi{-}\overset{O \atop \uparrow}{N}{=}N{-}\phi$

azoxybenzene

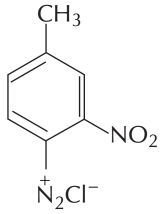
25. I= Sn/HCl

II=



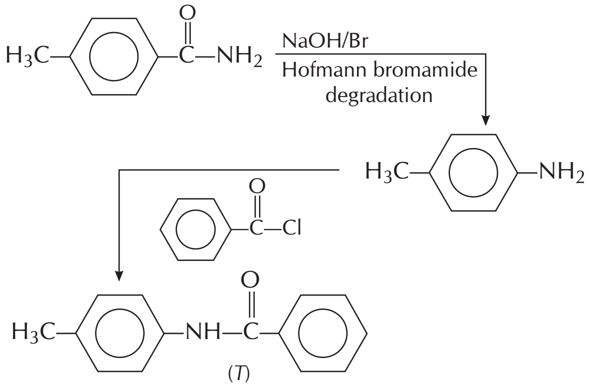
$III{=}H_2O/H^+$

IV=

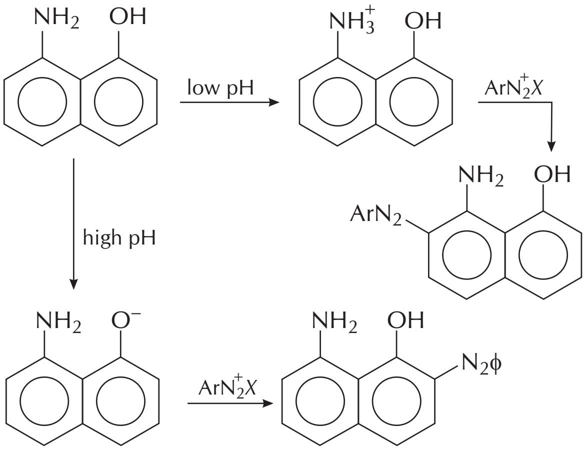


$V{=}H_3PO_2/H_2O$

26.



27. At low pH, it exist as cation whereas at high pH as anion



28. (A) Aniline is used for making azo dyes.

(B) TNT (trinitrotoluene) is an explosive.

(C) sulphanilamide is a sulpha drug.

(D) Nitrobenzene being inert towards Friedel-Crafts reaction, is used as a solvent for this reaction.

29. (a) $\underset{\text{alkyl isocyanide}}{RNC} \xrightarrow[{[H]}]{LiAlH_4} \underset{2^\circ\text{ amine}}{RNHCH_3}$

(b) $\underset{\text{alkyl cyanide}}{RCN} \xrightarrow[{[H]}]{LiAlH_4} \underset{1^\circ\text{ amine}}{RCH_2NH_2}$

(c) $\underset{\text{acid amide}}{RCONH_2} \xrightarrow[{[H]}]{LiAlH_4} \underset{1^\circ\text{ amine}}{RCH_2NH_2}$

(d) $\underset{1^\circ\text{ nitroalkane}}{RNO_2} \xrightarrow{Sn/HCl} \underset{1^\circ\text{ amine}}{RNH_2}$

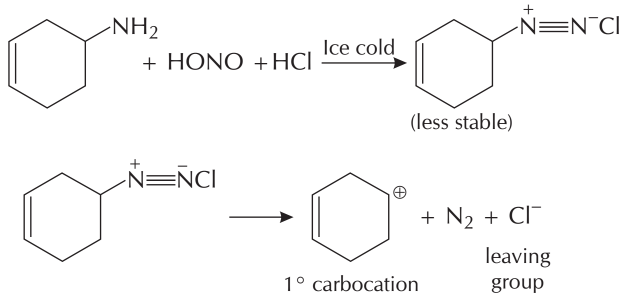
Thus, (*A*) can be alkyl cyanide or acid amide or 1° nitroalkane.

30. CH_3COCl and $(CH_3CO)_2O$ form acetanilide with aniline and thus, reduces the activety of $-NH_2$ group. Hence, treatment with these reagents result in the formation *p*-nitro derivative as major product. In the absence of these reagents, 2,4,6 trisubstituted derivative is the major product.

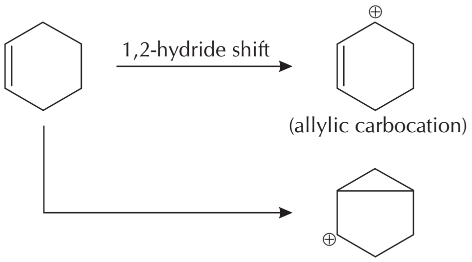
31. Bromination of acetanilide and coupling reactions of diazonium salts both are the examples of electrophilic substitution reaction.

32. 3° amines because of the absence of H-atoms, attached directly to N-atom, will not show positive Liebermann's nitroso test. Thus, $C_6H_5N(CH_3)_2$ being a 3° amine, does not show positive Liebermann's nitroso test.

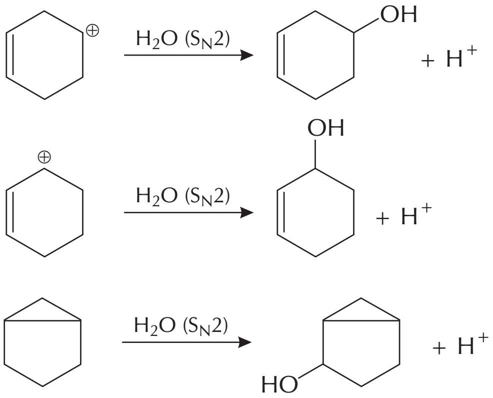
33.



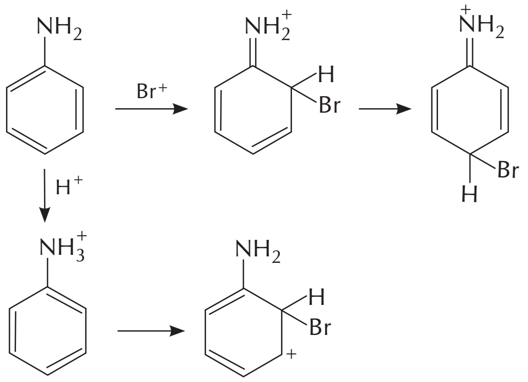
The carbocation formed rearranges itself to give more stable carbocation in the following manners,



Now, all these carbocation are converted into alcohols as



34.



35. Only chlorobenzene and bromobenzene are obtained by Sandmeyer's reaction, as for fluorobenzene, the reaction is explosive and in case of iodobenzene, the reaction is reversible.

36. For the reduction of nitro compounds, only a small amount of HCl is required along with Fe scrap. This is because $FeCl_3$ formed hydrolysed to give HCl which is utilised in the further reaction.

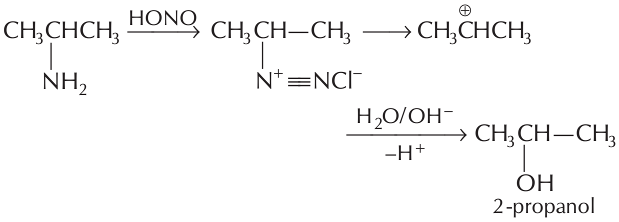
37. Hofmann bromamide degradation and Curtius degradation both involve the intramolecular alkyl shift and, thus result in the formation of 1° amines.

38. Alkyl group is +*I* showing group. In general, it increases the electron density over nitrogen, thus increase the availability of lone pair for donation. But in case of tertiary amines, in aqueous solution, the over crowding of three bulkier alkyl group results in increased strain, which decreases the availability of lone pairs for donation and thus results in decreased basicity. Hence, in aqueous solution, 3° amines are less basic as compared to 2° amines.

39. Primary amines are less basic as compared to secondary amines because of less electron density over N of $–NH_2$ in case of primary amines.

40. Acyl group being deactivating given only monosubstituted product whereas alkyl group is an activating group so it results in the formation of polysubstituted product.

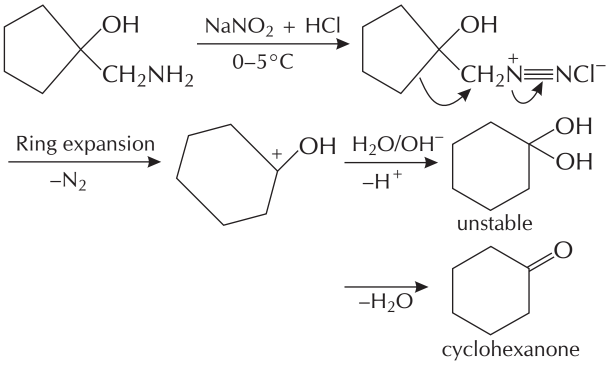
41.



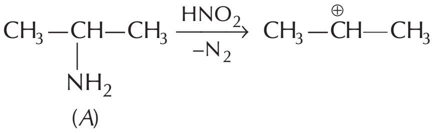
$$CH_3\underset{NH_2}{CH}CH_3 \xrightarrow{HONO} CH_3\underset{N^+\equiv NCl^-}{CH}—CH_3 \longrightarrow CH_3\overset{\oplus}{C}HCH_3 \xrightarrow[-H^+]{H_2O/OH^-} CH_3\underset{OH}{CH}—CH_3$$

2-propanol

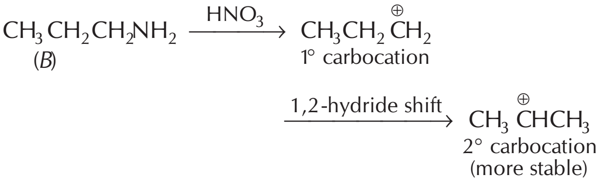
42.



43.



$$\underset{(A)}{CH_3—\underset{NH_2}{CH}—CH_3} \xrightarrow[-N_2]{HNO_2} CH_3—\overset{\oplus}{C}H—CH_3$$



$$\underset{(B)}{CH_3CH_2CH_2NH_2} \xrightarrow{HNO_3} \underset{1° \text{ carbocation}}{CH_3CH_2\overset{\oplus}{C}H_2} \xrightarrow{1,2\text{-hydride shift}} \underset{\substack{2° \text{ carbocation} \\ \text{(more stable)}}}{CH_3\overset{\oplus}{C}HCH_3}$$

***P*$_{44–46}$**

The mixture of amines when reacts with Hinsberg reagent, form the following products

$$RNH_2 + C_6H_5SO_2Cl \xrightarrow[-HCl]{} \underset{\text{soluble in NaOH}}{C_6H_5SO_2NHR}$$

$$\xrightarrow{NaOH} \underset{\substack{\text{(present in NaOH layer)} \\ (C)}}{C_6H_5SO_2N(Na)R}$$

$$R_2NH + C_6H_5SO_2Cl \xrightarrow[-HCl]{} \underset{\text{insoluble in NaOH}}{C_6H_5SO_2N\cdot R_2}$$

(thus, present in ethereal layer)

$$\underset{(A)}{C_6H_5SO_2N\cdot R_2} + H_3O^+ \xrightarrow{\Delta} \underset{\substack{2° \text{ amine} \\ (D)}}{R_2NH}$$

$$R_3N + C_6H_5SO_2Cl \longrightarrow \text{No reaction}$$

(thus, present in ethereal layer)

Hence,

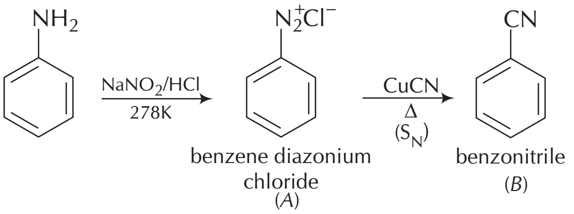
A = N,N-dialkyl benzene sulphonamide

B = R_3N

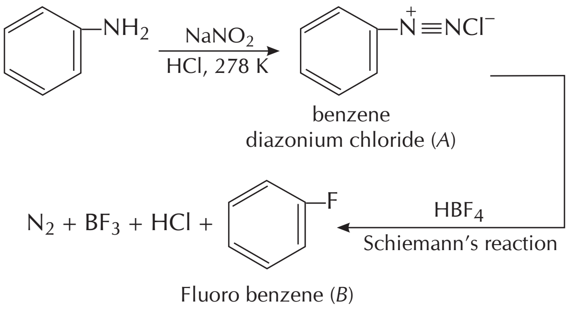
C = sodium salt of 1° amine (N-alkyl benzene sulphonamide)

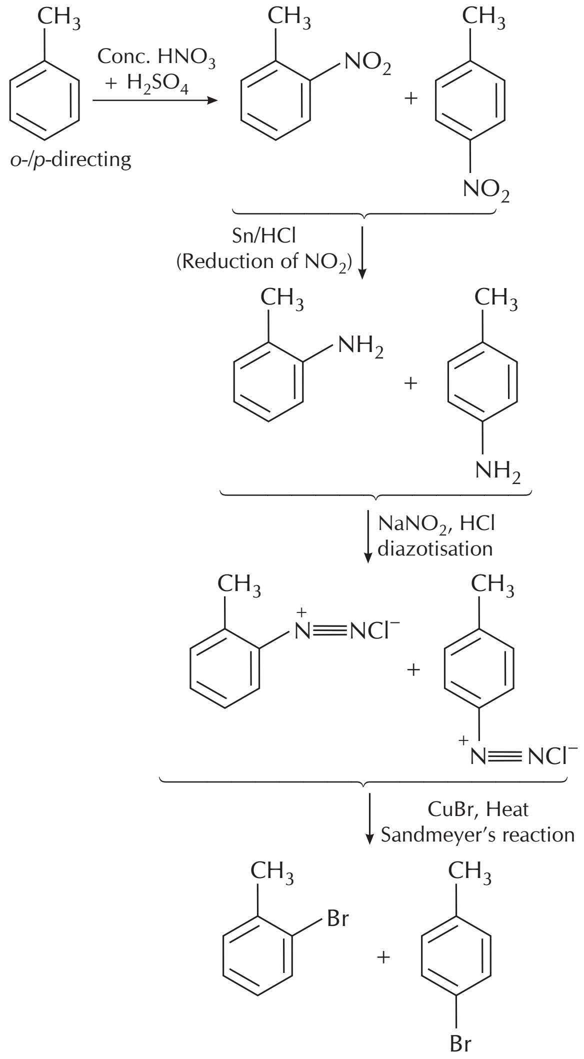
D = 2° amine (R_2NH)

47. Formation of *A* is by diazotisation and formation of *B* form *A* is by S_N reaction.



48.



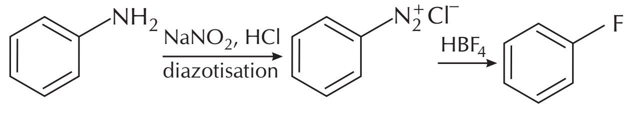
49. 

50. In aqueous solution, basicity order is $\underset{2^\circ}{\text{Dimethylamine}} > \underset{1^\circ}{\text{methylamine}} > \underset{3^\circ}{\text{trimethylamine}} > \text{aniline}$.

51. $CH_3CH_2NH_2 + CHCl_3 + KOH \rightarrow A + B + 3H_2O$

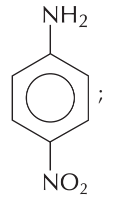
$$CHCl_3 + KOH \longrightarrow :CCl_2 + \underset{(B)}{KCl} + H_2O$$

$$CH_3CH_2NH_2 + :CCl_2 \longrightarrow \underset{\text{carbylamine }(A)}{CH_3CH_2NC} + 2HCl$$

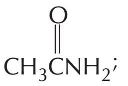
52. 

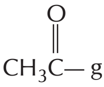
53. Wurtz reaction is used to prepare alkanes from alkyl halides.

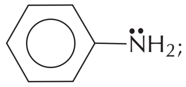
$$2R-X + 2Na \xrightarrow{\text{Dry ether}} R-R + 2NaX$$

54. (a) 

; $-NO_2$ group (electron withdrawing) decreases basic nature of aniline

(b) 
$CH_3\overset{O}{\overset{\|}{C}}NH_2$;

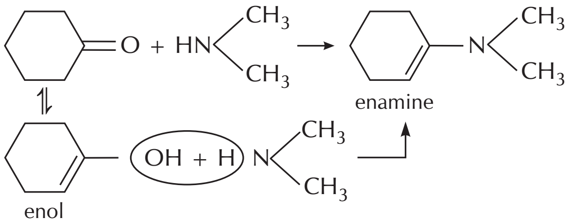

$CH_3\overset{O}{\overset{\|}{C}}-$ group is also electron withdrawing group.

(c) 

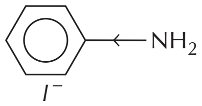
; phenyl group is also electron withdrawing.

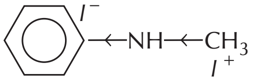
(d) Benzyl is electron repelling group increases basic nature.

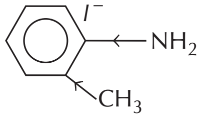
Thus, most basic compound is benzylamine.

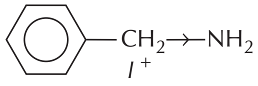
55. 

56. $-CH_3$ group [an electron releasing (+*I*) group] increases electron density at N-atom, hence basic nature is increased.

(a) 

(b) 

(c) 

(d) 

$-C_6H_5$ decreases electron density at N-atom, thus basic nature is decreased. (Lone pair on N in aniline compounds is delocalised alongwith π-electrons in benzene).

57. $NH_3CH_3NH_2, (CH_3)_2NH$

$$(CH_3)_2NH + H_2O \overset{K_1}{\rightleftharpoons} (CH_3)_2\overset{+}{N}H_2 + OH^-$$

I^+ effect maximum, stabilisation more, H-bond stability high hence most basic.

$$CH_3NH_2 + H_2O \overset{K_2}{\rightleftharpoons} CH_3\overset{+}{N}H_3 + OH^-$$

$$NH_3 + H_2O \overset{K_3}{\rightleftharpoons} NH_4^+ + OH^-$$

$$K_1 > K_2 > K_3$$

Hence, basicity order is

$$(CH_3)_2NH > CH_3NH_2 > NH_3$$

13 Polymers

JEE Main MILESTONE

- Various Terms Related to Polymers
- Classification of Polymers
- Plasticizers
- Polymerisation
- Rubber
- Polythene or Polyethylene
- Polyamides
- Polyesters
- Bakelite
- Others Important Polymers
- Molecular Mass of Polymers
- Biodegradable Polymers
- Monomers and Uses of Some Common Polymers

13.1 Various Terms Related to Polymers

In order to understand the composition, structure and characteristics of polymers, it is necessary to become aware with the following terms.

Monomers

The small molecules that combine together to give a polymer, are called monomers. *e.g.,* when a large number of ethene molecules combine together (under suitable conditions), a high molecular weight substance, called the **polymer**, is obtained. It is named as polyethene as it contains several ethene units.

$$n\mathrm{CH_2{=}CH_2} \xrightarrow[\text{Pressure}]{\mathrm{O_2},\ \text{heat}} \text{- - -}\mathrm{CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2}\text{- - -}$$

$$\text{or } \underset{\text{polyethylene}}{(\mathrm{-CH_2{-}CH_2-})_n}$$

The term polymer is coined from two Greek words : 'poly' means many and 'mer' means units or parts. Thus, ***polymers may be defined as the high molecular mass compounds which are prepared by the combination of a large number of one or more types of simple molecules or units.***

Repeating Units

The unit or part of a polymer, which is repeated at a regular interval is called **repeating unit**. Repeating unit may or may not be same as monomer, *e. g.*, in case of $(A)_n$ type polymer repeating unit, A is same as monomer and in case of $(AB)_n$ type polymer repeating unit, AB is different from monomers A and B.

Macromolecules

High molecular weight compounds are called macromolecules. Polymers because of their high molecular mass are also considered as macromolecules but *all macromolecules are not polymers*. The main difference between macromolecules and polymers is that the later have a repeating unit whereas the former may or may not, *e.g.*, polythene and chlorophyll both are macromolecules but only polythene due to the presence of $\left[CH_2-CH_2\right]$ repeating unit, is a polymer whereas chlorophyll due to the absence of repeating unit, is not a polymer.

Functionality of a Polymer

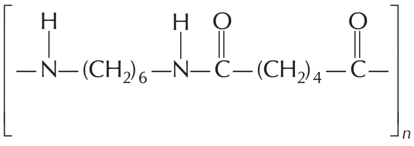
It is the number of reacting sites present in a molecule (monomer) that leads to the formation of polymer. *e.g.*, ethene ($CH_2=CH_2$) contains only one double bond, so it is monofunctional. $NH_2(CH_2)_4NH_2$ contains two reacting $-NH_2$ groups, so it is bifunctional.

Telomers

Polymers which contain foreign molecules such as *A* and *B* in addition to the repeating unit, are called telomers, *e.g.*, $A-M_n-B$.

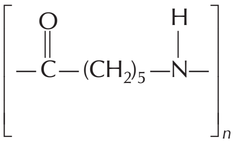
Sample Problem 1 *Which is not a polymer of only single monomer?* **[NCERT]**

(*a*)



$$\left[-\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\right]_n$$

(*b*)



$$\left[-\overset{O}{\overset{\|}{C}}-(CH_2)_5-\overset{H}{\overset{|}{N}}-\right]_n$$

(*c*) $\left[CF_2-CF_2\right]_n$

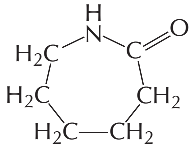
(*d*) *All of the above*

Interpret (c) (a) Since amide linkage —CONH— is present in (a), it is a polymer of diamine having 6C atoms and diacid having 6C atoms. Thus, its monomers are

(i) Hexamethylene diamine [$H_2N-(CH_2)_6-NH_2$] and

(ii) Adipic acid [$HOOC-(CH_2)_4-COOH$]

(b) also contains amide linkage but within the same molecule, so it contains $>$CO and amine group within a ring. Hence, its monomer is caprolactam.

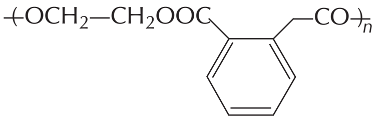


(c) contains the same monomer and repeating unit, so it is an addition polymer of a monomer containing double bond. Moreover, absence of functional group also shows the unsaturation. Hence, its monomer is tetrafluoroethene [$F_2C=CF_2$].

From the above it is clear that polymer given in option (a) have two monomers.

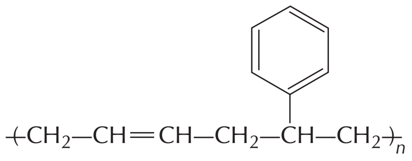
Sample Problem 2 *In which of the following polymers ethylene glycol is one of the monomer units?* **[NCERT Exemplar]**

(*a*)

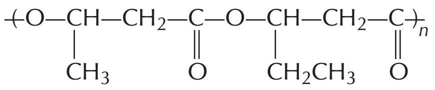


(*b*) $\left(CH_2-CH_2\right)_n$

(*c*)



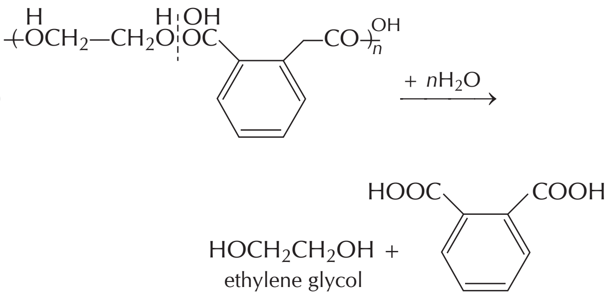
(*d*)



$$\left(O-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{O}{\underset{\|}{C}}-O-\underset{CH_2CH_3}{\underset{|}{CH}}-CH_2-\underset{O}{\underset{\|}{C}}\right)_n$$

Interpret (*a*) Since, in general, polymers are formed by the loss of small molecules like H_2O or without the loss of any molecule. So try to add H_2O or find unsaturation, to find the structures of monomers.

(a)



Hence, its one monomer unit is ethylene glycol.

(b) $(CH_2-CH_2)_n$ cannot be hydrolysed because of the absence of functional group, so its monomer must be unsaturated, *i.e.*, $CH_2=CH_2$.

(c) Similarly, $\left(CH_2-CH=CH-CH_2-\overset{C_6H_5}{\overset{|}{CH}}-CH_2\right)_n$ is a polymer of $CH_2=CH-CH=CH_2$ and $\overset{C_6H_5}{\overset{|}{CH}}=CH_2$ (styrene).

(d) Also, the given polymer on adding H_2O gives $HO-\underset{CH_3}{\underset{|}{CH}}CH_2-COOH$ and $HO-\underset{CH_2CH_3}{\underset{|}{CH}}CH_2COOH$ units.

Hence, only the polymer given in option (a) have ethylene glycol as monomer.

13.2 Classification of Polymers

Polymers are classified on different basis which are as follows

Classification on the Basis of Source of Availability

On this basis polymers are classified into following three catagories

(a) Natural Polymers

These are obtained from plants and animals. Some of these such as polysaccharides, proteins and nucleic acids are essential for the existence of life, so these are also known as **biopolymers**. These are generally biodegradable. Examples of such polymers are

(i) **Nucleic acids** (such as DNA, RNA) These are the polymers of nucleotides (*i.e.,* base + sugar + phosphate).

(ii) **Proteins** These are the polymers of amino acids, which are joined together by peptide bonds.

(iii) **Natural rubber** These are the polymers of derivatives of buta-1, 3-diene.

(iv) **Polysaccharides** (such as starch and cellulose) These are the polymers of monosaccharides, which are joined together through glycosidic linkages.

Caution Point *Enzymes are generally proteins, so these are also the polymers of amino acid monomers.*

(b) Semisynthetic Polymers

These are derived from natural polymers by chemical modifications. These are also called man made polymers. Their examples includes

(i) **Cellulose acetate** It is obtained by the acetylation of cellulose followed by partial hydrolysis. It is less inflammable and used in making photographic films, lacquers and varnishes.

(ii) **Rayon** It contains purified cellulose in the form of long fibres. When cellulose is treated with NaOH and CS_2, viscose, a colloidal dispersion, is obtained and when the viscose is forced through fine holes into dilute sulphuric acid, rayon is obtained. Rayon, a biodegradable polymer, absorbs moisture and is used for making textiles, carpets, tyre-cord etc. It has a shine like silk, so also known as artificial silk.

(iii) **Cellophane** When the viscose, obtained above, is forced through a long narrow slit into an acid bath and then, softens with glycerol, cellophane is obtained. Unlike plastics, it absorbs moisture.

(iv) **Cellulose nitrate** (gun cotton) These are obtained by the nitration of cellulose.

(c) Synthetic Polymers

These are man made polymers. Such polymers have high tensile strength. Due to their extensive use in daily life as well as in industry, these are of great importance, *e.g.,* polythene $-\!\!\left[CH_2-CH_2 \right]\!\!-_n$, polyvinyl chloride $-\!\!\left[CH_2-CHCl \right]_n$, polystyrene $-\!\!\left[CH_2-CHC_6H_5 \right]\!\!-_n$, nylon-66, bakelite, synthetic rubber etc.

Sample Problem 3 *Which of the following is not a semisynthetic polymer?* **[NCERT Exemplar]**

(a) *Cis-polyisoprene*
(b) *Cellulose nitrate*
(c) *Cellulose acetate*
(d) *Vulcanised rubber*

Interpret (a) *Cis*-polyisoprene is natural rubber which is obtained from rubber tree (natural source). So, it is a natural polymer, not a semisynthetic one.

Classification on the Basis of Structure

On this basis polymers are classified into following classes

(a) Linear Polymers

In linear polymers monomers are combined together in the form of long and straight chains. These chains are closely packed, due to which, these polymers have high melting points, high densities and high tensile strength, *e.g.,* high density polythene, polyvinyl chloride (PVC), polystyrene, polypropylene etc.

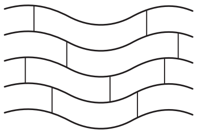
(b) Branched Chain Polymers

They contain linear chains with some branches. Due to branching, the molecules of polymer do not pack well. Consequently, these have low density, low melting point and low tensile strength, *e.g.,* low density polythene etc.

(c) Cross-linked or Network Polymers

These polymers usually are obtained from bi-or-tri functional monomers. In such polymers, the linear polymer chains are linked together through strong covalent bonds and results in a three dimensional network or cross-linked structure. Due to cross-linking, these polymers are hard, rigid and brittle, *e.g.,* bakelite, melamine etc.

(a) Linear chain (b) Branched chain



(c) Cross-linked

Fig. 13.1 General structure of different polymers

Classification on the Basis of Mode of Polymerisation

On this basis polymers are divided into following two classes

(a) Addition Polymers

These are usually obtained from unsaturated monomer molecules, *i.e.,* the molecules having double or triple bond. These are formed by successive addition of repeated monomers without the elimination of small molecules. The molecular mass of such polymers is whole number multiple of monomer. These are obtained by addition or chain growth polymerisation, so also known as **chain growth polymers**.

On the basis of monomers involved, these are further of two types

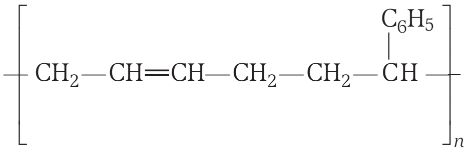
1. **Addition homopolymers** which are obtained by the repeated addition of single monomer unit, *e.g.,*

$$\underset{\text{ethene}}{nCH_2{=}CH_2} \longrightarrow \underset{\text{polyethene}}{\left[CH_2{-}CH_2\right]_n}$$

$$\underset{\text{vinyl chloride}}{nCH_2{=}CHCl} \longrightarrow \underset{\text{polyvinyl chloride}}{\left[CH_2{-}CHCl\right]_n}$$

2. **Addition copolymers** which are obtained by the repeated addition of more than one monomer units, *e.g.,*

$$\underset{\substack{\text{1,3-butadiene}\\(75\%)}}{nCH_2{=}CH{-}CH{=}CH_2} + \underset{\substack{\text{styrene}\\(25\%)}}{nC_6H_5CH{=}CH_2} \longrightarrow$$



$$\left[CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}\overset{\displaystyle C_6H_5}{\overset{|}{CH}}\right]_n$$

butadiene-styrene copolymer
(buna-S)

(b) Condensation Polymers

These are obtained when monomer molecules combine together with the loss of small molecules such as ammonia, water, alcohol etc. The molecular mass of such polymers is not a whole number multiple of monomer. These are the products of condensation polymerisation which generally occurs amongst the molecules possessing bi- or tri- functional groups, so are also called **step growth polymers**. These are usually copolymers but a few homopolymers are also known.

1. **Condensation copolymers** are obtained by the condensation of more than one monomer units, *e.g.,*

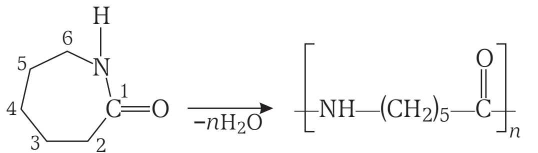
$$\underset{\substack{\text{hexamethylene}\\\text{diamine}}}{nH_2N(CH_2)_6NH_2} + \underset{\text{adipic acid}}{nHOOC(CH_2)_4COOH} \longrightarrow$$

$$\underset{\substack{\text{nylon-66}\\\text{(condensation copolymer)}}}{\left[NH(CH_2)_6NHCO(CH_2)_4CO\right]_n} + nH_2O$$

$$nHOOC{-}C_6H_4{-}COOH + nHO{-}(CH_2)_2{-}OH \xrightarrow[-nH_2O]{}$$

$$\underset{\text{terylene (dacron)}}{\left[OC{-}C_6H_4{-}COO{-}CH_2{-}CH_2{-}O\right]_n}$$

2. **Condensation homopolymers** are prepared by the condensation reaction between molecules of only one kind, *e.g.,*



caprolactum

nylon-6 or perlon
(condensation homopolymer)

Hot Spot 1

CLASSIFICATION ON THE BASIS of Magnitude of Intermolecular Forces

Although the chapter itself is not very important for JEE Main examination but question, if asked, may be from this topic as it is more important than the others. The level of question is easy and the question is generally direct.

On the basis of intermolecular forces polymers are classified into following classes

(a) Elastomers

As the name implies, these are the polymers that have elastic character (*i.e.,* have a property to regain their original shape after stretching). In such polymers, the polymer chains are held together by weak intermolecular forces which are responsible for their elastic character, *e.g.,* natural rubber, neoprene etc. In order to increase their elastic character, a few cross-links are also introduced in between the chains, *e.g.,* vulcanised rubber.

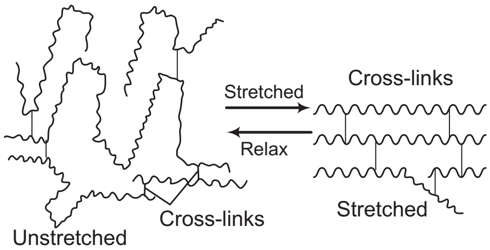


Fig. 13.2 Unstretched and stretched forms of an elastomer

(b) Fibres

These are long threads having high tensile strength, high modulus and less elasticity. These can be woven into fabric. These polymers have strong intermolecular forces such as hydrogen bonding, dipole-dipole interaction etc. Due to the presence of such strong forces of attraction, the polymer chains get closely packed and impart crystalline nature to polymers.

Thus, polymers show sharp melting points. As the crystalline nature increases, the polymers become denser, harder and more resistant to heat, *e.g.,* polyamides (nylon-66), polyesters (terylene) etc. However, in the presence of substituents as in poly (methyl methacrylates) or branches, no such close packing occurs, thus density gets reduced.

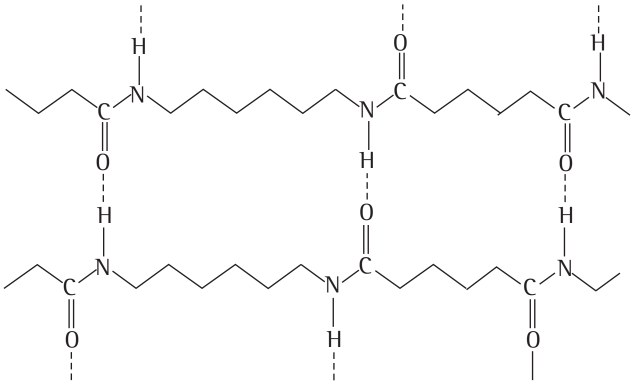


Fig. 13.3 Hydrogen bonding in nylon-6,6

(c) Thermoplastic Polymers

These are the linear or slightly branched polymers in which the intermolecular forces of attraction are intermediate between elastomers and fibres. These polymers soften on heating and become rigid on cooling. This is because of the absence of cross-linking between chains of such polymers. The process of softening, moulding and cooling can be repeated as often as, desired. These polymers are soluble in many organic solvents, *e.g.,* nitrocellulose, vinyl polymers such as polythene, perspex, polystyrene etc.

(d) Thermosetting Polymers

When heavily branched molecules or chains are heated, they result in hard infusible and insoluble three dimensional or extensively cross-linked products. These three dimensional or extensively cross-linked products are referred to as **thermosetting polymers**. Due to extensive cross-linking, these polymers have strongest intermolecular forces and are brittle as cross-linking reduces the mobility of polymer chains. On heating, such polymers result in chemical decomposition, thus these cannot be remelted or reused after hardening once *e.g.,* bakelite, urea-formaldehyde resin, melamine-formaldehyde etc. Remember that rigidity of polymers increases with cross-linking.

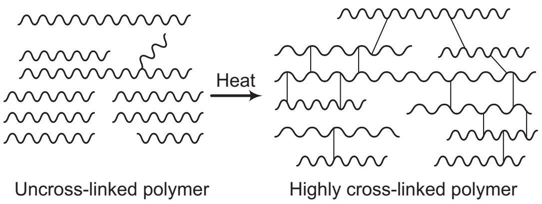


Fig. 13.4

(e) Oriented Polymers

There is an another class of polymers, termed as oriented polymers, which are stronger than steel and can conduct electricity almost like copper.

Sample **Problem 4** *Arrange the following polymers in increasing order of their intermolecular forces. Nylon-66, buna-S, polythene, neoprene.*

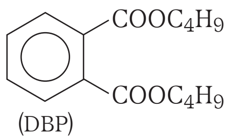
- (a) *Neoprene < buna-S < polythene < nylon-66*
- (b) *Neoprene < buna-S < nylon-66 < polythene*
- (c) *Polythene < nylon 66 < buna-S < neoprene*
- (d) *Polythene < buna-S < nylon-66 < neoprene*

Interpret (*a*) The order of intermolecular forces in different polymers is elastomers < plastics < fibres. So, in order to solve such problem first classify the given polymer into the above classes and then arrange them in increasing order of forces. Neoprene (synthetic rubber) is an elastomer, buna-S is also an elastomer, polythene is plastic and nylon 66 is a fibre. So, the increasing order of intermolecular forces of the given polymer is

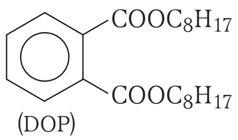
Neoprene < buna-S < polythene < nylon-66

13.3 Plasticizers

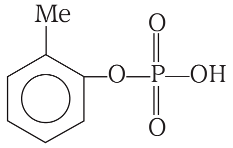
This name is given to those compounds, which when added to such plastics which do not soften very much with rise in temperature, make them soft and easily pliable. They do this because they lower the melting point (softening point) of the polymer thereby reducing the interparticle forces. Generally high boiling esters or high boiling haloalkanes are used as plasticizers. The plasticizers evaporate when exposed to air and light for a long time, leaving behind a hard and brittle plastic article, *e.g.,* tricresyl phosphate (TCP), dioctylphthalate (DOP), dibutylphthalate (DBP) and chlorinated paraffin wax (CPW) etc. *e.g.,* polyvinyl chloride (PVC) is a hard, stiff and glass like plastic. When a plasticizer such as dioctylphthalate (DOP) is added to it, it becomes soft and rubber like.



(DBP)



(DOP)



o-cresyl phosphate

Check Point 1

1. Is haemoglobin a polymer? Explain your answer.
2. Can we consider enzymes as polymer? [**NCERT**]
3. Explain, why do the melting point and tensile strength of polymers increase with rise in molecular mass?
4. Why does nylon-66 has a sharp melting point?
5. When dioctylphthalate is added to polyvinylchloride, it becomes soft. Explain, why?
6. Branched chain polymers have low melting point and low density. Explain, why?
7. Why elastomers have elastic property?

13.4 Polymerisation

The process or technique through which monomer units combine to give a polymer is known as **polymerisation**. The polymerisation reaction can't be controlled easily. According to **Carothers** (1931) polymerisation is best defined as "intermolecular combinations that are functionally capable of proceeding indefinitely".

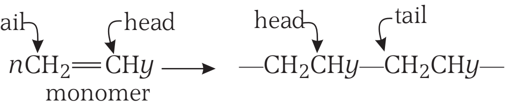
There are two principal methods through which monomers combine to give polymers. These are addition polymerisation and condensation polymerisation. Copolymerisation and coordination polymerisation, however, also are the methods of polymerisation.

Addition Polymerisation

It is the process in which molecules of same or different monomers combine together to give a polymer without the elimination of small molecules. Since, there is an increase in the length of chain (*i.e.,* chain grows) by this mode of polymerisation, it is also known as **chain growth polymerisation.** This mode of polymerisation is observed in molecules having multiple bonds, mainly in $CH_2{=}CHy$ type molecules (where, y may be —H, —X, —CO_2R, —CN etc.)

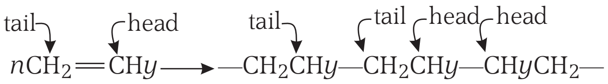
In chain growth polymerisation, there are three possible ways through which monomers can combine, *viz.*

(i) Head to tail manner



$$nCH_2{=}CHy \longrightarrow —CH_2CHy—CH_2CHy—$$

(ii) Head to head and tail to tail manner



$$nCH_2{=}CHy \longrightarrow —CH_2CHy—CH_2CHy—CHyCH_2—$$

(iii) In random manner which includes (i) and (ii) both.

Among these ways, 'Head to tail addition' is preferred for steric reasons because propagating unit attacks the less sterically hindered carbon. Moreover, groups that stabilise adjacent radicals also favour "head to tail addition".

The addition or chain growth polymerisation can proceed by the following two mechanisms (i) By the formation of free radicals, *i.e.,* free radical polymerisation and (ii) By the formation of ionic species, *i.e.,* ionic polymerisation. On the basis of structure of monomer and initiator used, each mechanism involve following three steps

(i) Initiation step, in which process starts,
(ii) Propagation step, in which chain grows,
(iii) Termination step, in which process terminates.

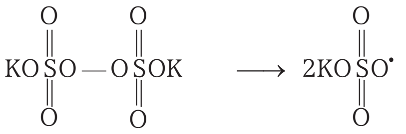
(a) Free Radical Addition Polymerisation

In this way of polymerisation there is generation of free radicals by free radical generators, called **initiator**. Any compound which readily undergoes homolytic cleavage to give such radicals that are sufficiently energetic to convert an alkene into radical, can act as a radical generator (initiator) for free radical polymerisation. Most commonly used free radical generators are organic and inorganic peroxides and salts of per acids. Examples of some free radical generators are summarised below

$$\underset{\text{benzoyl peroxide}}{(C_6H_5COO)_2} \longrightarrow 2C_6H_5COO^\bullet$$

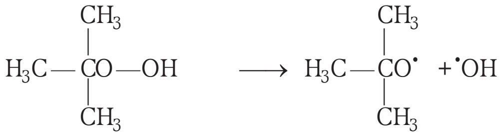
$$\underset{\text{acetyl peroxide}}{(CH_3COO)_2} \longrightarrow 2CH_3COO^\bullet$$

$$\underset{\text{hydrogen peroxide}}{H_2O_2} \longrightarrow 2\overset{\bullet}{O}H$$



$$\mathrm{KO}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\mathrm{O-O}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\mathrm{OK} \longrightarrow 2\mathrm{KO}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\mathrm{O}^\bullet$$

potassium perdisulphate



$$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}O-OH \longrightarrow H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}O^\bullet + {}^\bullet OH$$

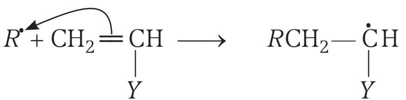
t-butyl hydrogen peroxide

Some free radicals are also generated in the presence of light.

This mode of polymerisation involves following three steps

Step I **Initiation step** In this step, a monomer unit gets excited either by exposing to light or by small amount of free radical generator, *e.g.,*

$$\underset{\text{(alkyl peroxide)}}{(RCOO)_2} \longrightarrow 2RCOO^\bullet \longrightarrow \underset{\substack{\text{(free radical}\\\text{generator)}}}{R^\bullet} + CO_2$$

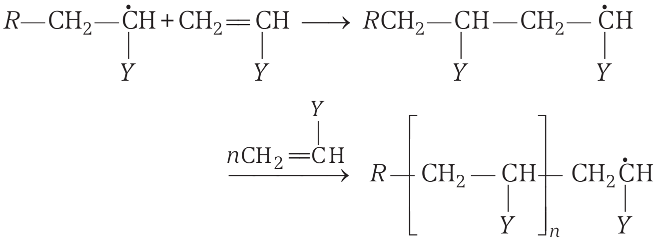


$$R^\bullet + CH_2{=}\underset{\underset{Y}{|}}{CH} \longrightarrow RCH_2-\underset{\underset{Y}{|}}{\dot{C}H}$$

excited monomer unit (free radical)

(where, Y = H, Cl, CN, —R etc.)

Step II **Propagation step** The excited monomer unit (or generated free radical) combines with another monomer unit, in this step and generate another free radical. This process of addition and generation continues and chain length increases, *e.g.,*



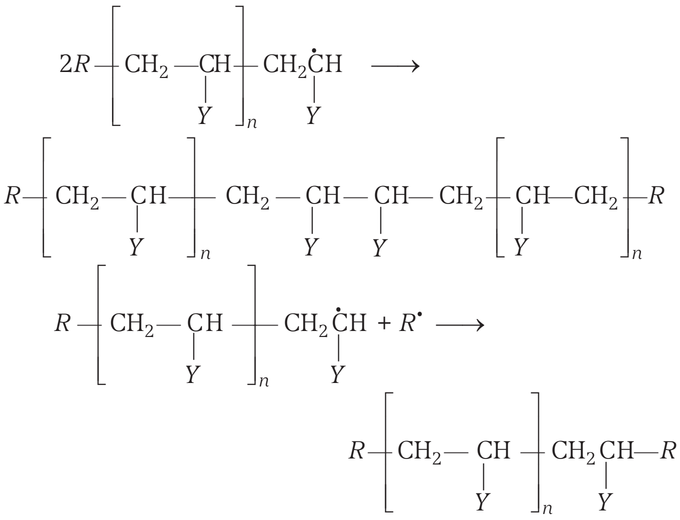
$$R-CH_2-\underset{\underset{Y}{|}}{\dot{C}H} + CH_2{=}\underset{\underset{Y}{|}}{CH} \longrightarrow RCH_2-\underset{\underset{Y}{|}}{CH}-CH_2-\underset{\underset{Y}{|}}{\dot{C}H}$$

$$\xrightarrow{nCH_2=\overset{\overset{Y}{|}}{C}H} R\left[CH_2-\underset{\underset{Y}{|}}{CH}\right]_n CH_2\underset{\underset{Y}{|}}{\dot{C}H}$$

(Because of the high molecular weight of polymers, the terminal groups are relatively unimportant in determining their physical properties. It is the rest part of polymers that determines their physical properties).

Step III **Termination step** In this step the growing chain is terminated by one of the following methods.

(i) When there is a coupling between the growing chains or between a growing chain and free radical generator, the chain gets terminated, *e.g.,*



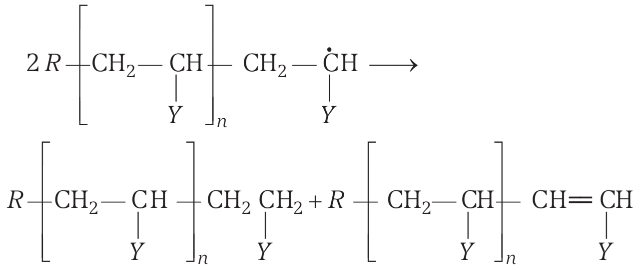
$$2R\left[CH_2-\underset{\underset{Y}{|}}{CH}\right]_n CH_2\underset{\underset{Y}{|}}{\dot{C}H} \longrightarrow$$

$$R\left[CH_2-\underset{\underset{Y}{|}}{CH}\right]_n CH_2-\underset{\underset{Y}{|}}{CH}-\underset{\underset{Y}{|}}{CH}-CH_2\left[\underset{\underset{Y}{|}}{CH}-CH_2\right]_n R$$

$$R\left[CH_2-\underset{\underset{Y}{|}}{CH}\right]_n CH_2\underset{\underset{Y}{|}}{\dot{C}H} + R^\bullet \longrightarrow$$

$$R\left[CH_2-\underset{\underset{Y}{|}}{CH}\right]_n CH_2\underset{\underset{Y}{|}}{CH}-R$$

(ii) When the growing chain undergoes disproportionation, the chain gets terminated, *i.e.,*

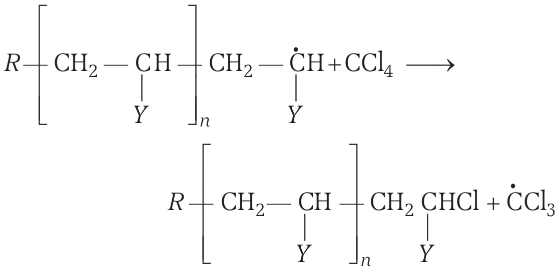


$$2R\left[CH_2-\underset{\underset{Y}{|}}{CH}\right]_n CH_2-\underset{\underset{Y}{|}}{\dot{C}H} \longrightarrow$$

$$R\left[CH_2-\underset{\underset{Y}{|}}{CH}\right]_n CH_2\underset{\underset{Y}{|}}{CH_2} + R\left[CH_2-\underset{\underset{Y}{|}}{CH}\right]_n CH{=}\underset{\underset{Y}{|}}{CH}$$

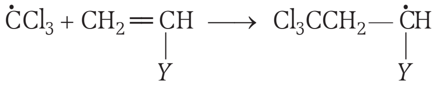
(iii) When reagents such as CCl_4 or CBr_4 are added, the growing chain gets terminated. These reagents are called **chain transfer agents** and the process is called

chain transfer. The molecular mass of a polymer can be controlled by this process. These reagents do not affect the rate of polymerisation but yield a polymer with lower average molecular mass and a small amount of chlorine, *e.g.,*



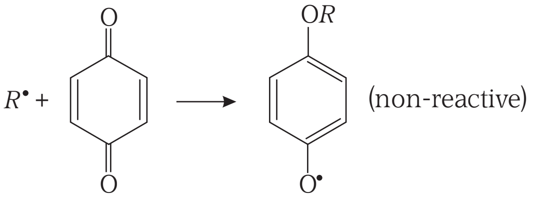
$$R\left[CH_2-\underset{Y}{\underset{|}{CH}}\right]_n CH_2-\underset{Y}{\underset{|}{\dot{C}H}}+CCl_4 \longrightarrow R\left[CH_2-\underset{Y}{\underset{|}{CH}}\right]_n CH_2\,\underset{Y}{\underset{|}{CHCl}}+\dot{C}Cl_3$$

The obtained free radical again generates excited monomer unit.



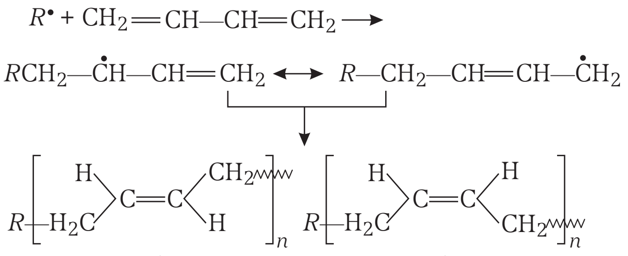
$$\dot{C}Cl_3+CH_2{=}\underset{Y}{\underset{|}{CH}} \longrightarrow Cl_3CCH_2-\underset{Y}{\underset{|}{\dot{C}H}}$$

When the radical, generated from chain transfer agent, is highly stable and unreactive, the original reaction chain gets terminated without the initiation of new one. Consequently, the process of polymerisation is inhibited. Therefore, these reagents are termed as **chain inhibitors**. Several amines, phenols, quinones act as chain inhibitor, *e.g.,* free radical polymerisation of a vinyl derivative is inhibited in the presence of benzoquinone.



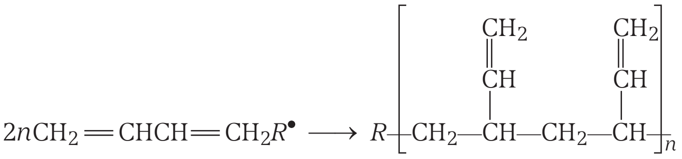
Conjugated dienes such as 1, 3-*butadiene can polymerise by one of the following two ways*

(i) **1,4-addition** When addition takes place at terminal carbon atoms (*i.e.,* at C_1 and C_4 in case of butadiene), the result is an unbranched polymer with a repeating unit having double bond. Therefore, the polymers can exist as *cis* form or trans form or a mixture of both, *e.g.,*



trans form *cis* form

(ii) **1,2-addition** When addition takes place at successive carbon atoms (*i.e.,* at C_1 and C_2 in case of butadiene), the result is a branched polymer.



$$2nCH_2{=}CHCH{=}CH_2R^\bullet \longrightarrow R\left[CH_2-\overset{\overset{\overset{CH_2}{\|}}{CH}}{\overset{|}{CH}}-CH_2-\overset{\overset{\overset{CH_2}{\|}}{CH}}{\overset{|}{CH}}\right]_n$$

(b) Ionic Addition Polymerisation

In this mode of polymerisation, there is generation of ionic species (as intermediate) such as cations and anions, instead of free radicals. Depending upon the nature of ionic species formed, ionic addition polymerisation further may be of two types.

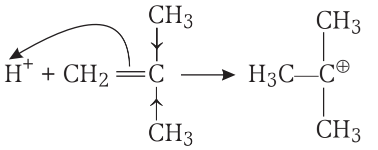
(i) **Cationic addition polymerisation** is the process, which involves formation of a carbocation as intermediate. The carbocation is generated by an initiator. Any compound which readily undergoes heterolytic cleavage to give a proton or cation that is able to convert an alkene into carbocation, can act as initiator for cationic polymerisation reaction. Commonly used carbocation generators or initiators are Lewis acids such as BF_3, $AlCl_3$ or $SnCl_4$ etc., and protonic acids such as H_2SO_4, HF etc.

Cationic addition polymerisation is facilitated in monomers having electron releasing groups such as CH_3, C_2H_5 etc. *Higher the stability of carbocation intermediate, more is the reactivity of monomer towards cationic addition polymerisation.* Like free radical addition polymerisation, cationic addition polymerisation also involves following three steps

Step I **Initiation step** In this step, the proton generated from either Lewis acid or protonic acid, attacks on monomer unit and a carbocation is formed.

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

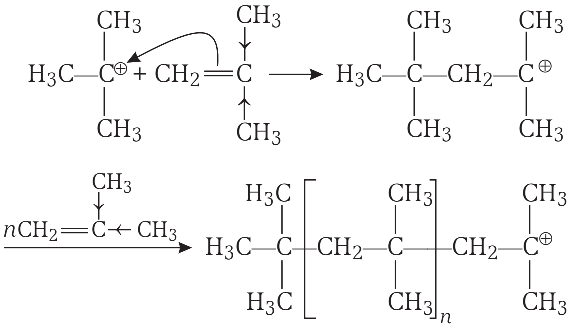
$$BF_3 + H_2O \rightleftharpoons H^+ + BF_3(OH^-)$$



$$H^+ + CH_2{=}\underset{CH_3}{\overset{CH_3}{C}} \longrightarrow H_3C-\underset{CH_3}{\overset{CH_3}{C^\oplus}}$$

carbocation (intermediate)

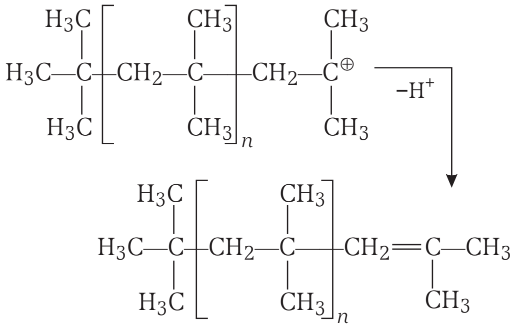
Step II **Propagation step**



$$H_3C-\underset{CH_3}{\overset{CH_3}{C^\oplus}}+CH_2{=}\underset{CH_3}{\overset{CH_3}{C}} \longrightarrow H_3C-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C^\oplus}}$$

$$\xrightarrow{nCH_2=\overset{CH_3}{C}\leftarrow CH_3} H_3C-\underset{H_3C}{\overset{H_3C}{C}}\left[CH_2-\underset{CH_3}{\overset{CH_3}{C}}\right]_n CH_2-\underset{CH_3}{\overset{CH_3}{C^\oplus}}$$

Step III **Termination step** The growing chain is generally terminated by the loss of a hydrogen ion (*i. e.*, proton).



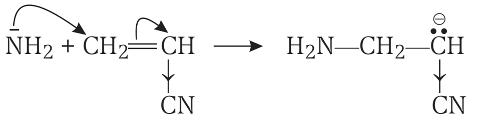
(ii) **Anionic addition polymerisation** is the process, in which intermediate formed is a carbanion. The initiator for this process are strong bases such as potassium amide (KNH_2), *n*-butyl lithium etc. Monomers (olefins) containing electron withdrawing groups (such as CN, C_6H_5 etc.) readily undergo anionic addition polymerisation.

The monomers that give more stable carbanion intermediate, readily undergo anionic addition polymerisation.

It involves the following three steps

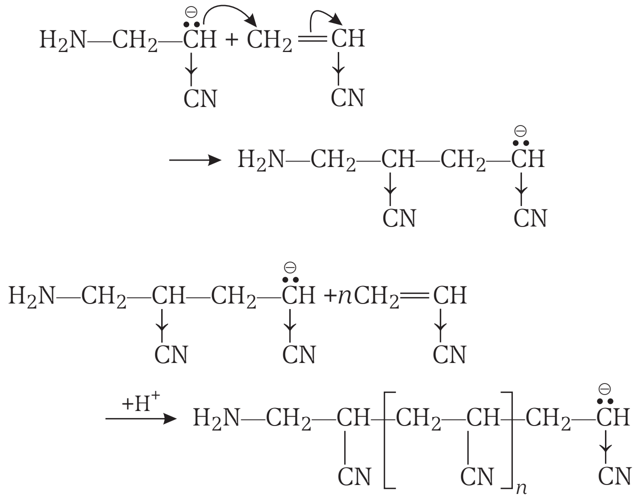
Step I **Initiation step** In this step, the nucleophiles, generated from strong bases, attack on monomer and generate carbanion.

$$KNH_2 \longrightarrow K^+ \bar{N}H_2$$

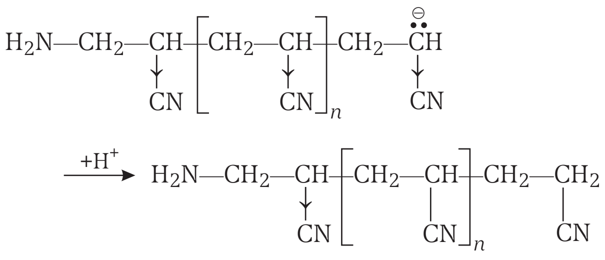


carbanion (intermediate)

Step II **Propagation step**



Step III **Termination step** The growing chain is terminated by the addition of a proton or a Lewis acid, present in the reaction mixture.



Check Point 2

1. Explain, why 'head to tail addition' is preferred in vinyl chloride?
2. Why does styrene undergo anionic polymerisation easily?
3. Will you prefer to polymerise acrylonitrile under anionic or cationic polymerisation condition? Explain your answer.
4. Which substances act as a radical initiator?

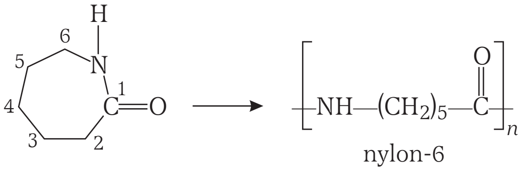
Condensation Polymerisation

In this mode of polymerisation, there is combination of molecules of same or different monomers in a controlled stepwise manner with the elimination of small molecules such as water, ammonia, alcohol etc., as by product. The monomers involved in this mode of polymerisation are not the same as those in addition polymerisation.

These monomers have functional groups such as alcohol, amine or carboxylic acid groups, instead of double bonds. The monomers having at least two functional groups, may be same or different, (*i.e.,* bifunctional monomers), polymerise by this mode of polymerisation. The product of each step is again a bifunctional molecule which can react with other monomer and dimer molecules until a long polymer chain is formed. Since, there is a repetitive condensation reaction between bifunctional monomers, the process is also known as **step growth polymerisation**.

On the basis of functional groups, there are two possible ways through which condensation polymerisation takes place.

(i) When monomer has two kinds of functional groups, it undergoes self polymerisation. *e.g.,*



caprolactum　　　　nylon-6

(ii) But if both the functional groups of monomer are same, an another monomer bearing different functional groups is required for condensation polymerisation, *e.g.,*

$$\underset{\text{adipic acid}}{HOOC(CH_2)_4COOH} + \underset{\text{hexamethylene diamine}}{H_2N\text{-}(CH_2)_6\text{-}NH_2} \xrightarrow[-H_2O]{} \underset{\text{nylon-66}}{\text{-}[NH(CH_2)_6NHCO(CH_2)_4CO]_n\text{-}}$$

The condensation polymerisation for two monomers A and B may be expressed as

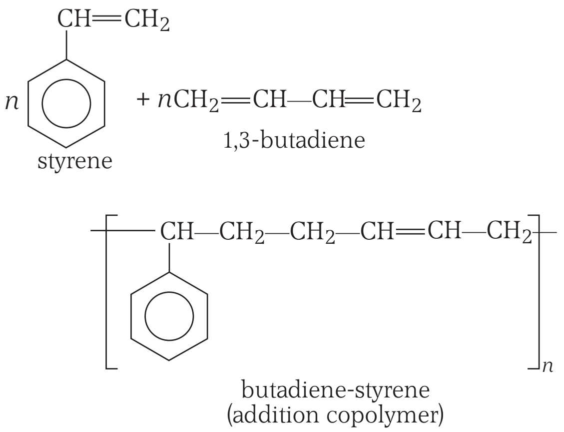
$$A + B \xrightarrow{\text{condense}} A-B$$
$$A-B+A \longrightarrow A-B-A$$
$$A-B-A+B \longrightarrow A-B-A-B$$

While in stepwise manner, it takes place in the following manner

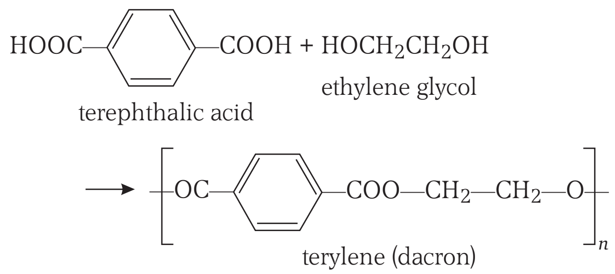
$$A + B \longrightarrow A-B$$
$$A-B+A-B \longrightarrow A-B-A-B$$
$$A-B-A-B+A-B-A-B \longrightarrow (A-B)_n$$

Copolymerisation

When two or more different monomer units are allowed to polymerise, a copolymer is formed which contains multiple units of each monomer used, in the same polymeric chain. The process by which copolymers are formed is referred to as **copolymerisation**. Indeed, it is not a distinct method from addition and condensation polymerisation. When two or more different monomer units combine through either addition or condensation polymerisation, an addition or condensation copolymer is obtained and the process is termed as **addition** (or chain growth) **copolymerisation or condensation** (or step growth) **copolymerisation**, *e.g.,*



butadiene-styrene
(addition copolymer)



The properties of copolymers are quite different from those of homopolymers (polymers that have only one type monomer units), *e.g.,* polystyrene, a homopolymer obtained from styrene, is a good insulator and can be easily moulded into toys, combs, radio parts etc., while styrene butadiene rubber (SBR), a copolymer of sytrene and butadiene (in 1 : 3 ratio), possesses high abrasion resistance, high load bearing capacity, thus used in manufacturing auto tyres, cable insulations etc. Moreover, it is very tough and a good substitute for natural rubber.

On the basis of arrangement of monomer units in the polymer chain during copolymerisation, the copolymers can be of the following four types

(i) **Random copolymers** are obtained when the monomer units are arranged randomly in the polymer chain, *e.g.,*

$$nA + nB \longrightarrow -A-A-A-B-B-A-B-B-B-A-A-$$

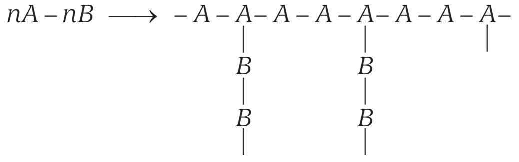
(ii) **Alternating copolymers** are obtained, when monomer units are at the alternate positions, in the polymer chain, *e.g.,*

$$nA + nB \longrightarrow -A-B-A-B-A-B-A-B-A-$$

(iii) **Block copolymers** are obtained, when different blocks of identical monomer units are at the alternate positions with each other, *e.g.,*

$$nA + nB \longrightarrow -(A-A-A)-(B-B-B)-(A-A-A)-$$

(iv) **Graft copolymers** are obtained, when homopolymer chains of one monomer units are grafted on the homopolymer chains of another monomer units, *e.g.,*

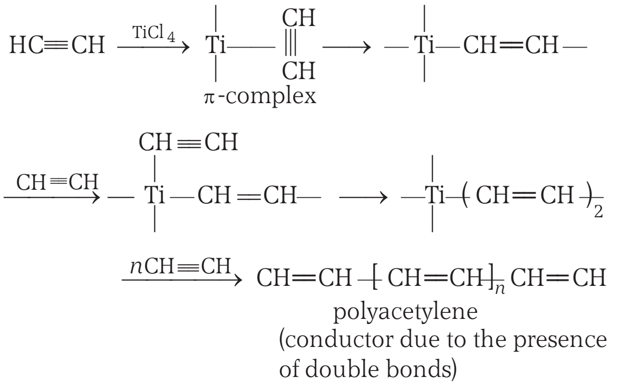


$$nA-nB \longrightarrow -A-\underset{\substack{| \\ B \\ | \\ B \\ |}}{A}-A-A-\underset{\substack{| \\ B \\ | \\ B \\ |}}{A}-A-A-\underset{|}{A}-$$

(Graft copolymers are prepared by radiating gamma rays on a completed homopolymer chain in the presence of an another monomer.)

Coordination Polymerisation

There is an another kind of polymerisation, which proceeds with the formation of coordination compound as intermediate. Thus, this polymerisation is called coordination polymerisation, *e.g.*, on treating with aluminium-titanium initiator $[(C_2H_5)_3Al + TiCl_4]$, monomer first forms a coordination complex with titanium by donating its π-electrons. The π-complex, thus, formed reacts with a large number of monomer units stepwise and leads to the formation of polymer.



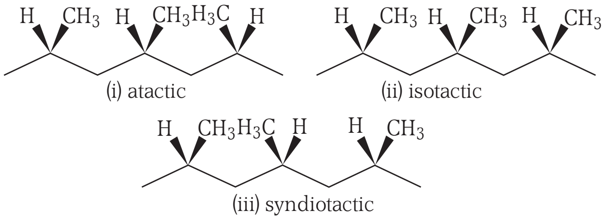
This process was found by Ziegler and Natta, that's why it is also known as *Ziegler-Natta* polymerisation and the catalyst used is called *Ziegler-Natta* catalyst.

The major advantage of this polymerisation is that the polymer obtained has specific stereochemistry, *e.g.*, propene can polymerise to give any of the three possible stereochemical arrangements

(i) **Atactic** (or random arrangement) in which methyl groups are arranged randomly.

(ii) **Isotactic** (or same arrangement), in which methyl groups are present on same side of *zig-zag* backbone.

(iii) **Syndiotactic** (or alternate arrangement), in which methyl groups lie alternately on the opposite sides of *zig-zag* backbone.



(i) atactic
(ii) isotactic
(iii) syndiotactic

Sample **Problem 5** *Which form of polypropene exist as enantiomer?*

(*a*) *Isotactic*
(*b*) *Syndiotactic*
(*c*) *Atactic*
(*d*) *All of these*

Interpret (*d*) All forms of polypropene (PP) would exist in equal amount of enantiomers, with net specific rotation of zero. So each form would exist as racemates.

Check Point 3

1. Which type of monomers undergo condensation polymerisation?
2. By which mode of polymerisation, caprolactum polymerises and why?
3. Which type of copolymers are largely found?

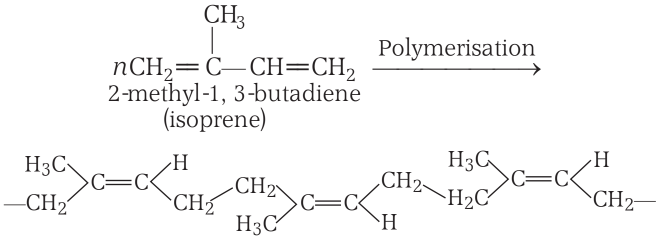
Some Important Polymers

13.5 Rubber

Rubbers are the polymer of derivatives of buta-1, 3-diene. These have elastic properties due to which these are also included in class 'elastomers'. On the basis of origin, rubbers can be of two types.

Natural Rubber

Because of its origin from natural sources, it is a natural polymer. It is prepared from rubber latex (contains 35% rubber) which is a colloidal dispersion of rubber in water and is obtained from rubber trees (*Hevea brasiliensis*). On treating latex with acids such as acetic acid, formic acid etc., crude rubber coagulates which either on masticating or on adding necessary agents gives natural rubber. Natural rubber is linear 1, 4-polymer of isoprene (2-methyl-1, 3-butadiene). In other words, natural rubber is *cis*-polyisoprene or *cis*-1,4-polyisoprene.



cis-1,4-polyisoprene (natural rubber)

The weight average molecular weight $(\overline{M}_w)$ of rubber is in the range 1,30,000–3,40,000. *Its trans form is known as gutta percha.*

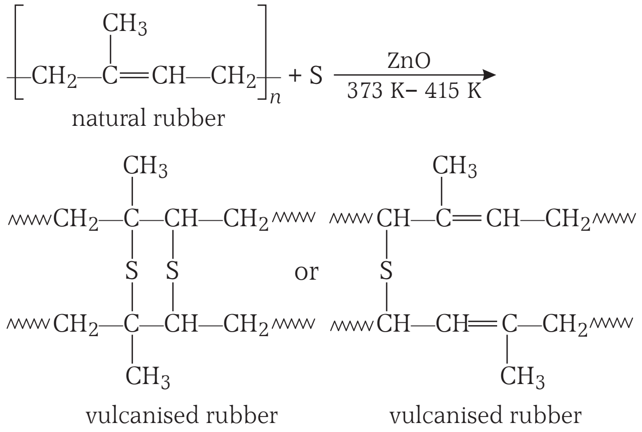
Properties of Natural Rubber

Natural rubber is insoluble in water, dilute acids and alkalies but soluble in organic solvents such as benzene, chloroform, petrol etc. It absorbs a large amount of water and has low tensile strength and elasticity.

Vulcanisation

To improve the undesirable properties, natural raw rubber is heated with sulphur or sulphur compounds at 373 K to 415 K in the presence of ZnO. The process is called **vulcanisation of rubber** and was introduced by **Charles Goodyear.** On vulcanisation, sulphur introduces cross-links at the reactive sites of double bonds and makes the rubber stiffened, more elastic and resistant to oxidation and organic solvents. The stiffness of rubber depends upon the amount of sulphur added, *e.g.,* when 5% sulphur is used as a cross-linking agent, the obtained vulcanised rubber is used for manufacturing tyres but if 30% sulphur is used, the obtained vulcanised rubber (ebonite) is used in making battery case.

Zinc oxide used in the vulcanisation process, is an additive which accelerates the rate of vulcanisation because vulcanisation originally is a slow process.



$$\underset{\text{natural rubber}}{\left[-CH_2-\overset{\overset{\large CH_3}{|}}{C}=CH-CH_2-\right]_n} + S \xrightarrow[373\text{ K}-\ 415\text{ K}]{ZnO}$$

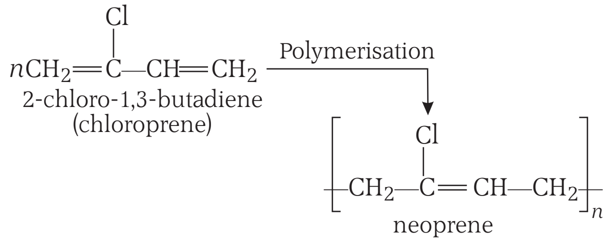
To protect rubber from deterioration on exposure to air, an additive such as diphenyl amine is also added.

Synthetic Rubbers

These are synthesised from certain organic compounds. These are either homopolymer of buta-1, 3-diene derivatives or copolymer of buta-1, 3-diene or its derivatives with another unsaturated organic monomers, such as acrylonitrile, styrene etc. These are more resistant and have high tensile strength. *e.g.,*

(a) Neoprene

It is the most commonly used synthetic rubber. It is a homopolymer of chloroprene (2-chloro-1, 3-butadiene). It is also known as **duprene** and is obtained by the free radical polymerisation or *Ziegler-Natta* polymerisation of chloroprene.



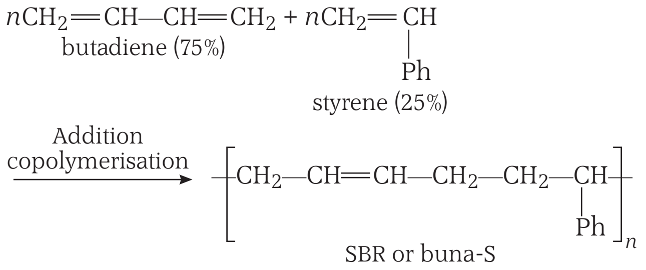
$$\underset{\substack{\text{2-chloro-1,3-butadiene}\\ \text{(chloroprene)}}}{nCH_2=\overset{\overset{\large Cl}{|}}{C}-CH=CH_2} \xrightarrow{\text{Polymerisation}} \underset{\text{neoprene}}{\left[-CH_2-\overset{\overset{\large Cl}{|}}{C}=CH-CH_2-\right]_n}$$

It is a thermoplastic and need not to be vulcanised. As it is resistant towards air, heat, light, chemicals, acids below 50% strength, it is superior to natural rubber.

It is used in manufacture of gaskets, hoses and conveyor belts etc.

(b) **Buna-S** (Styrene-butadiene rubber, SBR)

It is also called GRS (general purpose styrene rubber). It is obtained by the copolymerisation of 75% butadiene and 25% styrene in the presence of sodium metal.



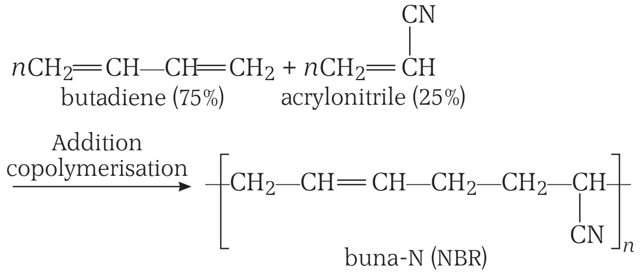
$$\underset{\text{butadiene (75\%)}}{nCH_2=CH-CH=CH_2} + \underset{\text{styrene (25\%)}}{nCH_2=\underset{\underset{\large Ph}{|}}{CH}} \xrightarrow[\text{copolymerisation}]{\text{Addition}} \underset{\text{SBR or buna-S}}{\left[-CH_2-CH=CH-CH_2-CH_2-\underset{\underset{\large Ph}{|}}{CH}-\right]_n}$$

It is an elastomer.

It is generally compounded with carbon black and vulcanised with sulphur. It is extremely resistant to wear and tear and finds use in manufacture of tyres and other mechanical rubber goods.

(c) **Buna-N** (NBR or GRA)

It is obtained by the copolymerisation of 75% butadiene and 25% acrylonitrile (vinyl cyanide) in the presence of peroxide catalyst or sodium metal.



$$\underset{\text{butadiene (75\%)}}{nCH_2=CH-CH=CH_2} + \underset{\text{acrylonitrile (25\%)}}{nCH_2=\overset{\overset{\large CN}{|}}{CH}} \xrightarrow[\text{copolymerisation}]{\text{Addition}} \underset{\text{buna-N (NBR)}}{\left[-CH_2-CH=CH-CH_2-CH_2-\underset{\underset{\large CN}{|}}{CH}-\right]_n}$$

It is more rigid, responds less to heat and very resistant to swelling action of petrol, oils and other organic solvents.

(d) Thiokol or Polysulphide Rubber

It is obtained by the condensation copolymerisation of ethylene dichloride and sodium tetrasulphide (Na_2S_4).

(e) Butyl Rubber

It is obtained by the copolymerisation of iso-butylene and isoprene.

13.6 Polythene or Polyethylene

It is a polymer of ethene ($CH_2 {=\!=} CH_2$). Depending upon the conditions of temperature, pressure and nature of catalyst.

Polythene are of two types.

Low Density Polythene

It is prepared by free radical addition polymerisation of ethene at 350 to 570 K, under 1000–2000 atm pressure and in the presence of traces of oxygen or a peroxide.

$$\underset{\text{ethene}}{nCH_2{=}CH_2} \xrightarrow[\text{350–570 K; 1000–2000 atm}]{\text{Traces of oxygen or peroxide}} \text{low density polythene (highly branched)}$$

The branching does not allow the polymer to undergo close packing and thus, the density of the polymer is low.

It is inert, tough but flexible and poor conductor of electricity. Therefore, it is used for insulating electric wires, for manufacturing squeeze bottles and toys.

High Density Polythene

It is also inert but relatively tough and hard with high tensile strength, hence used for manufacturing containers, house wares etc. It is formed by the polymerisation of ethene in the presence of catalyst, such as triethyl aluminium and titanium tetrachloride, at 330–350 K and atmospheric pressure.

$$\underset{\text{ethene}}{nCH_2{=}CH_2} \xrightarrow[\text{catalyst}]{\text{330–350 K, 1 atm}} \text{high density polythene}$$

(with linear chains)

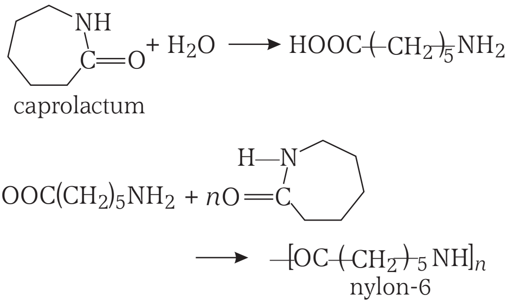
The polymer, thus, obtained consists of practically linear molecules which get packed closely and thus, density is high.

13.7 Polyamides

Polymers having amide linkages —(CONH)— are called nylons (or polyamides) [here, Ny=Newyork and Lon=London] as nylon-66 was simultaneously prepared in New York and London. These are prepared by condensation copolymerisation of diamines with dicarboxylic acids or by condensation homopolymerisation of lactam.

Nylon-6 or Perlon

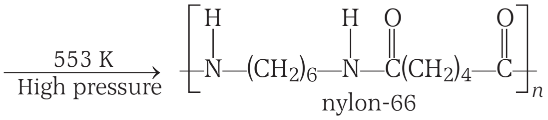
It is prepared by the polymerisation of amino caproic acid at high temperature and is used for manufacturing fabrics, tyre cords etc. Since, caprolactum is more easily available, it is widely used for preparing nylon-6. For this, it is first hydrolysed with water to form amino acid.



Nylon-66

It is prepared by the condensation copolymerisation of hexamethylenediamine and adipic acid under high pressure and at high temperature.

$$nH_2N{-}(CH_2)_6{-}NH_2 + nHOOC{-}(CH_2)_4{-}COOH$$



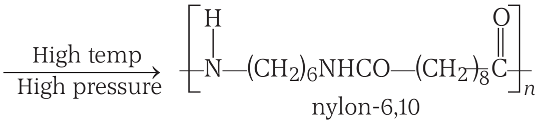
$$\xrightarrow[\text{High pressure}]{\text{553 K}} \underset{\text{nylon-66}}{\left[\overset{H}{\overset{|}{N}}{-}(CH_2)_6{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}(CH_2)_4{-}\overset{O}{\overset{\|}{C}} \right]_n}$$

It is used in making bristles for brushes and in textile industry.

Nylon-6, 10

It is prepared by the condensation copolymerisation of hexamethylenediamine and sebaic acid under high pressure and at high temperature.

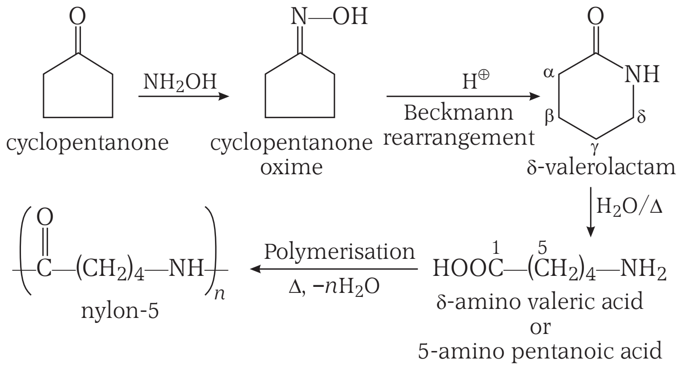
$$nH_2N(CH_2)_6NH_2 + HOOC{-}(CH_2)_8{-}COOH$$



$$\xrightarrow[\text{High pressure}]{\text{High temp}} \underset{\text{nylon-6,10}}{\left[\overset{H}{\overset{|}{N}}{-}(CH_2)_6NHCO{-}(CH_2)_8\overset{O}{\overset{\|}{C}} \right]_n}$$

It is used in mountaineering ropes, tyre cords and fabrics,

Nylon-5



It is used in the manufacture of fabrics and mountaineering ropes.

Naming the Nylons

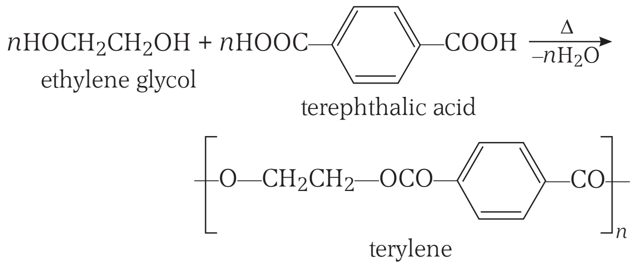
To write the name of nylon, first the number of carbon atoms of amines are written followed by the number of carbon atoms of acid, *e.g.,* in nylon-6, 10 amine contains six carbon atoms and the acid contains ten carbon atoms.

13.8 Polyesters

Polymers having ester linkage (—COO—) are called polyesters. These are prepared by the condensation reaction between dialcohols and diacids.

Terylene or Dacron

It is obtained by heating a mixture of ethylene glycol and terephthalic acid at 420–460 K and in the presence of catalyst such as mixture of zinc acetate and antimony trioxide.

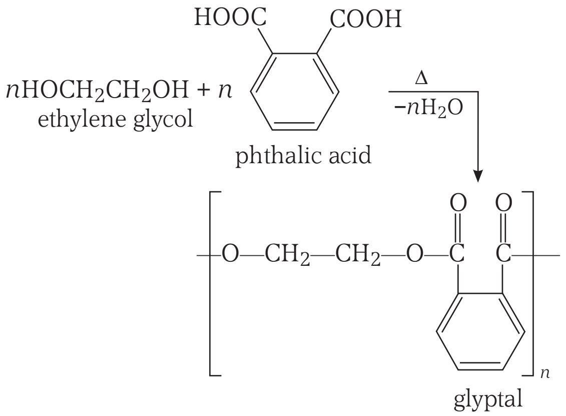


It is a crease resistant fibre, so used in blending with cotton and wool fibres, in making wash and wear fabrics, safety belts etc.

Caution Point *The film mode of terylene is called mylar.*

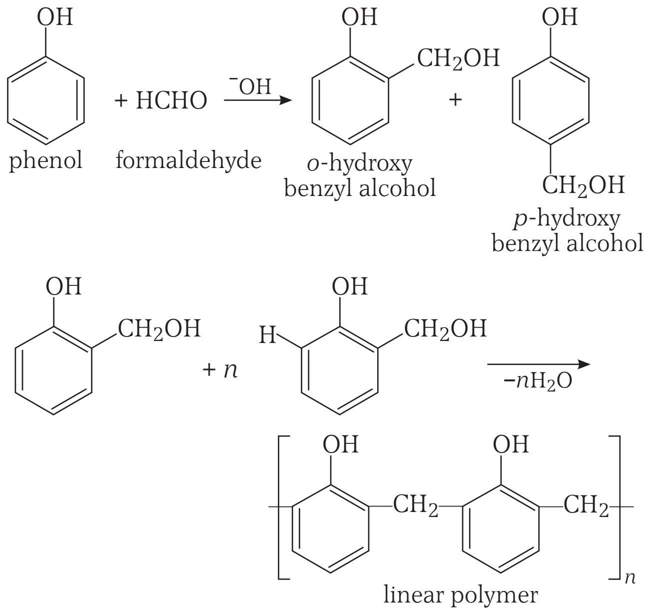
Glyptal or Alkyd Resin

It is a polymer of ethylene glycol and phthalic acid and is used in making paints and lacquers.

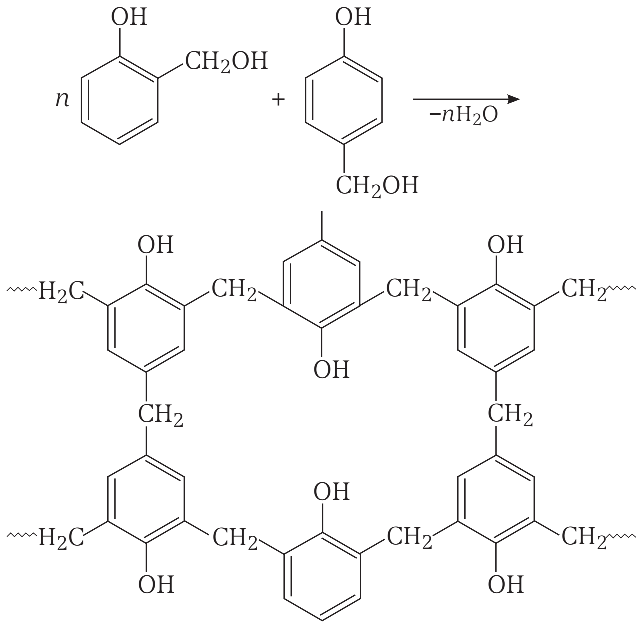


13.9 Bakelite

It is a condensation polymer of phenol and formaldehyde. When phenol is condensed with formaldehyde in the presence of a base, initially a mixture of *o*- and *p*-hydroxy benzyl alcohol is obtained. Out of which, *o*- forms again undergo self-condensation to give a linear polymer, called **novolac.**



Here, both the isomers again undergo condensation polymerisation and a highly cross-linked polymer, called 'bakelite' is obtained.



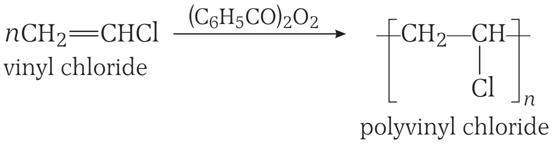
bakelite

Bakelite with low degree of polymerisation is used in making glues, in varnishes and lacquers. Bakelite with high degree of polymerisation is widely used for making electrical goods, fountain pen barrels, combs etc.

13.10 Others Important Polymers

Polyvinyl Chloride (PVC)

It is prepared by heating vinyl chloride in an inert solvent in the presence of benzoyl peroxide.



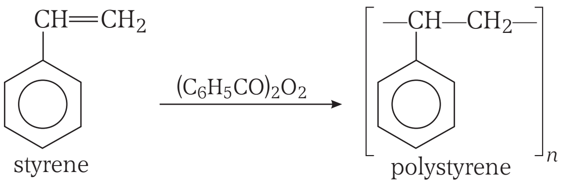
$$nCH_2{=}CHCl \xrightarrow{(C_6H_5CO)_2O_2} \left[-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}- \right]_n$$

It is a thermoplastic and its plasticity can be increased by addition of a plasticiser (ester of phthalic acid). It is an electrical insulator and is resistant to fire and chemicals.

It is used for making sheets, pipes, waterproof outer clothing (rain coats), table clothes, plastic dolls, gramophone records, floor covering and electrical insulating coating on electrical cables.

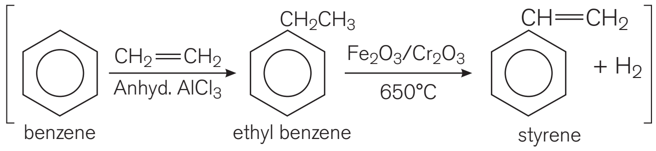
Polystyrene (Styron)

It is manufactured by polymerisation of styrene in the presence of benzoyl peroxide.



Polystyrene is used in the manufacture of food containers, cosmetic bottles, television and radio cabinets, plastic cups, packaging and toys.

Caution Point *Styrene is obtained from benzene as follows :*



Teflon or Polytetrafluoroethylene (PTFE)

It is manufactured by heating tetrafluoroethylene under pressure in the presence of ammonium peroxydisulphate.

$$nCF_2{=}CF_2 \xrightarrow[\text{High pressure}]{(NH_4)_2S_2O_8} \underset{\text{teflon (PTFE)}}{[-CF_2-CF_2-]_n}$$

It is chemically inert and heat resistant polymer. It is very tough and electrical resistant. It is used for making seals and gaskets which have to withstand high temperature. It is also used for insulation of electrical items and for making non-stick surface coating and lubricant particularly for cooking utensils.

Caution Point *Polymonochlorotrifluoroethylene (PCTFE) can also be used at the place of teflon.*

$$\underset{\text{chlorotrifluoroethylene}}{nClFC{=}CF_2} \longrightarrow \underset{\text{PCTFE}}{[-ClFC-CF_2-]_n}$$

13.11 Molecular Mass of Polymers

Polymerisation is quite complicated in nature. During the formation of polymers, the degree of polymerisation or the length of the polymer chain depends upon the availability of the monomer molecules near the growing polymer chain and also the reaction conditions employed. As a result in the synthetic polymers, the chains of different lengths may unite with one another. Hence, an average value of molecular mass is taken. But the same is not true for the natural polymers such as proteins, where the chains are of identical lengths and hence, their molecular masses are singular and not average in nature.

There are two ways of expressing molecular mass of a polymer. These are number average molecular mass and weight average molecular mass.

Number Average Molecular Mass

When the total mass of all the molecules of a sample is divided by the total number of molecules, the result obtained is called the number-average molecular mass.

It is obtained by following expression,

$$\overline{M}_n = \frac{\Sigma N_i M_i}{\Sigma N_i}$$

Osmotic pressure method is used to determine number average molecular mass.

Weight Average Molecular Mass

It is average of the molecular mass of the groups of the molecules having particular molecular masses multiplied by their respective molecular masses.

The expression for weight average molecular mass is

$$\overline{M}_w = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i}$$

It is determined by light scattering and ultracentrifugation methods.

where, N_i = number of molecules

M_i = molecular mass

Sample Problem 6 *Calculate the average molecular mass* $\overline{M}_n$ *and* $\overline{M}_w$ *of a polymer sample in which* 30% *molecules have a molecular mass of* 20000, 40% *have* 30000, *and the rest* 30% *have* 60,000.

(a) 36000, 43333
(b) 30000, 44000
(c) 48000, 55566
(d) 35000, 25001

Interpret (a) $\overline{M}_n$ and $\overline{M}_w$ of this sample will be

$$\overline{M}_n = \frac{(30 \times 20000) + (40 \times 30000) + (30 \times 60000)}{(30 + 40 + 30)}$$

$$= 36000$$

$$\overline{M}_w = \frac{30(20000)^2 + 40(30000)^2 + 30(60000)^2}{30 \times 20000 + 40 \times 30000 + 30 \times 60000} = 43333$$

Polydispersity Index (PDI)

The ratio of weight average molecular mass and number average molecular mass is called poly dispersity index (PDI).

$$\text{PDI} = \frac{\overline{M}_w}{\overline{M}_n}$$

For natural polymers, PDI = 1,

$\therefore$ $\overline{M}_w = \overline{M}_n$ and polymer is monodispersed.

For synthetic polymers, PDI > 1,

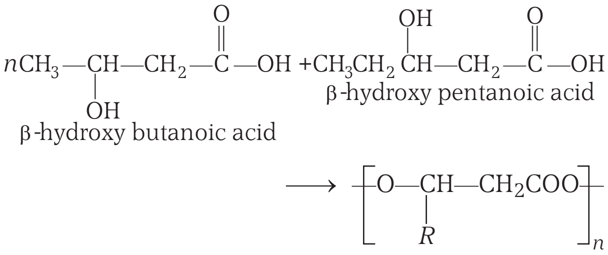
$\therefore$ $\overline{M}_w > \overline{M}_n$ and polymer is polydispersed.

Caution Point *Polymers with narrrow range of molecular masses are called monodisperse and that with wide range are called polydisperse polymers.*

13.12 Biodegradable Polymers

The polymers that can be dissociated into small segments by enzymes, (produced by microorganisms) are called biodegradable polymers. These are developed to reduce environmental problems caused by solid non-biodegradable polymer wastes. Chain growth polymers, because of the presence of inert C—C bond (towards enzyme catalysed reactions), usually are non-biodegradable but step growth polymers having functional groups may be biodegradable, *e. g.*,

(i) **PHBV** (poly β-hydroxy butyrate-co-β-hydroxy-valerate), a polyester, is a copolymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid.



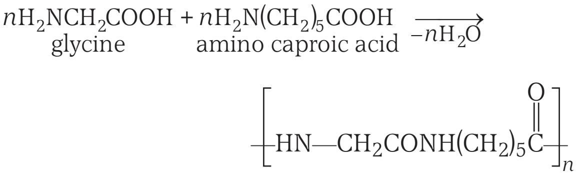
$$\underset{\beta\text{-hydroxy butanoic acid}}{n\text{CH}_3\text{—}\underset{\text{OH}}{\text{CH}}\text{—CH}_2\text{—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—OH}} + \underset{\beta\text{-hydroxy pentanoic acid}}{\text{CH}_3\text{CH}_2\overset{\text{OH}}{\text{CH}}\text{—CH}_2\text{—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—OH}} \longrightarrow \left[\text{O—}\underset{R}{\text{CH}}\text{—CH}_2\text{COO}\right]_n$$

PHBV

(where, $R = CH_3$, C_2H_5 etc.)

β-hydroxy butanoic acid gives stiffness and β-hydroxy pentanoic acid imparts flexibility to PHBV. It is used in orthopaedic devices and in controlled drug release.

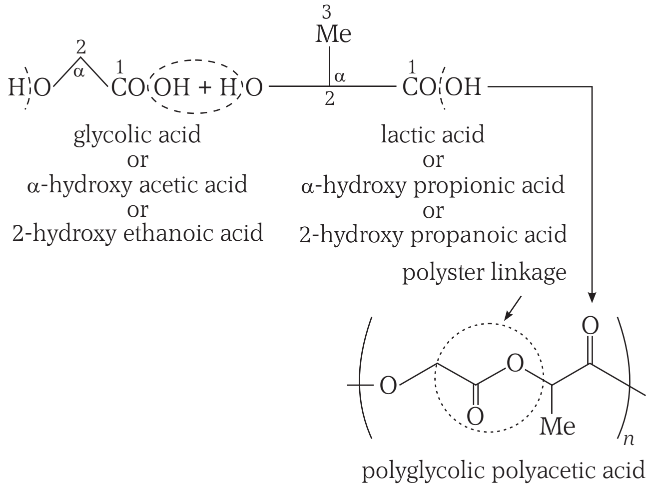
(ii) **Nylon-2-nylon-6** is a polyamide copolymer of glycine H_2NCH_2—COOH and amino caproic acid $[H_2N(CH_2)_5COOH]$.



$$\underset{\text{glycine}}{n\text{H}_2\text{NCH}_2\text{COOH}} + \underset{\text{amino caproic acid}}{n\text{H}_2\text{N(CH}_2)_5\text{COOH}} \xrightarrow[-n\text{H}_2\text{O}]{} \left[\text{HN—CH}_2\text{CONH(CH}_2)_5\overset{\text{O}}{\overset{\|}{\text{C}}}\right]_n$$

nylon-2-nylon-6

(iii) **Polyglycolic acid and polyacetic acid** comprise commercially successful biodegradable polymers such as sutures. Dextron was the first bioabsorbable or biodegradable suture prepared from the biodegradable polyesters. It is used for post-operative stitches.



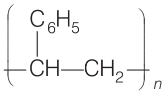
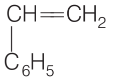
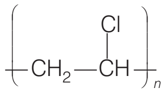
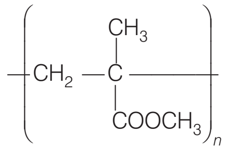
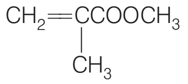
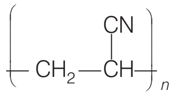
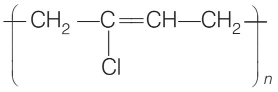
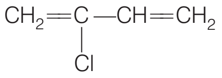
Check Point 4

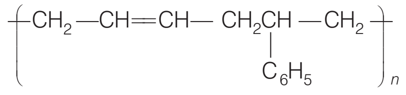
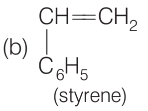
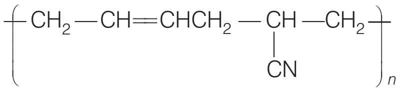
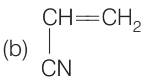
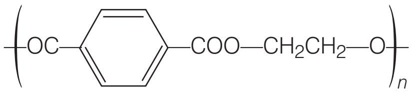
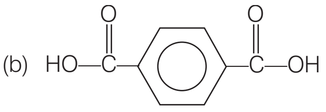
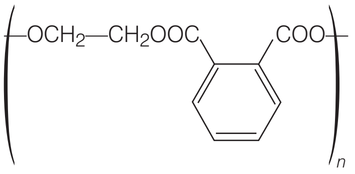
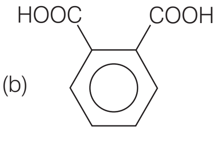
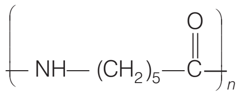
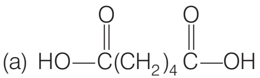
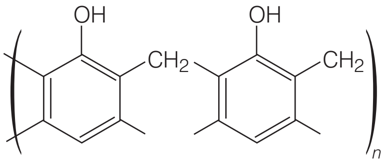
1. Why is polyacetylene a conducting polymer?
2. How do double bonds in rubber molecules influence their structure and reactivity?
3. What does 66 indicate in nylon-66? In what way it is different from nylon-6?
4. What is the PDI value of proteins?

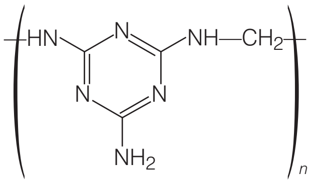
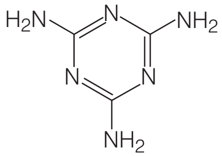
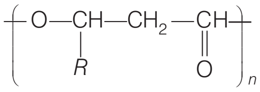
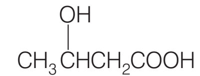
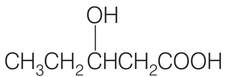
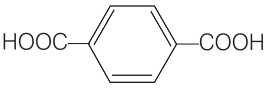
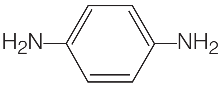
13.13 Monomers and Uses of Some Common Polymers

Some polymers with their monomer units and uses are tabulated below.

Table 13.1 **Polymers, Their Monomers and Uses**

S.N.	Polymer name and structure	Monomer	Nature of polymer	Uses
1.	Polythene $\left(CH_2-CH_2\right)_n$	$CH_2=CH_2$ (ethene)	Addition homopolymer	As insulator, anticorrosive, packing material, for household and laboratory wares.
2.	Polystyrene  $\left(CH(C_6H_5)-CH_2\right)_n$	 $CH(C_6H_5)=CH_2$ (styrene)	Addition homopolymer	As insulator, wrapping material, manufacture of toys and household articles.
3.	Polyvinyl chloride (PVC)  $\left(CH_2-CH(Cl)\right)_n$	$CH_2=CHCl$ (vinyl chloride)	Addition homopolymer	In manufacture of raincoats, hand bags, vinyl flooring and leather clothes.
4.	Polytetrafluoro ethylene (PTFE) or teflon $\left(CF_2-CF_2\right)_n$	$CF_2=CF_2$ (tetra fluoroethene)	Addition homopolymer	As lubricant, insulator, and in making cooking wares.
5.	Polymethyl methacrylate (PMMA or Plexi glass)  $\left(CH_2-C(CH_3)(COOCH_3)\right)_n$	 $CH_2=C(CH_3)COOCH_3$ (methyl methacrylate)	Addition homopolymer	As substitute of glass and making decorative materials.
6.	Polyacrylonitrile (Orlon)  $\left(CH_2-CH(CN)\right)_n$	$CH_2=CHCN$ (vinyl cyanide)	Addition homopolymer	In making synthetic fibres and synthetic wool.
7.	Neoprene  $\left(CH_2-C(Cl)=CH-CH_2\right)_n$	 $CH_2=C(Cl)-CH=CH_2$ (2-chloro-but-1,3-diene)	Addition homopolymer	As insulator, making conveyor belts and printing rollers.

S.N.	Polymer name and structure	Monomer	Nature of polymer	Uses
8.	Buna-S (Styrene-butadiene rubber, SBR)  $\left(\text{CH}_2\text{—CH=CH— CH}_2\text{CH(C}_6\text{H}_5\text{)—CH}_2\right)_n$	(a) $CH_2{=}CH—CH{=}CH_2$ (buta-1,3-diene) (b)  $CH{=}CH_2(C_6H_5)$ (styrene)	Addition copolymer	In making automobile tyres, footwear and bubble gums.
9.	Buna-N (nitrile rubber, NBR)  $\left(\text{CH}_2\text{—CH=CHCH}_2\text{—CH(CN)—CH}_2\right)_n$	(a) $CH_2{=}CH—CH{=}CH_2$ (buta-1,3-diene) (b)  $CH{=}CH_2(CN)$ (acrylonitrile)	Addition copolymer	In making oil seals, manufacture of hoses and tank linings.
10.	Terylene or dacron 	(a) $HO—CH_2—CH_2—OH$ ethylene glycol or ethane-1,2-diol and (b)  terephthalic acid or benzene-1,4-dicarboxylic acid	Codensation or step growth copolymer, linear polymer	For making wash and wear fabrics, tyres cords, safety belts, tents, sea belts and sails.
11.	Glyptal or alkyd resin 	(a) $HO—CH_2—CH_2—OH$ ethylene glycol (b)  phthalic acid	Condensation copolymer, thermoplastic	As binding material in preparation of mixed plastics and paints.
12.	Nylon-6 or perlon  $\left(\text{NH—(CH}_2)_5\text{—}\overset{\text{O}}{\overset{\Vert}{\text{C}}}\right)_n$	Caprolactum	Condensation homopolymer, linear polymer	In making fibres, plastics, tyre cords and ropes.
13.	Nylon-66 $\left(\text{NH(CH}_2)_6\text{NHCO(CH}_2)_4\text{CO}\right)_n$	(a)  $\text{HO—}\overset{\text{O}}{\overset{\Vert}{\text{C}}}\text{(CH}_2)_4\overset{\text{O}}{\overset{\Vert}{\text{C}}}\text{—OH}$ adipic acid (b) $H_2N—(CH_2)_6—NH_2$ hexamethylene diamine	Condensation copolymer, linear polymer	In making bristles for brushes, synthetic fibres, parachutes, ropes and carpets, as a substitute for metal in bearings and gears. Crincked nylon is used for making elastic hosiery.
14.	Bakelite 	(a) HCHO formaldehyde (b) C_6H_5OH phenol	Condensation copolymer, crosslink or network polymer, thermosetting polymer	For making gears, protective coating and electrical fittings.
15.	Urea formaldehyde resin $\left(\text{NHCO—NH—CH}_2\right)_n$	(a) HCHO formaldehyde (b) NH_2CONH_2 urea	Condensation copolymer	For making unbreakable cups and laminated sheets.

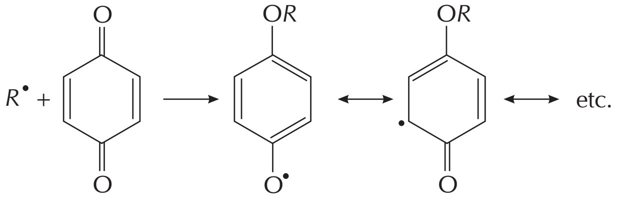
S.N.	Polymer name and structure	Monomer	Nature of polymer	Uses
16.	Melamine-formaldehyde resin or melmac 	(a)  melamine (b) HCHO formaldehyde	Condensation copolymer, highly branched thermosetting polymer	In making plastic crockery, unbreakable cups and plates.
17.	Poly-β-hydroxy butyrate-co-β-hydroxy valerate (PHBV)  $\left(\text{O}-\underset{R}{\text{CH}}-\text{CH}_2-\overset{}{\underset{\text{O}}{\underset{\Vert}{\text{CH}}}}\right)_n$	(a)  $\text{CH}_3\overset{\text{OH}}{\overset{\vert}{\text{CH}}}\text{CH}_2\text{COOH}$ β-hydroxy butanoic acid (b)  $\text{CH}_3\text{CH}_2\overset{\text{OH}}{\overset{\vert}{\text{CH}}}\text{CH}_2\text{COOH}$ β-hydroxy pentanoic acid	Condensation copolymer, biodegradable polymer	As packaging material in orthopaedic devices and for controlled drug release
18.	Kevlar (nylon polymer)	(a)  terephthalic acid (b)  1,4-diamino benzene	Condensation copolymer	For making bullet proof vests.
19.	Lexan or polycarbonate (polyester)	(a) diethyl carbonate (b) bisphenol-*A*	Condensation copolymer	In making bullet proof windows and safety helmets
20.	Polyurethanes	(a) toluene diisocyanate (b) ethylene glycol	Condensation copolymer	For making washable and long lasting mattresses, cushions.
21.	VINYON	(a) $CH_2{=\!=}CHCl$ vinyl chloride 90% (b) $CH_2{=\!=}CHCOOCH_3$ vinyl acetate (10%)	Addition copolymer	
22.	DYNEL	(a) acrylonitrile (b) vinyl chloride	Copolymer	For making synthetic hair wigs.
23.	SARAN	(a) vinyl chloride (b) vinylidine chloride ($CH_2{=\!=}CCl_2$)	Copolymer	For wrapping food materials.
24.	ABS rubber	(a) acrylonitrile (b) buta-1,3-diene (c) styrene	Copolymer	Bumpers, crash helmets, telephones, luggage.
25.	SAN rubber	(a) $CH_2{=\!=}CHC_6H_5$ (styrene) (b) $CH_2{=\!=}CHCN$ acrylonitrile	Addition copolymer	In dish washer safe objects, vacuum cleaner parts.

WORKED OUT Examples

Example 1 *How does the presence of benzoquinone inhibit the free radical polymerisation of a vinyl derivative?*

(a) *By trapping radical intermediate*
(b) *By forming less reactive radical*
(c) *Both (a) and (b)*
(d) *None of the above*

Solution (a) Benzoquinone traps the radical intermediate to form a non-reactive radical, which is highly stabilised by resonance. Due to the lack of reactivity of this intermediate, further progress of the chain reaction is interrupted and the reaction stops.

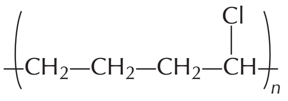


Example 2 *A copolymer of ethene and vinyl chloride contains alternate monomers of each type. What is the mass percentage of vinyl chloride in this copolymer?*

(a) 75% (b) 69% (c) 82% (d) 39%

Solution (b) The structure of copolymer is

$$n(CH_2{=}CH_2) + n(CH_2{=}CHCl) \longrightarrow$$



$$\left(\!-CH_2-CH_2-CH_2-\overset{\overset{\large Cl}{|}}{CH}-\!\right)_n$$

Molecular mass of ethene = 28

Molecular mass of vinyl chloride = 62.5

Empirical formula mass of copolymer = 28 + 62.5 = 90.5

Mass percentage of vinyl chloride in the copolymer

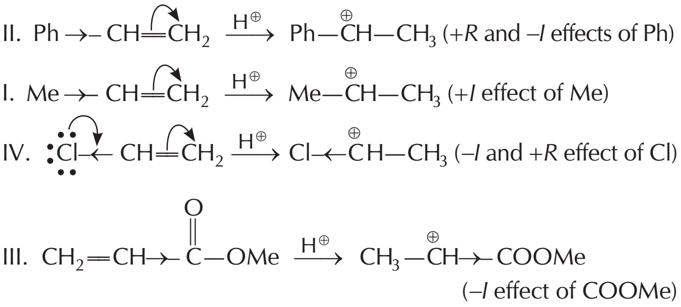
$$= \frac{62.5 \times 100}{90.5} = 69.06$$

Example 3 *Give the decreasing order of reactivities of the following monomers towards cationic addition polymerisation.*

I. $MeCH{=}CH_2$ *II.* $PhCH{=}CH_2$
III. $CH_2{=}CH{-}COOMe$ *IV.* $CH_2{=}CH{-}Cl$

(a) *I > II > III > IV* (b) *II > I > IV > III*
(c) *II > I > III > IV* (d) *I > II > IV > III*

Solution (b) Cationic polymerisation is favoured by the presence of electron donating group (*e.g.*, Me group). The more the electron donating group, the more stable is the intermediate carbocation, and as a result more favoured is the cationic polymerisation. Stability of $(\rightarrow\!C^{\oplus})$ is



$$\text{II. } Ph \rightarrow\!- CH{=}CH_2 \xrightarrow{H^{\oplus}} Ph-\overset{\oplus}{C}H-CH_3 \text{ (+}R\text{ and }–I\text{ effects of Ph)}$$

$$\text{I. } Me \rightarrow\!- CH{=}CH_2 \xrightarrow{H^{\oplus}} Me-\overset{\oplus}{C}H-CH_3 \text{ (+}I\text{ effect of Me)}$$

$$\text{IV. } :\!\ddot{Cl}\!\leftarrow\!- CH{=}CH_2 \xrightarrow{H^{\oplus}} Cl\!\leftarrow\!-\overset{\oplus}{C}H-CH_3 \text{ (}–I\text{ and +}R\text{ effect of Cl)}$$

$$\text{III. } CH_2{=}CH\!\rightarrow\!-\overset{\overset{\large O}{\|}}{C}-OMe \xrightarrow{H^{\oplus}} CH_3-\overset{\oplus}{C}H\!\rightarrow\!-COOMe$$

(–*I* effect of COOMe)

The decreasing reactivity order towards cation polymerisation is (II) > (I) > (IV) > (III).

Example 4 *Give the decreasing order of reactivities of the following monomers towards anionic addition polymerisation.*

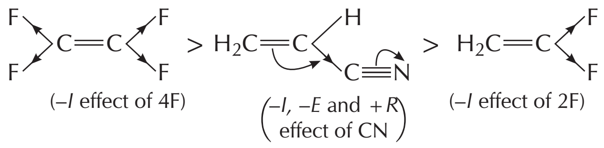
I. $Me{-}CH{=}CH_2$ *II.* $PhCH{=}CH_2$
III. $CH_2{=}CH{-}CN$ *IV.* $H_2C{=}CCl_2$
V. $H_2C{=}CF_2$ *VI.* $F_2C{=}CF_2$

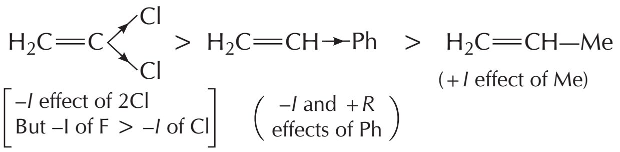
The correct order is

(a) *VI > III > V > IV > II > I*
(b) *VI > V > III > IV > II > I*
(c) *VI > IV > V > III > II > I*
(d) *VI > V > IV > II > I > III*

Solution (a) Anionic polymerisation is favoured by the presence of electron donating group (*e.g.*, —*X*, —COO*R*, —CN, etc.). The more the electron donating group, the more stable is the intermediate carbanion, and consequently more favoured is the anionic polymerisation.

Stability of $\left(\rightarrow\!C^{\ominus}\right)$ is





$$H_2C{=}CCl_2 > H_2C{=}CH \rightarrow Ph > H_2C{=}CH{-}Me$$

$\left[\begin{array}{l}-I \text{ effect of 2Cl}\\ \text{But } -I \text{ of F} > -I \text{ of Cl}\end{array}\right]$ $\left(\begin{array}{c}-I \text{ and } +R\\ \text{effects of Ph}\end{array}\right)$ $(+I \text{ effect of Me})$

The decreasing reactivity order towards anionic polymerisation is (VI) > (III) > (V) > (IV) > (II) > (I).

Example 5 *Propene polymerises in isotactic, snydiotactic, and atactic forms, while vinylidene chloride* ($CH_2{=}CCl_2$) *does not, this is because*

(*a*) *polyproprene is chiral but vinylidene chloride does not*

(*b*) *polypropprene contains conjugated double bonds but vinylidene chloride does not*

(*c*) *polypropprene is reactive but vinylidene chloride is inert*

(*d*) *All of the above*

Solution (*a*) Polypropene has chiral C atoms and, therefore, exists in different forms as mentioned. Polyethylidene chloride, on the other hand, does not have chiral C atom and thus, does not exist in the forms mentioned.

Example 6 *A polydisperse mixture of a polymer can be described by the following composition of molar mass data*

(Mass %)	25.0	50.0	25.0
M (kg mol^{-1})	1.00	1.20	1.40

Calculate the polydispersity index for the mixture.

(*a*) 1 (*b*) 1.02

(*c*) 2.02 (*d*) 0.03

Solution (*b*) $$\overline{M}_n = \frac{\Sigma N_i M_i}{\Sigma N_i} \qquad \text{...(i)}$$

and $$\overline{M}_w = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i} \qquad \text{...(ii)}$$

Each of the mass% values must be converted to value of N_i. Assuming 100.0 g of the mixture, the amounts of each polymer are

$$\text{Moles} = \frac{\text{Wt.}}{\text{M}},$$

$$N_1 = \frac{25}{1000} = 2.50 \times 10^{-2} \text{ mol}$$

$$N_2 = \frac{50}{1200} = 4.17 \times 10^{-2} \text{ mol}$$

$$N_3 = \frac{25}{1400} = 1.79 \times 10^{-2} \text{ mol}$$

Substituting the values in Eq. (i) and (ii), we get

$$\overline{M}_n = \frac{\left[\begin{array}{l}(2.50 \times 10^{-2} \text{ mol})(1.00 \text{ kg mol}^{-1})\\ + (4.17 \times 10^{-2} \text{ mol})(1.20 \text{ kg mol}^{-1})\\ + (1.79 \times 10^{-2} \text{ mol})(1.40 \text{ kg mol}^{-1})\end{array}\right]}{2.50 \times 10^{-2} \text{ mol} + 4.17 \times 10^{-2} \text{ mol} + 1.79 \times 10^{-2} \text{ mol}}$$

$$= 1.18 \text{ kg mol}^{-1}$$

$$\overline{M}_w = \frac{\left[\begin{array}{l}(2.50 \times 10^{-2} \text{ mol})(1.00)^2 + (4.17 \times 10^{-2})\,(1.20)^2\\ + (1.79 \times 10^{-2})(1.40)^2 \text{ kg}^2 \text{ mol}^{-1}\end{array}\right]}{\left[\begin{array}{l}(2.50 \times 10^{-2})(1.00) + (4.17 \times 10^{-2})(1.20)\\ + (1.79 \times 10^{-2})(1.40)\end{array}\right] \text{kg}}$$

$$= 1.20 \text{ kg mol}^{-1}$$

Polydispersity index = $\overline{M}_w / \overline{M}_n$.

Substituting the results gives

$$\text{Polydispersity index} = \frac{1.20 \text{ kg mol}^{-1}}{1.18 \text{ kg mol}^{-1}}$$

$$= 1.02$$

Start Practice for JEE Main

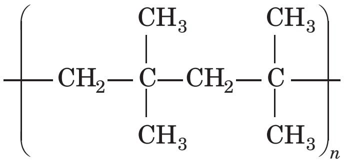
Round I (Topically Divided Problems)

General Terms and Classification of Polymers

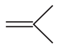
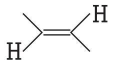
1. A high molecular weight molecule, made up of a large number of smaller units, is known as
(a) monomer (b) macromolecule
(c) polymer (d) Both (b) and (c)

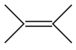
2. With increase in which of the following factors, tensile strength of a polymer increases?
(a) Crystallinity (b) Melting point
(c) Molecular weight (d) All of these

3. Which is not true about polymers?
(a) Polymers have high viscosity
(b) Polymers scatter light
(c) Polymers do not carry any charge
(d) Polymers have low molecular weight

4. 

$\left(-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{\underset{CH_3}{C}}- \right)_n$ is a polymer having monomer units. **[NCERT Exemplar]**

(a) 
(b) 
(c) 

(d) 

5. Which factor imparts crystalline nature to a polymer like nylon? **[NCERT Exemplar]**
(a) Hydrogen bonding (b) Covalent bonding
(c) Ionic bonding (d) All of these

6. Which of the following polymers of glucose is stored by animals? **[NCERT Exemplar]**
(a) Cellulose (b) Amylose
(c) Amylopectin (d) Glycogen

7. Which of the following is not a biopolymer?
(a) Proteins (b) Rubber
(c) Cellulose (d) RNA

8. Teflon is an example of polymer which is a/an
(a) polyamide (b) addition polymer
(c) polyester (d) formaldehyde resin

9. Which of the following are addition polymers? **[NCERT Exemplar]**
(a) Nylon
(b) Melamine formaldehyde resin
(c) Orlon
(d) All of the above

10. Which of the following polymers are condensation polymers? **[NCERT Exemplar]**
(a) Bakelite (b) Teflon
(c) Butyl rubber (d) None of these

11. Which among the following is step-growth polymer?
(a) PTFE (b) PVC
(c) Polyester (d) Polythene

12. Which of the following is an elastomer?
(a) Vulcanised rubber (b) Dacron
(c) Polystyrene (d) Malamine

13. Which of the following polymers are used as fibre?
1. Polytetrafluoroethane
2. Polychloroprene
3. Nylon
4. Terylene

The correct answer is **[NCERT Exemplar]**
(a) 1 and 2 (b) 2 and 3
(c) 3 and 4 (d) All of these

14. Nylon-66 is not a
(a) condensation polymer (b) polyamide
(c) homopolymer (d) copolymer

15. The strongest molecular forces are present in
(a) elastomers (b) thermoplastics
(c) fibres (d) thermosetting polymers

16. The compound which cannot be used as a plasticizer, is
(a) di-*n*-butylphthalate
(b) tricresyl phosphate
(c) di-*n*-octyphthalate
(d) diethyl phthalate

17. The functionality of propene and adipic acid are respectively. **[NCERT]**
(a) 1, 1 (b) 0, 1
(c) 0, 2 (d) 1, 2

Polymerisation, Its Mechanism and Types

18. When two or more chemically different monomers take part in polymerisation, it is called
(a) addition polymerisation
(b) copolymerisation
(c) chain polymerisation
(d) homopolymerisation

19. Nylon-66 is obtained by the condensation polymerisation of
(a) adipic acid and hexamethylene diamine
(b) phenol and formaldehyde
(c) terephthalic acid and ethylene glycol
(d) sebacic acid and hexamethylene

20. Low density polythene is prepared by
(a) free radical polymerisation
(b) cationic polymerisation
(c) anionic polymerisation
(d) Ziegler-Natta polymerisation

21. The compound that inhibits the growth of polymer chain during vinyl polymerisation, is
(a) carbon tetrachloride (b) *p*-benzoquinone
(c) benzophenone (d) carbon dioxide

22. A chain transfer agent is
(a) C_6H_5OH (b) $NH(C_6H_5)_2$
(c) CCl_4 (d) CH_3OH

23. The best way to prepare polyisobutylene is
(a) coordination polymerisation
(b) cationic polymerisation
(c) anionic polymerisation
(d) free radical polymerisation

24. Bakelite is a condensation polymer of phenol and formaldehyde. The initial step between the two compounds is an example of
(a) free radical reaction
(b) aldol condensation
(c) aromatic nucleophilic substitution
(d) aromatic electrophilic substitution

25. Number average molecular mass, $\overline{M}_n$ and weight average molecular mass ($\overline{M}_w$) of synthetic polymers are related as
(a) $\overline{M}_n = (\overline{M}_w)^{1/2}$ (b) $\overline{M}_n = \overline{M}_w$
(c) $\overline{M}_w > \overline{M}_n$ (d) $\overline{M}_w < \overline{M}_n$

26. For natural polymers PDI is generally
(a) 0 (b) 1 (c) 100 (d) 1000

Rubber

27. The chemical name of isoprene is
(a) 2-methyl-1,3-butadiene (b) 2-chloro-1,3-butadiene
(c) 2-methoxypropene (d) None of these

28. Synthetic polymer that resembles natural rubber is
(a) chloroprene (b) isoprene
(c) neoprene (d) glyptal

29. The correct statement about thiokol rubber is that
(a) it is a natural polysulphide rubber
(b) it is resistant to oils and abrasion
(c) it is prepared by addition polymerisation
(d) All of the above are correct

30. Heating of rubber with sulphur is called
(a) vulcanisation (b) galvanisation
(c) sulphonation (d) bessemerisation

31. Which of the following type of forces are present in vulcanised rubber?
(a) Weakest intermolecular forces
(b) Hydrogen bonding
(c) Three dimensional network of bonds
(d) Metallic bonding

32. By the addition of 3% to 10% sulphur in rubber
(a) soft rubber is obtained
(b) hard rubber is obtained
(c) no change takes place
(d) soluble rubber is obtained

33. The main point of difference between buna N and buna S is **[NCERT]**
(a) the former is homopolymer whereas the later is copolymer
(b) former contains buta-1,3-diene but later does not
(c) former contains acrylonitrile but later contains styrene
(d) All of the above

Some Important Polymers

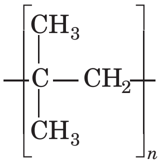
34. Amongst the following the branched chain polymer is
(a) polystyrene
(b) low density polythene
(c) high density polythene
(d) polyester

35. Which of the following statement is not true about low density polythene? [**NCERT** Exemplar]
(a) Tough
(b) Hard
(c) Poor conductor of electricity
(d) Highly branched structure

36. The catalyst used in the polymerisation of high density polythene is
(a) titanium oxide
(b) titanium isoperoxide
(c) lithium tetrachloride and triphenyl aluminium
(d) titanium tetrachloride and trimethyl aluminium

37. The commercial name of polyacrylonitrile is [**NCERT** Exemplar]
(a) dacron (b) orlon (acrilan)
(c) PVC (d) bakelite

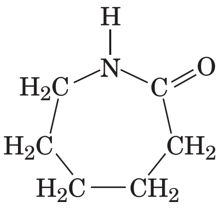
38. Monomer of



$\left[\overset{CH_3}{\underset{CH_3}{C}} - CH_2 \right]_n$ is
(a) 2-methylpropene (b) styrene
(c) propylene (d) ethene

39. Which of the following type of forces are present in nylon-66?
(a) van der Waals' forces of attraction
(b) Hydrogen bonding
(c) Three dimensional network of bonds
(d) Metallic bonding

40. Which of the following polymer can be formed by using the following monomer unit? [**NCERT** Exemplar]



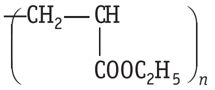
(a) Nylon-66 (b) Nylon 2-nylon 6
(c) Melamine polymer (d) Nylon-6

41. Esterification of terephthalic acid with glycol produces
(a) nylon
(b) buna rubber
(c) polyurethane
(d) terylene

42. In which of the following polymers, empirical formula resembles with monomer?
(a) Bakelite (b) Teflon
(c) Nylon-66 (d) Dacron

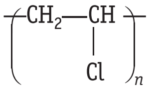
43. Orlon is a hard, horny and a high melting material. Which of the following represents its structure?

(a)



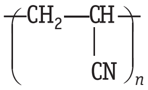
$\left(-CH_2 - \underset{COOC_2H_5}{CH} \right)_n$

(b)



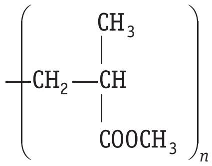
$\left(-CH_2 - \underset{Cl}{CH} - \right)_n$

(c)



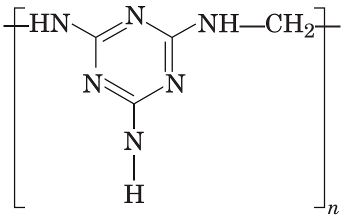
$\left(-CH_2 - \underset{CN}{CH} - \right)_n$

(d)



$\left(-CH_2 - \overset{CH_3}{\underset{COOCH_3}{CH}} \right)_n$

44. The monomers of the following polymer are



(a) hexamethylene diamine and decanedioic acid
(b) hexamethylene diamine and methanal
(c) melamine and methanal
(d) melamine and ethanal

45. Which of the following polymers does not involve cross-linkages?
(a) Vulcanised rubber (b) Melamine
(c) Bakelite (d) Polystyrene

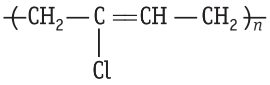
46. Which of the following has an ester linkage?
(a) Nylon-66 (b) Dacron
(c) PVC (d) Bakelite

47. Among the following, the wrong statement is
(a) PMMA is plexiglass
(b) SBR is natural rubber
(c) PTFE is teflon
(d) LDPE is low density polythene

48. Which of the following is a biodegradable polymer?
(a) Cellulose (b) Polythene
(c) Polyvinyl chloride (d) Nylon-6

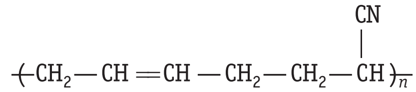
49. Which of the following polymer is biodegradable? [**NCERT** Exemplar]

(a)



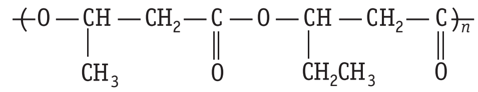
$\left(CH_2 - \underset{Cl}{C} = CH - CH_2 \right)_n$

(b)



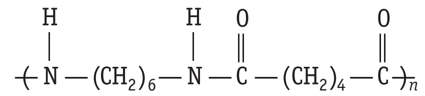
$\left(CH_2 - CH = CH - CH_2 - CH_2 - \overset{CN}{CH} \right)_n$

(c)



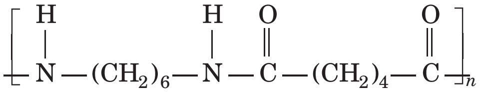
$\left(O - \underset{CH_3}{CH} - CH_2 - \underset{\underset{O}{\|}}{C} - O - \underset{CH_2CH_3}{CH} - CH_2 - \underset{\underset{O}{\|}}{C} \right)_n$

(d)



$\left(\overset{H}{N} - (CH_2)_6 - \overset{H}{N} - \overset{O}{\overset{\|}{C}} - (CH_2)_4 - \overset{O}{\overset{\|}{C}} \right)_n$

50. The monomer of



$$\left[\overset{\overset{H}{|}}{N} - (CH_2)_6 - \overset{\overset{H}{|}}{N} - \overset{\overset{O}{\|}}{C} - (CH_2)_4 - \overset{\overset{O}{\|}}{C} \right]_n$$

is/are **[NCERT]**

(a) sebacic acid and tetramethylenediamine

(b) adipic acid and hexamethylene diamine

(c) sebacic acid and hexamethylene diamine

(d) adipic acid and dimethylenediamine

Round II (Mixed Bag)

Only One Option Correct

1. Which of the following has been used in the manufacture of non-inflammable photographic films?

(a) Cellulose nitrate

(b) Cellulose xanthate

(c) Cellulose perchlorate

(d) Cellulose acetate

2. Polystyrene, dacron and orlon are classified respectively as

(a) chain growth; step growth; step growth

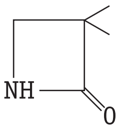
(b) chain growth; chain growth; step growth

(c) chain growth; step growth; chain growth

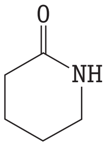
(d) step growth; step growth; chain growth

3. Lactam from which nylon-4 is synthesised, is

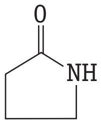
(a)



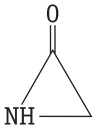
(b)



(c)



(d)



4. Given the polymers,
A = Nylon 6 6; B = Buna-S; C = Polythene.

Arrange these in increasing order of their intermolecular forces (lower to higher).

(a) $A < B < C$ (b) $B > C > A$

(c) $B < C < A$ (d) $A < C < B$

5. Arrange the following monomers in order of decreasing ability to undergo cationic polymerisation

I. $NO_2C_6H_5—CH=CH_2$ II. $CH_2=CH—C_6H_5CH_3$
III. $CH_2=CH—C_6H_5OCH_3$

(a) I > II > III

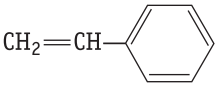
(b) III > II > I

(c) II > I > III

(d) I > III > II

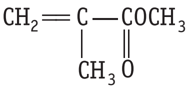
6. Head-to-tail addition takes place in chain-growth polymerisation when monomer is

(a)



(b) $CH_2=CH—CH=CH_2$

(c)



$CH_2 = \underset{CH_3}{\underset{|}{C}} — \underset{O}{\underset{\|}{C}}OCH_3$

(d) $CH_2=CH—C \equiv N$

7. Which of the following vinyl derivatives is most reactive towards anionic polymerisation?

(a) $CH_2=CHCH_3$ (b) $CH_2=CHC_2H_5$

(c) $CH_2=CHCl$ (d) $CH_2=CHC \equiv N$

8. Select the correct statement.

(a) Vinyon is a copolymer of vinyl chloride and vinyl acetate

(b) Saran is a copolymer of vinyl chloride and vinylidine chloride

(c) Butyl rubber is a copolymer of isobutylene and isoprene

(d) All of the above are correct

9. Which is not a polyacrylate?

(a) PMMA (b) Acrilan

(c) Poly acrylonitrile (d) PCTFE

10. The polymer used in making synthetic hair wigs is made up of

(a) $CH_2=CHCl$

(b) $CH_2=CHCOOCH_3$

(c) $C_6H_5CH=CH_2$

(d) $CH_2=CH—CH=CH_2$

11. Which is a polymer of three different monomers?

(a) ABS

(b) SBR

(c) NBR

(d) Nylon-2-nylon-6

12. Which pair of polymers have similar properties?

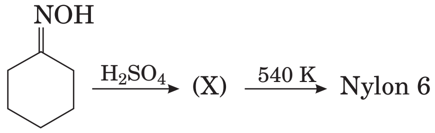
(a) Nylon, PVC

(b) PAN,PTFE

(c) PCTFE, PTFE

(d) Bakelite, alkyl resin

13. In the reaction sequence



(X) is

(a) cyclohexanone
(b) caprolactum
(c) $HO(CH_2)_6NH_2$
(d) hexamethylene diisocyanate

14. Which of the following monomers form biodegradable polymers?

I. 3-hydroxybutanoic acid + 3-hydroxypentanoic acid
II. Glycine + amino caproic acid
III. Ethylene glycol + pthalic acid
IV. Caprolactum

The correct answer is [**NCERT** Exemplar]

(a) I, II only (b) II, III only
(c) I, II and III (d) II, III and IV

15. Which of the following polymers can have strong intermolecular forces?

I. Nylon II. Polystyrene
III. Rubber IV. Polyesters

The correct answer is [**NCERT** Exemplar]

(a) I, IV (b) II, III
(c) I, III (d) All of these

16. Vulcanisation makes rubber

I. more elastic
II. soluble in inorganic solvent
III. crystalline
IV. more stiff

The correct options are [**NCERT** Exemplar]

(a) I and IV only (b) I and III only
(c) II and III only (d) II, III and IV only

17. Match the polymers given in Column I with the preferred mode of polymerisation followed by their monomers.

Column I		Column II	
A.	Nylon-66	1.	Free radical polymerisation
B.	PVC	2.	*Ziegler-Natta* polymerisation or coordination polymerisation
C.	HDP	3.	Anionic polymerisation
		4.	Condensation polymerisation

The correct answer is [**NCERT** Exemplar]

	A	B	C		A	B	C
(a)	4	3	1	(b)	4	2	3
(c)	4	1	2	(d)	4	2	1

18. Match the polymers given in Column I with their commerical names given in Column II.

Column I		Column II	
A.	Polyester of glycol and phthalic acid	1.	Novolac
B.	Copolymer of 1, 3-butadiene and styrene	2.	Glyptal
C.	Phenol and formaldehyde resin	3.	Buna-S
D.	Polyester of glycol and terephthalic acid	4.	Buna-N
E.	Copolymer of 1, 3-butadiene and acrylonitrile	5.	Dacron

[**NCERT** Exemplar]

Codes

	A	B	C	D	E		A	B	C	D	E
(a)	4	3	2	1	5	(b)	2	3	1	5	4
(c)	2	1	3	4	5	(d)	2	1	3	5	4

More than One Option Correct

19. Which of the following polymers have vinylic monomer units? [**NCERT** Exemplar]

(a) Acrilan (b) Polystyrene
(c) Nylon (d) Teflon

20. Which of the following polymers, need atleast one diene monomer for their preparation? [**NCERT** Exemplar]

(a) Dacron (b) Buna-S (c) Neoprene (d) Novolac

21. Which of the following are characteristics of thermosetting polymers? [**NCERT** Exemplar]

(a) Heavily branched cross linked polymers.
(b) Linear slightly branched long chain molecules
(c) Become infusible on moulding so cannot be reused
(d) Soften on heating and harden on cooling, can be reused

22. Which of the following polymers are thermoplastic? [**NCERT** Exemplar]

(a) Teflon (b) Natural rubber
(c) Neoprene (d) Polystyrene

23. Among the following chain transfer reagent are

(a) Carbon tetrachloride (b) Benzoyl peroxide
(c) Benzoquinone (d) Carbon tetrabromide

Assertion and Reason

Directions (Q. No. 24 to 28) *Each of these questions contains two statements : Statement* I (*Assertion*) *and Statement* II (*Reason*). *Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes* (*a*), (*b*), (*c*), (*d*) *given below :*

(a) Statement I is true; Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true; Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

24. **Statement I** Olefinic monomers undergo addition polymerisation.

Statement II Polymerisation of vinylchloride is initiated by peroxides or persulphates. [NCERT Exemplar]

25. **Statement I** Rayon is a semi synthetic polymer and is taken as a better choice than cotton fabric.

Statement II Mechanical and aesthetic properties of cellulose can be improved by acetylation. [NCERT Exemplar]

26. **Statement I** Polyvinyl alcohol is obtained by polymerisation of vinyl alcohol.

Statement II Polyvinyl alcohol is prepared by hydrolysis of polyvinyl acetate.

27. **Statement I** Network polymers are thermosetting.

Statement II Network polymers have high molecular mass. [NCERT Exemplar]

28. **Statement I** PMMA is used for making lenses and light covers.

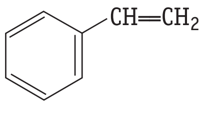
Statement II It has excellent light transmission properties.

Comprehension Based Questions

Directions (Q. Nos. 29 to 31) A polymer is a large molecule made by linking together repeating units of small molecules called monomers. The process of linking them up is called polymerisation. On the basis of mode of polymerisation, polymers are of two types; Addition polymers and condensation polymers. Addition polymers are formed by repeated addition of monomer molecules possessing double or triple bonds. Addition polymers may be homopolymer (single monomeric species) or copolymers (two different monomers). The condensation polymers are formed by repeated condensation reaction between two different bifunctional or trifunctional monomeric units with the elimination of small molecules such as H_2O, alcohol etc.

29. Which one of the following cannot form addition polymers?

(a) $CH_2{=}CH_2$

(b) 

(c) $HOOC(CH_2)_4COOH$

(d) None of these

30. Condensation polymers are formed from monomers
(a) which have bifunctional groups
(b) which have multiple $(C{=}C)$ or $(C{\equiv}N)$ or $(C{\equiv}C)$ bonds
(c) in which elimination can take place
(d) in which addition can take place

31. Which type of polymer is the Buna-S rubber?
(a) Copolymer
(b) Addition polymer
(c) Condensation polymer
(d) It is not a polymer

Directions (Q. Nos. 32 to 33) Neoprene is synthetic rubber which is obtained by polymerisation of 2-chloro-1,3 butadiene. In it the configuration of polymer is *trans*. Its properties are improved by vulcanisation, which is infact the hardening of rubber by heating is presence of sulphur causes cross-linking of separate polymer chains through disulphide bonds and thus vulcanised chains are locked together in one giant molecule. Cross-linking prevents the polymer from being torn when it is stretched, and the cross-links provide a reference framework for the material to return to when the stretching force is removed.

32. The tensile strength, elasticity and resistance to abrasion can be increased by a process called
(a) diazotisation
(b) vulcanisation
(c) isomerisation
(d) polymerisation

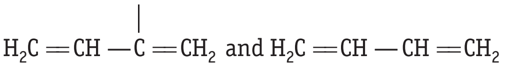
33. In vulcanisation of rubber,
(a) sulphur reacts of form new compound
(b) sulphur crosslinks are introduced
(c) sulphur forms a very thin protective layer over rubber
(d) All of the above

Previous Years' Questions

34. Thermosetting polymer, bakelite is formed by the reaction of phenol with [AIEEE 2008, 2011]
(a) CH_3CH_2CHO
(b) CH_3CHO
(c) $HCHO$
(d) $HCOOH$

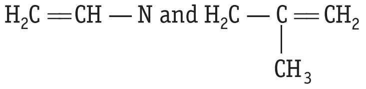
35. The polymer containing strong intermolecular forces, *e.g.*, hydrogen bonding, is [AIEEE 2010]
(a) teflon
(b) nylon-66
(c) polystyrene
(d) natural rubber

36. Buna-N synthetic rubber is a copolymer of [AIEEE 2009]

(a) 
$H_2C{=}CH{-}\overset{\overset{\displaystyle Cl}{|}}{C}{=}CH_2$ and $H_2C{=}CH{-}CH{=}CH_2$

(b) $H_2C{=}CH{-}CH{=}CH_2$ and $H_5C_6{-}CH{=}CH_2$

(c) $H_2C{=}CH{-}CN$ and $H_2C{=}CH{-}CH{=}CH_2$

(d) 
$H_2C{=}CH{-}N$ and $H_2C{-}\underset{\underset{\displaystyle CH_3}{|}}{C}{=}CH_2$

37. Which of the following is fully fluorinated polymer? [AIEEE 2005]

(a) PVC
(b) Thiokol
(c) Teflon
(d) Neoprene

38. Nylon threads are made up of [AIEEE 2003]

(a) polyvinyl polymer
(b) polyester polymer
(c) polyamide polymer
(d) polyethylene polymer

39. Monomers are converted to polymer by [AIEEE 2002]

(a) hydrolysis of monomers
(b) condensation reaction between monomers
(c) protonation of monomers
(d) None of the above

Answers

Round I

1. (d)	**2.** (c)	**3.** (d)	**4.** (a)	**5.** (a)	**6.** (d)	**7.** (b)	**8.** (b)	**9.** (c)	**10.** (a)
11. (c)	**12.** (a)	**13.** (c)	**14.** (c)	**15.** (d)	**16.** (d)	**17.** (d)	**18.** (b)	**19.** (a)	**20.** (a)
21. (b)	**22.** (b)	**23.** (b)	**24.** (d)	**25.** (c)	**26.** (b)	**27.** (a)	**28.** (c)	**29.** (b)	**30.** (a)
31. (a)	**32.** (b)	**33.** (c)	**34.** (b)	**35.** (c)	**36.** (d)	**37.** (b)	**38.** (a)	**39.** (b)	**40.** (d)
41. (d)	**42.** (b)	**43.** (c)	**44.** (c)	**45.** (d)	**46.** (b)	**47.** (b)	**48.** (a)	**49.** (d)	**50.** (b)

Round II

1. (d)	**2.** (c)	**3.** (c)	**4.** (c)	**5.** (b)	**6.** (d)	**7.** (c)	**8.** (d)	**9.** (d)	**10.** (a)
11. (a)	**12.** (c)	**13.** (b)	**14.** (a)	**15.** (a)	**16.** (a)	**17.** (c)	**18.** (b)	**19.** (b,d)	**20.** (b,c)
21. (a,c)	**22.** (a,d)	**23.** (a,d)	**24.** (b)	**25.** (a)	**26.** (d)	**27.** (b)	**28.** (a)	**29.** (c)	**30.** (a)
31. (a)	**32.** (b)	**33.** (b)	**34.** (c)	**35.** (b)	**36.** (c)	**37.** (c)	**38.** (c)	**39.** (b)	

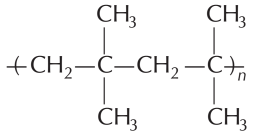
the Guidance

Round I

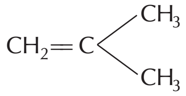
1. A high molecular weight molecule, made up of a large number of smaller units is called polymer and it is also known as macromolecule However, all macromolecules are not polymers.

2. With increase in molecular weight of a polymer, other properties such as tensile strength, crystallinity, melting point etc., increase.

3. Polymers are large molecules with high molecular weight, and a repeating unit. They do not carry any charge. They have high viscosity and can scatter light.

4. 

$$\left[CH_2-C(CH_3)_2-CH_2-C(CH_3)_2 \right]_n$$

is a polymer having monomer units 

$$CH_2{=}C(CH_3)_2$$

5. Strong intermolecular forces like hydrogen bonding lead to close packing of chains that imparts crystalline character.

6. Glycogen is a polymers of glucose which is stored by animals.

7. Since proteins, cellulose and RNA control various activities of plants and animals, they are called biopolymers.

8. Teflon is prepared by the combination of a large number of tetrafluoroethylene molecules, without the elimination of any small molecule. Therefore, it is an example of addition homopolymer.

$$nCF_2{=}CF_2 \longrightarrow \underset{\text{teflon}}{\left[CF_2-CF_2 \right]_n}$$

9. Orlon is an addition polymer as its molecular mass is integral multiple of molecular mass of its monomer.

12. Among the given, only vulcanised rubber has elastic character, so it is an elastomer.

13. Nylon and terylene are fibres whereas PTFE is a thermoplastic and polychloroprene is an elastomer.

14. Nylon-66 is obtained by the condensation of hexamethylene diamine with adipic acid. Since, two different monomers involve in its preparation, it is a copolymer, not a homopolymer.

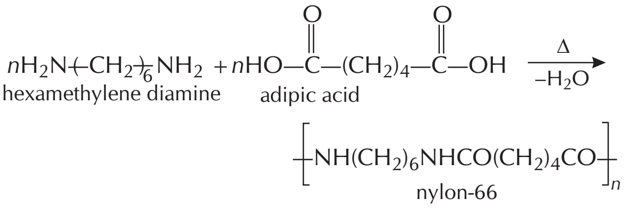
15. Due to the presence of extensive cross-linking, thermosetting polymers have strongest molecular forces.

16. Generally high boiling esters or haloalkanes act as plasticizer.

17. Functionality of a monomer means the number of bonding sites present in it. *e.g.,* functionality of ethene, propene, styrene, acrylonitrile is one and that of ethylene glycol, adipic acid, hexamethylene diamine is two.

18. When two or more chemically different monomers take part in polymerisation, it is called copolymerisation.

19. Nylon-6 6 is obtained by condensation copolymerisation of adipic acid and hexamethylene diamine.

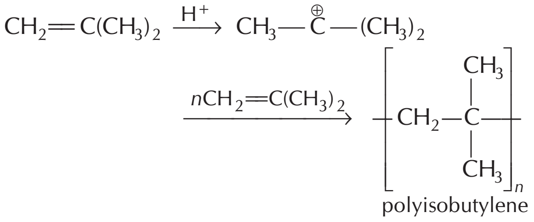


$$nH_2N\text{+}CH_2\text{+}_6NH_2 + nHO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[-H_2O]{\Delta} \left[NH(CH_2)_6NHCO(CH_2)_4CO\right]_n$$

20. Ethene on free radical polymerisation gives low density polythene.

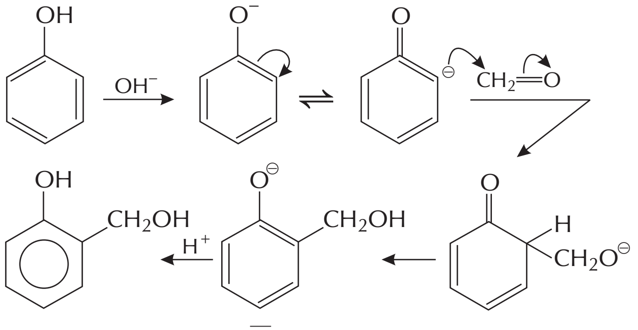
21. Certain amines, phenols and quinones are used to inhibit the growth of polymer chain.

23. Since 3° carbocations are most stable, the best way to obtain polyisobutylene is acid catalysed or cationic polymerisation in the presence of Lewis acid or protonic acid.



$$CH_2{=}C(CH_3)_2 \xrightarrow{H^+} CH_3-\overset{\oplus}{C}-(CH_3)_2 \xrightarrow{nCH_2=C(CH_3)_2} \left[CH_2-\underset{CH_3}{\overset{CH_3}{C}}\right]_n$$

24. It is aromatic electrophilic substitution.



25. $$PDI = \frac{\overline{M}_w}{\overline{M}_n}$$

For synthetic polymer, PDI > 1

$\therefore \quad \overline{M}_w > \overline{M}_n$

26. Polydispersity index (PDI) $= \frac{\overline{M}_w}{\overline{M}_n}$

For natural polymers, PDI = 1

$\therefore \quad \overline{M}_w = \overline{M}_n$

27. Isoprene is $CH_2{=}C(CH_3)-CH{=}CH_2$ (2-methyl-1, 3-butadiene).

28. Neoprene (synthetic rubber) resembles with natural rubber.

$$\text{+}CH_2-CH{=}C(Cl)-CH_2\text{+}_n$$

neoprene

$$\text{+}CH_2-CH{=}C(CH_3)-CH_2\text{+}_n$$

natural rubber

29. Thiokol is a synthetic polysulphide rubber which is obtained by the condensation polymerisation of ethylene dichloride and sodium polysulphide. It is resistant to oils and abrasion.

30. Heating of rubber with sulphur or sulphur compounds at 373 K to 415 K in the presence of ZnO is called vulcanisation.

31. Vulcanised rubber is highly elastic, so intermolecular forces present in it, are weakest.

32. Additon of 3-10% sulphur to rubber, makes it hard.

33. Buna-N and buna-S both are synthetic rubber and copolymers. The difference lies in their compostiion.

Buna-N constituents are buta-1, 3-diene and acrylonitrile.

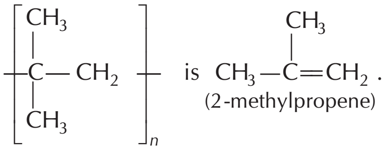
Buna-S constituents are buta-1, 3-diene and styrene.

34. Low density polythene is a branched chain polymer.

36. High density polythene is obtained, when ethene undergoes *Ziegler-Natta* polymerisation. In this process, *Ziegler-Natta* catalyst, a mixture of titanium tetrachloride ($TiCl_4$) and trimethyl aluminium [$(CH_3)_3Al$] is used to catalyse the polymerisation.

37. The commercial name of polyacrylonitrile is orlon (acrilan).

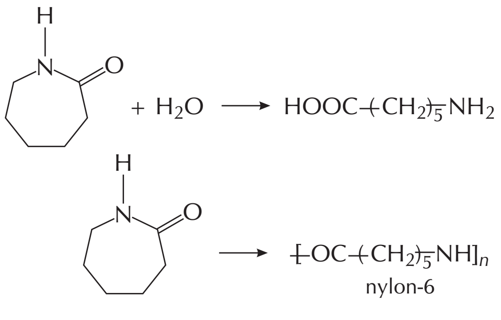
38. Monomer of



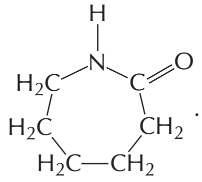
$$\left[\underset{CH_3}{\overset{CH_3}{C}}-CH_2\right]_n \text{ is } CH_3-\overset{CH_3}{C}{=}CH_2 .$$

(2-methylpropene)

40. Caprolactum is widely used for preparing nylon-6, for this it is first hydrolysed with water to form amino acid.

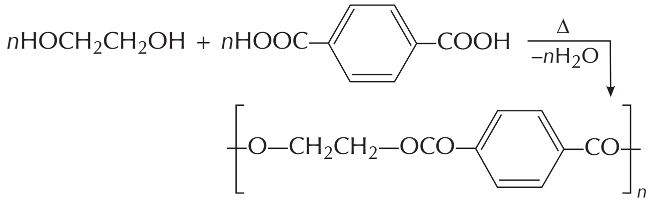


So, it is clear that nylon-6 (polymer) can be formed by the using of the caprolactum



monomer unit

41. Esterification of terephthalic acid with ethylene glycol produces terylene.



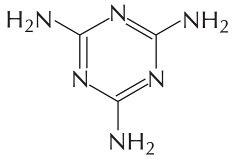
terylene or dacron

42. In addition homopolymers such as teflon, empirical formula resembles with monomer.

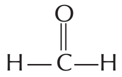
43. Orlon is a polymer of vinyl cyanide or acrylonitrile ($CH_2{=}CHCN$).

44. Break—NH—CH_2 bond and add H_2O to get the structure of monomers.

(a) 2, 4, 6-triamino-1, 3, 5-triazine or melamine

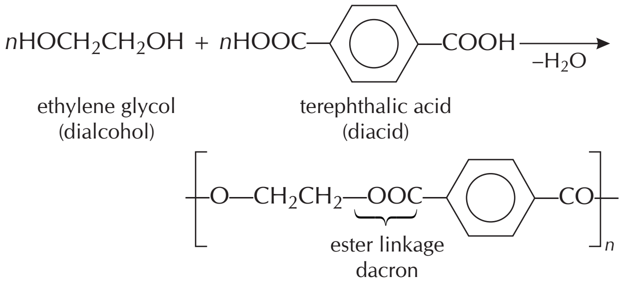


(b) Formaldehyde or methanal (HCHO)



45. Polystyrene contains only linear chains.

46. When a diacid is condensed with dialcohol, the polymer obtained contains ester linkage.



47. SBR (styrene-butadiene) is a synthetic rubber.

48. Cellulose is a biodegradable polymer.

Round II

1. Cellulose acetate has been used in the manufacture of non-inflammable photographic films.

2. Polystyrene and orlon, being vinyl derivative, are chain growth polymers while dacron is a step growth polymer.

3. For the synthesis of nylon-4, lactam with four carbon atoms is required.

4. Buna-S is an elastomer, thus has weakest intermolecular forces. Nylon-66, is a fibre, thus has strong intermolecular forces like H-bonding. Polythene is a thermoplastic polymers, thus the intermolecular forces present in polythene are in between elastomer and fibres. Thus, the order of intermolecular forces of these polymers is

Buna-S < Polythene < Nylon-66

5. Electron releasing groups such as CH_3, —OCH_3 activate the monomer towards cationic polymerisation as these groups provide stability to the carbocation formed. Thus, the correct order is

$$CH_2{=}CHC_6H_5(OCH_3) > CH_2{=}CH-C_6H_5(CH_3) > NO_2C_6H_5-CH{=}CH_2$$

6. Vinyl derivatives containing electron releasing group readily undergo head to tail addition polymerisation.

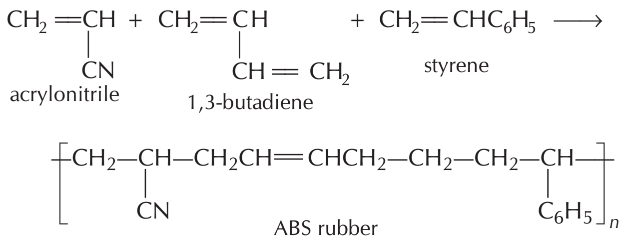
7. Electron withdrawing groups make the monomer more reactive towards anionic polymerisation.

8. All options are correct.

9. PCTFE (poly monochloro tetrafluoro ethylene), $\lbrack ClFC-CF_2 \rbrack_n$ is not a polyacrylate.

10. SARAN, a polymer of vinyl chloride ($CH_2{=}CHCl$). and vinylidene chloride, is used for making synthetic hair wigs.

11. ABS is acrylonitrile-butadiene-styrene rubber which is obtained by copolymerisation of acrylonitrile, 1, 3-butadiene and styrene.



$$\underset{\text{acrylonitrile}}{CH_2{=}\underset{|}{CH}\!-\!CN} + \underset{\text{1,3-butadiene}}{CH_2{=}CH-CH{=}CH_2} + \underset{\text{styrene}}{CH_2{=}CHC_6H_5} \longrightarrow \underset{\text{ABS rubber}}{\lbrack CH_2-\underset{CN}{CH}-CH_2CH{=}CHCH_2-CH_2-CH_2-\underset{C_6H_5}{CH} \rbrack_n}$$

12. PCTFE and PTFE both have same carbon backbone.

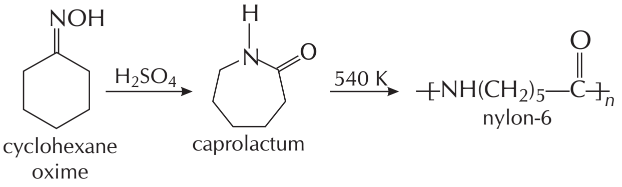
$$+ClFC-CF_2+_n$$

PCTFE (polymonochloro tetrafluoroethylene)

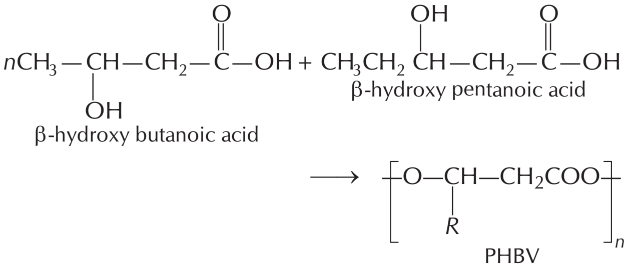
$$+F_2C-CF_2+_n$$

PTFE (polytetrafluoroethylene)

13. Caprolactum is the monomer of nylon-6.



14. Monomers 3-hydroxy butanoic acid and 3-hydroxypentanoic acid react each other and form biodegradable PHBV. Glycine and amino caproic acid also react to form biodegradable polymers nylon-2-nylon-6.

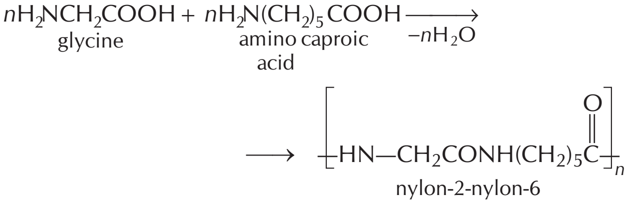


$$nCH_3-\underset{OH}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-OH+CH_3CH_2\overset{OH}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-OH$$

β-hydroxy butanoic acid β-hydroxy pentanoic acid

$$\longrightarrow \left[O-\underset{R}{CH}-CH_2COO\right]_n$$

PHBV



$$nH_2NCH_2COOH+nH_2N(CH_2)_5COOH\xrightarrow[-nH_2O]{}$$

glycine amino caproic acid

$$\longrightarrow \left[HN-CH_2CONH(CH_2)_5\overset{O}{\overset{\|}{C}}\right]_n$$

nylon-2-nylon-6

15. Nylon and polyesters have strong intermolecular forces (*i.e.*, hydrogen bonding).

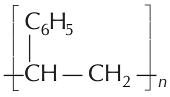
16. Vulcanisation makes the rubber more elastic and more stiff.

17. Nylon-66 is a condensation polymer.*i.e.,* obtained by condensation polymerisation.

PVC is obtained by free radical polymerisation whereas HDP (high density polythene) is a result of *Zieglar-Natta* polymerisation.

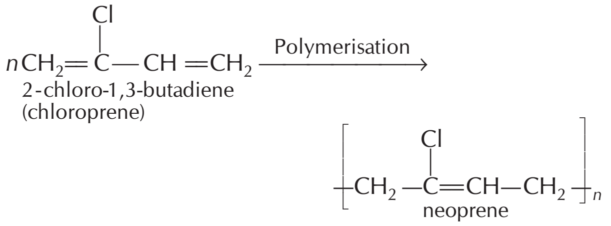
18. Glyptal is a polymer of glycol and phthalic acid Buna-S is obtained by copolymerisation of 1, 3-butadiene and styrene.

Novolac is a linear polyester of phenol formaldehyde resin Dacron is a polyester of glycol and terephthalic acid Buna-N is a copolymer of 1, 3-butadiene and acryclonitrile.



19. Polystyrene $\left[\underset{}{\overset{C_6H_5}{\overset{|}{CH}}}-CH_2\right]_n$ teflon $+CF_2-CF_2+_n$ and acrilan polymers have vinylic monomer, units.

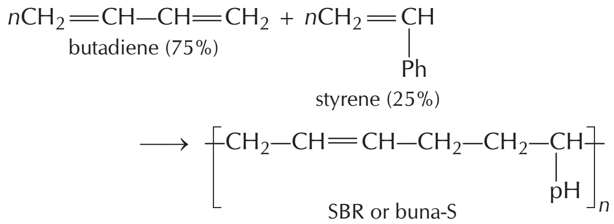
20. Buna-S and neoprene polymers need atleast one diene monomer for their preparation.



$$nCH_2=\overset{Cl}{\overset{|}{C}}-CH=CH_2\xrightarrow{\text{Polymerisation}}\left[CH_2-\overset{Cl}{\overset{|}{C}}=CH-CH_2\right]_n$$

2-chloro-1,3-butadiene (chloroprene)

neoprene



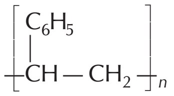
$$nCH_2=CH-CH=CH_2+nCH_2=\underset{Ph}{\underset{|}{CH}}$$

butadiene (75%) styrene (25%)

$$\longrightarrow\left[CH_2-CH=CH-CH_2-CH_2-\underset{pH}{\underset{|}{CH}}\right]_n$$

SBR or buna-S

21. The polymer which become infusible on moulding *i.e.*, can't be used further and are heavily branched (cross-linked) are called thermosetting ploymers.



22. Teflon $+CF_2-CF_2+_n$ polystyrene $\left[\overset{C_6H_5}{\overset{|}{CH}}-CH_2\right]_n$ and polythene $+CF_2-CF_2+_n$ are thermoplastic polymers.

23. Carbon tetrachloride and carbon tetrabromide act as chain transfer reagent in vinyl polymerisation.

24. Olefinic monomers being unsaturated undergo addition polymerisation. Polymerisation of vinylchloride is initiated by peroxides/ persulphates.

25. Rayon is a semisynthetic polymer which is obtained from cellulose through acetylation process. It is taken as a better choice than cotton fabric.

26. Polyvinyl alcohol cannot be prepared by polymerisation of vinyl alcohol since it readily tautomerises to acetaldehyde.

27. Network polymers are thermosetting. They have the high molecular mass.

28. Statement I is the correct explanation of Statement II.

29. $HOOC(CH_2)_2COOH$ form condensation polymers.

30. Condensation polymers one formed from monomers adipic acid and hexamethylene diamine.

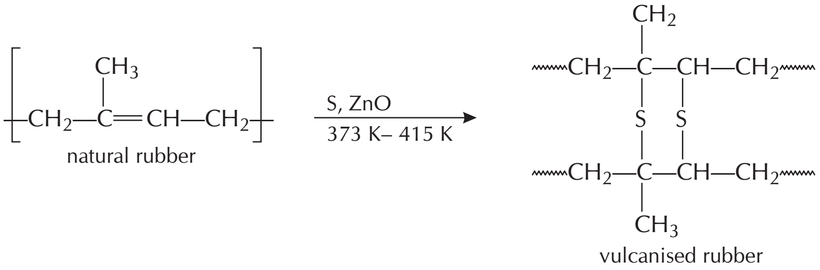
$$nNH_2(CH_2)_6NH_2+n(CH_2)_4(COOH)_2\longrightarrow +NH(CH_2)_6NHCO(CH_2)_4CO+_n+nH_2O$$

nylon-66

31. Buna-S is copolymer.

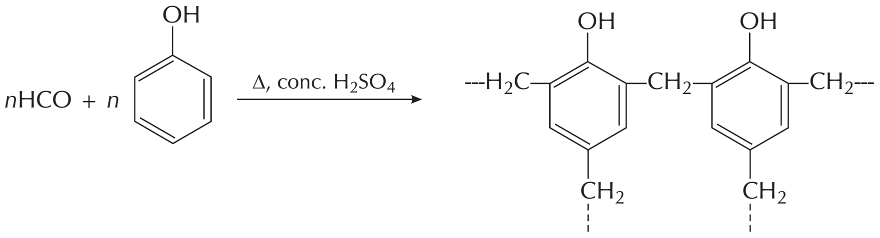
32. Vulcanisation is responsible for tensile strength, elasticity and resistance to abrasion of rubber.

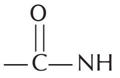
33. During vulcanisation process, sulphur cross-links are introduced at the reactive sites of double bonds,



34. Bakelite is a thermosetting plastic formed by reaction of phenol with HCHO in the presence of conc. H_2SO_4.

It is thus cross-linked polymer, condensation taking place at *o*-and *p*-positions.



35. In nylon-66 hydrogen bonds are formed between  $-\overset{\overset{\large O}{\|}}{C}-NH$ group of successive chains.

36. Buna-N actually abbreviated from where Bu represents 1, 3- butadiene, Na represents Na, sodium and N represents nitrile (acrylonitrile).

Thus, buna-N is co-polymer of 1, 3-butadiene and acrylonitrile usually polymerise in the presence of sodium.

37. Teflon is $\left[\!-CF_2-CF_2-\!\right]_n$

38. Nylon threads are made up of polyamide.

39. Condensation is the process of aggregation of more than one molecule without losing any atom or group (sometimes smaller group or atoms H_2O, R—OH etc., are released).

$$\underset{\text{(monomer)}}{n\,CH_2{=}CH_2} \longrightarrow \underset{\text{polymer}}{-CH_2-(CH_2-CH_2)-CH_2-}$$

14 Biomolecules

JEE Main MILESTONE

- Carbohydrates
- α-Amino Acids
- Proteins
- Enzymes
- Vitamins
- Nucleic Acids

14.1 Carbohydrates

These are naturally occurring organic substances. These are present in both plants and animals. Initially these are produced in plants by a process known as photosynthesis. In this process, sunlight is absorbed by a green pigment called chlorophyll (present in the green plants). The photochemical energy thus obtained is used to convert carbon dioxide and water into carbohydrates and oxygen.

$$xCO_2 + yH_2O \xrightarrow[\text{Chlorophyll}]{\text{Sunlight}} C_x(H_2O)_y + xO_2$$

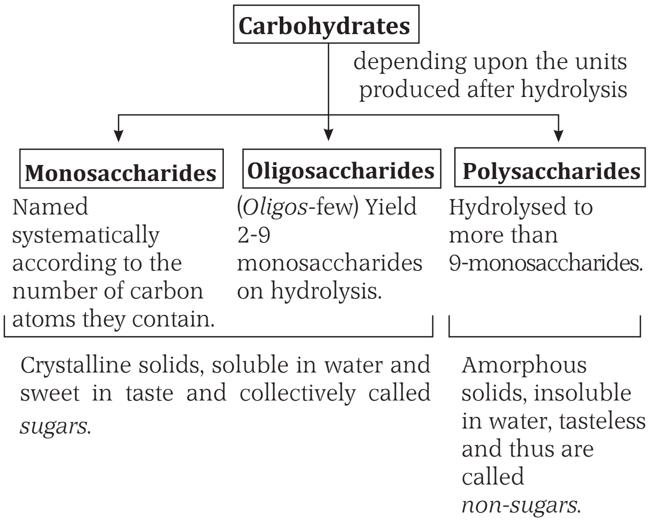
Animals do not synthesise carbohydrates.

Previously it was believed that carbohydrates are the substances with general formula $C_x(H_2O)_y$ *i.e.,* hydrates of carbon. However, a number of compounds have been discovered which are carbohydrates by chemical behaviour, but do not possess the formula $C_x(H_2O)_y$, *e.g.,* rhamnose ($C_6H_{12}O_5$) and deoxyribose ($C_5H_{10}O_4$). Similarly, all compounds possessing to the formula $C_x(H_2O)_y$ are not necessarily carbohydrates, *e.g.,* HCHO, CH_3COOH etc. Hence, this definition has been changed now. According to modern definition *optically active polyhydroxy aldehydes or polyhydroxy ketones or compounds which can be hydrolysed to one of these are called carbohydrates.*

Biomolecules are complex life less substances which forms the basis of life i.e., they not only build up living creatures but are also responsible for their growth and maintenance. The size and complexity gives almost unlimited potential for diversity of molecules, but it also makes organic molecules much more fragile and easy to destroy than the smaller and simpler inorganic molecules.

Classification of Carbohydrates

Carbohydrates are also known as **saccharides** and classified according to their behaviour towards hydrolysis.



Carbohydrates are also classified as either **reducing sugars** or **non-reducing sugars.** The sugars that reduce the Tollen's reagent and Fehling's solution are called **reducing sugars.** Reducing sugars include all the monosaccharides, both aldoses as well as ketoses with a $—CH_2OH$ next to the carbonyl group. The disaccharides may be reducing or non-reducing depending upon the position of linkages between two monosaccharide units. If the glycosidic linkage involves the carbonyl functions of both the monosaccharides units, the resulting disaccharide would be **non-reducing** (as sucrose). If one of the carbonyl functions in the anyone of the monosaccharide units is free, the resulting disaccharide would be reducing sugar (as maltose, lactose, cellobioase.). All polysaccharides are non-reducing sugars.

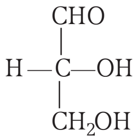
Sample Problem 1 *Carbohydrates are classified on the basis of their behaviour on hydrolysis and also as reducing or non-reducing sugar. Sucrose is a* **[NCERT Exemplar]**

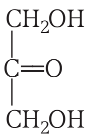
(a) *monosaccharide* (b) *disaccharide*
(c) *reducing sugar* (d) *non-reducing sugar*

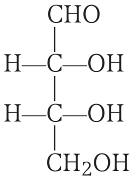
Interpret (*b,d*) Sucrose is the most common disaccharide. It consists of a D-glucose subunit and a D-fructose subunit linked by a glycosidic bond between C-1 of glucose (in the α-position) and C-2 of fructose (in the β-position). Sucrose is a non-reducing sugar because it does not have a hemiacetal or hemiketal group, so it is not in equilibrium with the readily oxidisable open chain aldehyde or ketone form in aqueous solution.

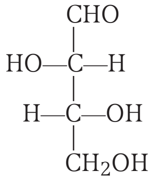
Monosaccharides : General Features

These are the simplest carbohydrates which cannot be hydrolysed to smaller molecules. All these are polyhydroxy compounds containing either an aldehydic (—CHO) group and are called **aldoses** (the aldehydic group being monovalent is present at the end of the chain) or a ketonic ($>C{=}O$) group and are called **ketoses** (the ketonic group is present next to terminal carbon atom). The simplest monosaccharides are **trioses** such as glyceraldehyde (aldose), dihydroxyacetone (ketose) and aldotetros such as erythrose and threose.


D(+)-glyceraldehyde
(An aldotriose)

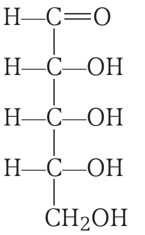

dihydroxyacetone
(A ketotriose)

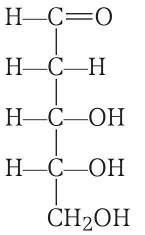

D(–) erythrose

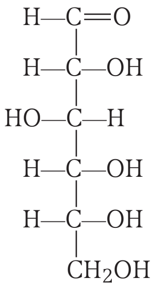

D(–) threose

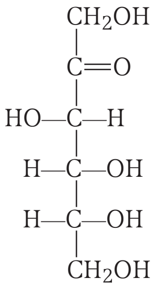
Any natural sugar degrade to D-(+) glyceraldehydes. But some synthetic carbohydrate degrade to L-(–) glyceraldehyde. Ketotriose does not considered as a monosaccharide because it is optically inactive.

However, the naturally occurring monosaccharides are pentoses (5 C atoms) and hexoses (6 C atoms) out of these, the most common are ribose, 2-deoxyribose, glucose (aldoses) and fructose (ketose).

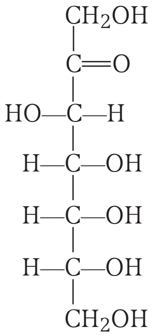

D(–)-ribose


D(–) 2-deoxyribose


D(+)-glucose


D(–)-fructose

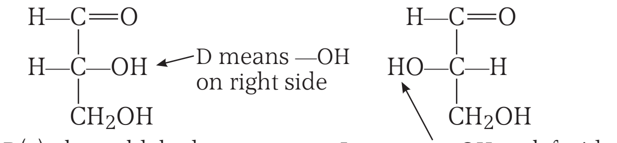
Sedoheptulose, a ketoheptose sugar (7 carbon atoms) has the same structure as fructose with an extra carbon.


D-sedoheptulose

Similarly, L-glycero-D-manno-heptose (aldoheptose) is a constituent of polysaccharides in Gram-negative bacteria.

Configuration of Carbohydrates

D or L letter before the name of any carbohydrate indicate the relative configuration of a particular stereo-isomer. Glyceraldehyde, a simplest saccharide exists in two enantiomeric forms.



D(+)-glyceraldehyde

L-means —OH on left side.

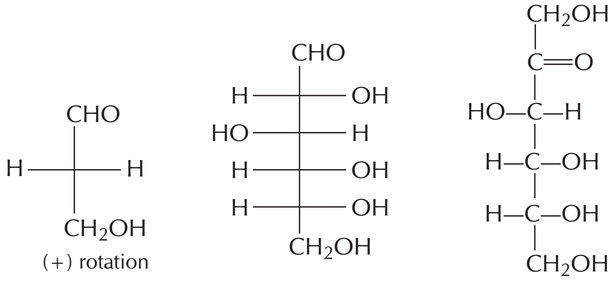
These two forms serve as a reference point for designating and drawing all other monosaccharides. The monosaccharides having the same configuration as of D-glyceraldehyde at the asymmetric carbon which is adjacent to —CH_2OH group but the most distant from carbonyl group (aldehyde or ketone group) are designated as D-form and those having the same configuration as of L-glyceraldehyde are designated as L-forms. The natural glucose and fructose are D-forms.

The maximum number of optical isomers of a carbohydrate is equal to 2^n.

where, n = number of chiral carbons.

Caution Point *The (+) and (–) signs only indicates the direction of rotation of plane polarized light by a specific enantiomer and it does not give any information about the arrangement of —OH group on the asymmetric carbon atom which is adjacent to —CH_2OH group.*

Sample **Problem 2** *Optical rotations of some compounds along with their structures are given below. Which of them have D configuration.* **[NCERT Exemplar]**

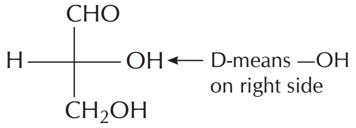


(I) (II) (III)

(*a*) I, II, III (*b*) II, III

(*c*) I, II (*d*) III

Interpret (*a*) The monosaccharides having the same configuration as of D-glyceraldehyde at the asymmetric carbon which is adjacent to —CH_2OH group but the most distant from carbonyl group are designated as D-configuration.

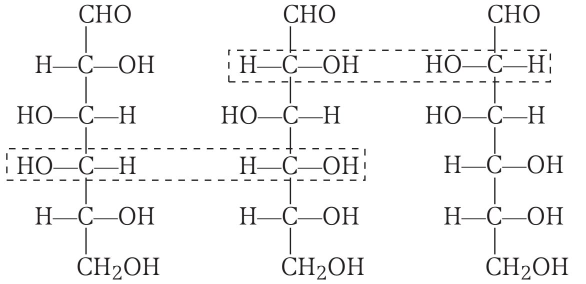


D-(+)-glyceraldehyde

Therefore, all the given species have D-configuration.

Epimers

A more selective term, **epimer** is used to designate diastereomers that differ in configuration at only one chiral centre. Thus, glucose is epimeric with D (+)-mannose and D(+)-galactose as shown below :

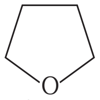

D(+)-galactose D(+)-glucose D(+)-mannose

Similarly, ribose and arabinose are epimers at C-2 and arabinose and lyxose are epimers at C-3.

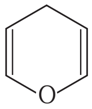
Caution Point *Arabinose and xylose are not epimers, since their configuration differ at both C-2 and C-3.*

Ring Structure of Monosaccharides

The ring form of monosaccharides is favoured in aqueous solution. Structures of pentoses and hexoses are cyclic involving five or six membered rings containing an oxygen atom. The five membered ring containing an oxygen atom, because of its similarity with **furan** is called the **furanose form** and the six membered ring containing an oxygen atom because of its similarity with **pyran** is called the **pyranose form**.



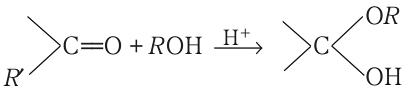
furan



pyran

During ring formation, reaction between an aldehyde and an alcohol forms a **hemiacetal.** A **hemiketal** is an analogous product formed by reaction of a ketone with an alcohol.

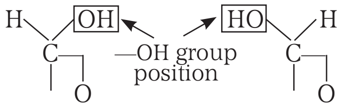
Formation of a hemiacetal or a hemiketal



(where, $R' = \mathrm{H}$ or R)
If aldehyde (*i.e.*, $R' = \mathrm{H}$) ⟶ hemiacetal,
If ketone (*i.e.*, $R' = R$) ⟶ hemiketal

As a result of ring formation

(i) Carbon number 1–(C_1) becomes asymmetric (chiral) and hence, monosaccharides exist in two stereoisomeric forms, α and β-form. In the α-form, the —OH at C_1 is towards right while in the β-form, the —OH at C_1 is towards left.



α-position β-position

A pair of stereoisomers which differ in configuration only around C_1 carbon are called **anomers** and the C_1 is called the **anomeric carbon** (or glycosidic carbon).

Glucose ($C_6H_{12}O_6$)

Glucose is a monosaccharide, aldohexose and reducing sugar. It is found in ripe grapes (hence named **grape-sugar**), honey and most sweet fruits. It is also a normal constituent of blood and occurs in the urine of diabetics. The blood normally contains 65 to 110 mg of glucose per 100 mL (hence named blood sugar). In the combined state, it occurs in glucosides, dissacharides and polyssacharides.

Methods of Preparation

(i) **From sucrose** Cane sugar (sucrose) on acid hydrolysis in the presence of alcohol, gives a mixture of glucose and fructose.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

Glucose being less soluble in alcohol than fructose separates out by crystallising on cooling (fractional crystallisation).

(ii) **From starch** Glucose is obtained on a large scale by the hydrolysis of starch with dilute H_2SO_4 or dilute HCl under pressure.

$$\underset{\text{starch}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[393\text{ K, 2-3 atm}]{H^+} \underset{\text{glucose}}{nC_6H_{12}O_6}$$

After neutralisation with $CaCO_3$ and filteration, filterate is decolourised by boiling with animal charcoal and then concentrated under reduced pressure and crystallised.

(iii) **From lactose or maltose**

$$\underset{\text{lactose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{galactose}}{C_6H_{12}O_6}$$

$$\underset{\text{maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{glucose}}{2C_6H_{12}O_6}$$

Physical Properties of Glucose

(i) Glucose is a white crystalline solid (m.p. 146°C). It also occurs in the form of monohydrate, $C_6H_{12}O_6 \cdot H_2O$ (mp 86°C).

(ii) Glucose is readily soluble in water, sparingly soluble in alcohol and insoluble in ether.

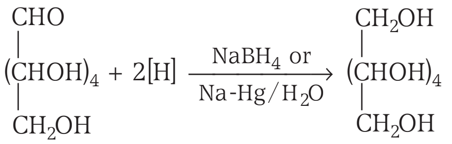
(iii) It is optically active and dextrorotatory (hence named dextrose). It shows mutarotation (The change in specific rotation of an optically active compound in solution with time, to an equilibrium value is called mutarotation)

(iv) It has a very sweet taste but is about three fourth as sweet as sucrose (cane-sugar).

Chemical Properties of Glucose

(i) **Reduction**

(a) On reduction with $NaBH_4$ or Na-Hg, glucose yields sorbitol.



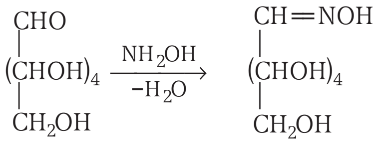
$$\begin{array}{l} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} + 2[H] \xrightarrow[\text{Na-Hg}/H_2O]{NaBH_4\text{ or}} \begin{array}{l} CH_2OH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

sorbitol

(b) On reduction with HI and red P, it gives a mixture of *n*-hexane and 2-iodohexane.

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow[\Delta]{\text{Red P/HI}} \underset{n\text{-hexane}}{CH_3CH_2CH_2CH_2CH_2CH_3}$$
$$+ \underset{\text{2-iodohexane}}{CH_3CHICH_2CH_2CH_2CH_3}$$

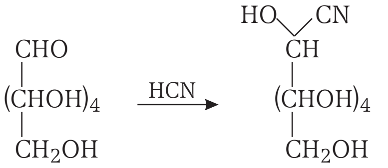
(ii) **Reaction with hydroxylamine** Glucose forms glucose oxime with hydroxylamine.



$$\begin{array}{l} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow[-H_2O]{NH_2OH} \begin{array}{l} CH{=}NOH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

glucose oxime

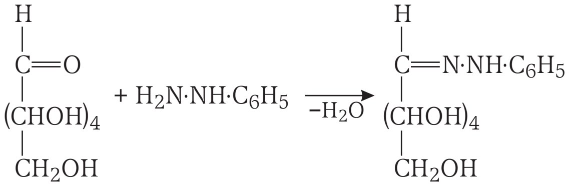
(iii) **Reaction with hydrogen cyanide** An addition product, glucose cyanohydrin is formed.



$$CHO(CHOH)_4CH_2OH \xrightarrow{HCN} CH(OH)(CN)(CHOH)_4CH_2OH$$

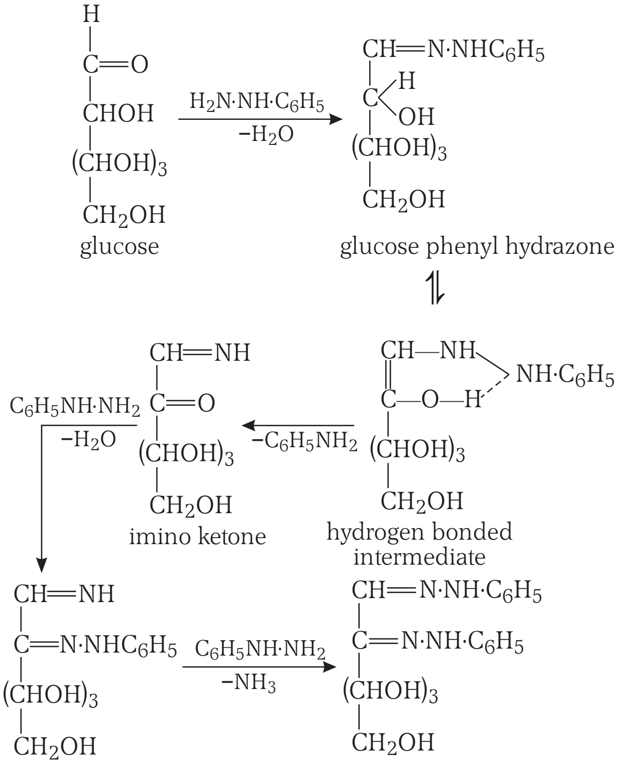
glucose cyanohydrin

(iv) **Reaction with phenyl hydrazine** When treated with equimolar quantities of phenyl hydrazine, glucose yields a phenyl hydrazone.



$$\underset{\text{glucose}}{HC{=}O(CHOH)_4CH_2OH} + H_2N{\cdot}NH{\cdot}C_6H_5 \xrightarrow[-H_2O]{} \underset{\text{glucose phenyl hydrazone}}{HC{=}N{\cdot}NH{\cdot}C_6H_5(CHOH)_4CH_2OH}$$

- However, when glucose is warmed with excess of phenyl hydrazine, crystalline product, glucosazone is formed.



$$\underset{\text{glucose}}{HC{=}O\,CHOH(CHOH)_3CH_2OH} \xrightarrow[-H_2O]{H_2N{\cdot}NH{\cdot}C_6H_5} \underset{\text{glucose phenyl hydrazone}}{CH{=}N{\cdot}NHC_6H_5\,CH(OH)(CHOH)_3CH_2OH}$$

$$\rightleftharpoons \underset{\text{hydrogen bonded intermediate}}{CH{-}NH\cdots NH{\cdot}C_6H_5 \,\|\, C{-}O{-}H\,(CHOH)_3CH_2OH} \xrightarrow{-C_6H_5NH_2} \underset{\text{imino ketone}}{CH{=}NH\,C{=}O(CHOH)_3CH_2OH}$$

$$\xrightarrow[-H_2O]{C_6H_5NH{\cdot}NH_2} CH{=}NH\,C{=}N{\cdot}NHC_6H_5(CHOH)_3CH_2OH \xrightarrow[-NH_3]{C_6H_5NH{\cdot}NH_2} CH{=}N{\cdot}NH{\cdot}C_6H_5\,C{=}N{\cdot}NH{\cdot}C_6H_5(CHOH)_3CH_2OH$$

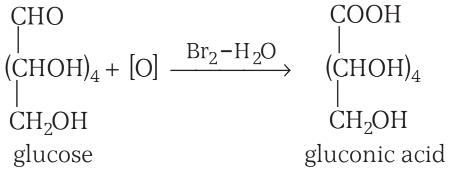
glycosazone
(yellow crystalline solid)

Osazone formation is given by only α-hydroxy aldehyde and α-hydroxy ketones. (Glucose, fructose and mannose form the same osazone, *i.e.,* glucosazone).

Glucosazone is a yellow crystalline solid, sparingly soluble in water and has sharp melting point. Due to these properties, it is used to identify glucose.

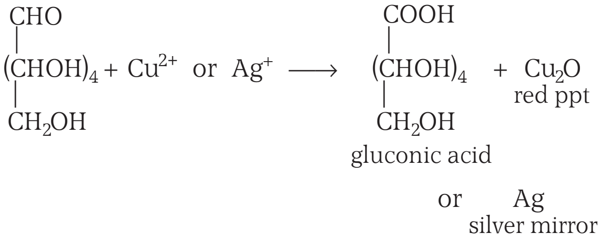
(v) **Oxidation**

(a) With bromine water, glucose gives gluconic acid.



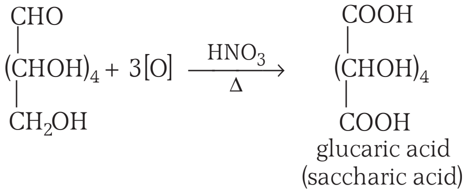
$$\underset{\text{glucose}}{CHO(CHOH)_4CH_2OH} + [O] \xrightarrow{Br_2-H_2O} \underset{\text{gluconic acid}}{COOH(CHOH)_4CH_2OH}$$

(b) Glucose on oxidation with Fehling's solution and Tollen's reagent gives coloured precipetate and gluconic acid.



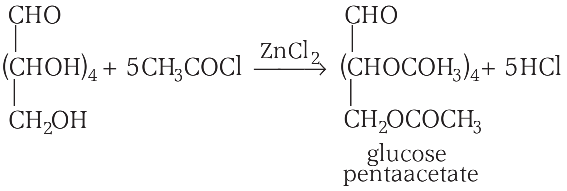
$$CHO(CHOH)_4CH_2OH + Cu^{2+} \text{ or } Ag^+ \longrightarrow \underset{\text{gluconic acid}}{COOH(CHOH)_4CH_2OH} + \underset{\text{red ppt}}{Cu_2O} \text{ or } \underset{\text{silver mirror}}{Ag}$$

(c) On oxidation with strong acids like nitric acid, glucose gives glucaric (saccharic) acid.



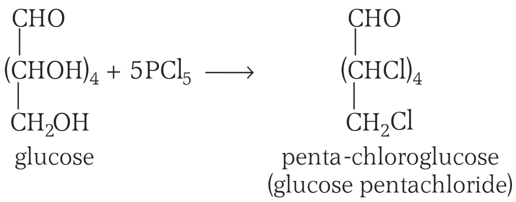
$$CHO(CHOH)_4CH_2OH + 3[O] \xrightarrow[\Delta]{HNO_3} \underset{\text{glucaric acid (saccharic acid)}}{COOH(CHOH)_4COOH}$$

(vi) **Reaction with acetyl chloride** Glucose reacts with acetyl chloride to form glucose penta-acetate.



$$CHO(CHOH)_4CH_2OH + 5CH_3COCl \xrightarrow{ZnCl_2} \underset{\text{glucose pentaacetate}}{CHO(CHOCOH_3)_4CH_2OCOCH_3} + 5HCl$$

(vii) **Reaction with PCl_5** Glucose reacts with PCl_5 to form penta-chloro glucose.

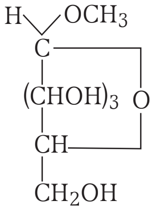


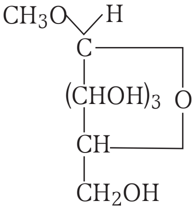
$$\underset{\text{glucose}}{CHO(CHOH)_4CH_2OH} + 5PCl_5 \longrightarrow \underset{\text{penta-chloroglucose (glucose pentachloride)}}{CHO(CHCl)_4CH_2Cl}$$

$+ 5POCl_3 + 5HCl$

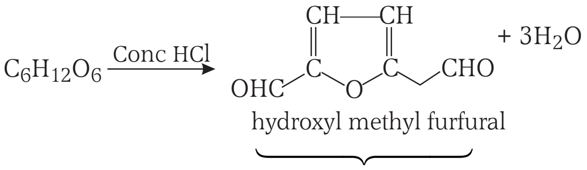
(viii) **Reaction with methanol** D(+)-glucose when treated with methanol in presence of dry HCl gas, reacts with its one mole only and yields monomethyl ether which is actually a mixture of α- and β- forms indicating that one of the —OH group is different from others.

$$C_6H_{11}O_5 - \boxed{OH + H}\, OCH_3 \xrightarrow{\text{dry HCl}} \underset{\substack{\alpha\text{- and }\beta\text{-methyl} \\ \text{glucoside}}}{C_6H_{11}O_5OCH_3} + H_2O$$


α-methyl-glucoside


β-methyl-glucoside

(ix) **Reaction with conc. HCl** On treatment with conc. HCl, glucose forms hydroxymethyl furfural which further produces laevulic acid.



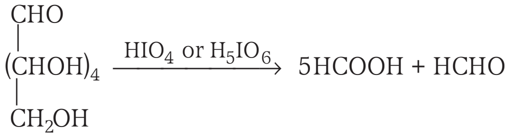
hydroxyl methyl furfural

$CH_3COCH_2CH_2COOH + H_2O$
laevulic acid

(x) **Reaction with metallic hydroxides** Glucose reacts with metallic hydroxides like $Ca(OH)_2$, $Ba(OH)_2$, $Sr(OH)_2$ etc. to form metallic glucosates, which are soluble in water.

$$C_6H_{11}O_5 - \boxed{OH + H}\, O—Ca—OH \longrightarrow \underset{\text{calcium glucosate}}{C_6H_{11}O_5—O—Ca—OH} + H_2O$$

(xi) **Reaction with periodic acid** Periodic acid splits glucose into formic acid and formaldehyde.



$$\begin{matrix} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{matrix} \xrightarrow{HIO_4 \text{ or } H_5IO_6} 5HCOOH + HCHO$$

(xii) **Fermentation** Glucose when fermented by zymase, yields ethanol.

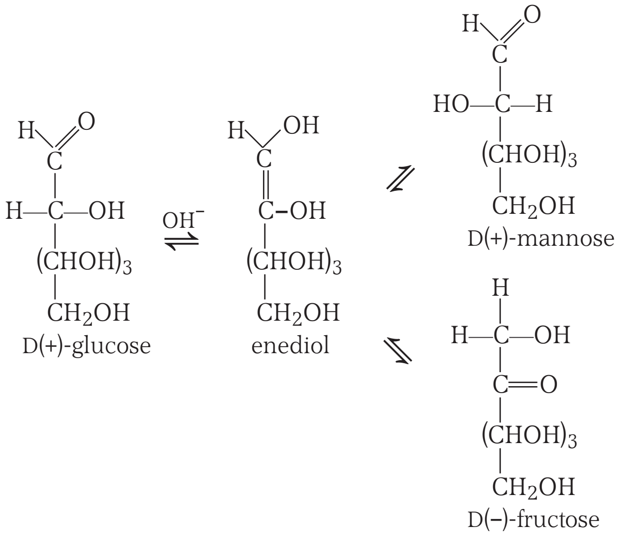
$$\underset{\text{glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

(xiii) **Dehydration** On strong heating or on treating with warm conc. H_2SO_4, glucose is dehydrated to give a black mass (sugar carbon).

$$C_6H_{12}O_6 \xrightarrow{\text{Conc. } H_2SO_4} \underset{\text{black carbon}}{6C} + 6H_2O$$

(xiv) **Reaction with alkalies** When warmed with conc. alkali, glucose first turns yellow, then brown and finally gives a resinous mass.

A dilute solution of glucose when warmed with dilute alkali, is converted into an optically inactive solution of D(+)-glucose, D(+)-mannose and D(–)- fructose. This is known as **Lobry-de-Bruyn-van Ekenstein rearrangement**,



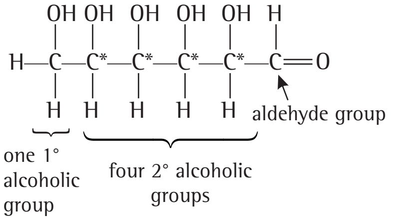
Hot Spot 1

STRUCTURE of Glucose

Structure of glucose is an important topic for JEE main examination. Generally questions are seen from this topic. The level of question is from easy to average.

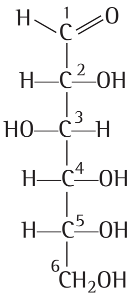
- By the usual analytical methods, the molecular formula of glucose is found to be $C_6H_{12}O_6$.
- Formation of 2-iodohexane and *n*-hexane [Reaction (i)b] indicates that six carbon atoms in glucose are present in a straight chain.
- Formation of glucose penta acetate (Reaction-vi) indicates the presence of 5—OH groups. Since it exists as a stable compound, five —OH groups should be attached to different carbon atoms.
- Formation of glucose oxime and glucose cyanohydrin (reaction (iii) and (iv)) respectively confirms the presence of carbonyl group in glucose.
- Formation of gluconic acid in presence of mild oxidising agent like Br_2—H_2O (Reaction (ii)-a) indicates that glucose contains an aldehydic group. Since aldehydic group is monovalent, it must be present on the end of the chain.

On the basis of point discussed above, it was suggested that glucose has an **open chain structure.** The open chain structure, for the first time, was proposed by **Baeyer.** Glucose contains one —CHO group, one 1° alcoholic group and four 2° alcoholic groups as



(C* = asymmetric centres)

There are four dissimilar chiral carbon atoms in the molecule, but a definite configuration to these asymmetric centres has not been assigned. The configuration of D-glucose was proved by **Emil Fischer.**

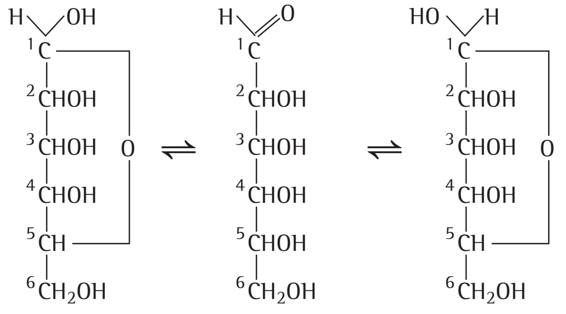


D(+)-glucose

Evidence against open chain structure However, there are some evidences which do not support the open chain structure of glucose. These are

1. Even though an aldedhyde gorup is present, the glucose does not react with $NaHSO_3$, NH_3, 2,4-DNP and Grignard reagent.
2. Glucose does not respond to Schiff's reagent test.
3. Glucose penta-acetate does not react with hydroxyl-amine. This indicates the absence of free —CHO group in glucose.
4. Glucose exists in two stereoisomeric forms *i.e.,* α and β anomers. α-glucose (mp 146°C) with specific rotation +111° is obtained by crystallising glucose from alcohol or acetic acid solution whereas β-glucose (mp 150°C) with specific rotation 19.2° is obtained by crystallising glucose form pyridine solution.
5. An aqueous solution of glucose shows mutarotation, *i.e.,* if either of the two forms is dissolved in water and allowed to stand, the specific rotation of the solution changes gradually until a final value of +52.5° is reached. It means that the specific rotation gradually decreases from +111° to +52.5° in case of α-glucose and increases from +19.2° to +52.5° in case of β-glucose. This phenomena is known as **mutarotation.**

Cyclic Structure of Glucose This behaviour could not be explained by the open chain structure for glucose. It was proposed that one of the —OH groups may add to the —CHO group to form a cyclic hemiacetal structure. According to **Fischer** in this process, glucose forms a stable cyclic hemiacetal between —CHO group and the —OH group of the fifth carbon atom in pyranose structure.

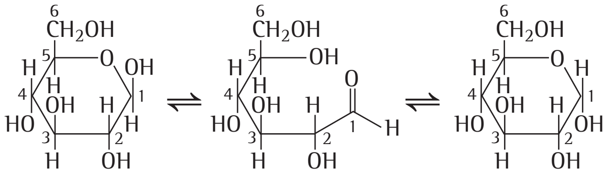


α-D(+)-glucose $[\alpha]_D$ = 111° (36%)

open-chain $[\alpha]_D$ = 52.5° (0.02%)

β-D(+)-glucose $[\alpha]_D$ = 19.2° (64%)

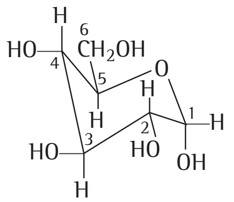
Fischer projections are not the best way to show the structure of a glucose. The cyclic structure of glucose is more correctly represented by **Haworth projection formula.**



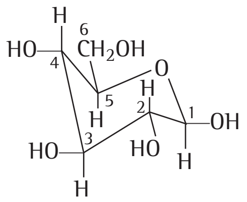
β-D(+)-glucose (64%) Δ(+)-glucose (open chain) (0.02%) α-D(+)-glucose (36%)

The two cyclic hemiacetal forms of glucose differ only in the configurtion of the hydroxyl group at C-1 called anomeric carbon. Such isomers, *i.e.*, α-form and β-form are called anomers.

Glucose is sometimes illustrated as a **chair form** because it is a more accurate representation of bond-angles of the molecule (**Reeves**, 1950).



α-anomer



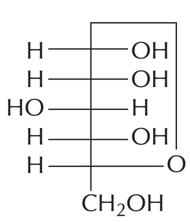
β-anomer (stable)

In β-anomer, the glycosidic hydroxyl group is equatorial and as a general rule, the conformation with greatest number of large groups in equatorial orientation is the most stable form. Thus, β-anomer predominates in the equilibrium mixture. The **boat form** of glucose is unstable.

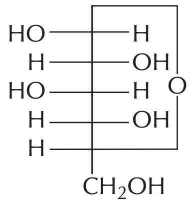
Sample **Problem 3**

Three cyclic structures of monosaccharides are given below which of these are anomers?

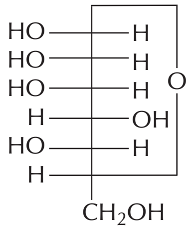
[NCERT Exemplar**]**



(I)



(II)



(III)

(*a*) *I and II* (*b*) *II and III*

(*c*) *I and III* (*d*) *III is anomer of I and II*

Interpret (*a*) Cyclic hemiacetal forms of monosaccharide which differ only in the configuration of the hydroxyl group at C-1 are anomers.

Sample **Problem 4**

Which of the following reactions of glucose can be explained only by its cyclic structure?

[NCERT Exemplar**]**

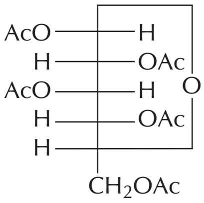
(*a*) *Glucose forms pentaacetate*

(*b*) *Glucose reacts with hydroxylamine to form an oxime*

(*c*) *Pentaacetate of glucose does not react with hydroxylamine*

(*d*) *Glucose is oxidised by nitric acid to gluconic acid*

Interpret (*c*)



Glucose pentaacetate does not have a free —OH group at C-1 and so can't be converted to the open chain form to give —CHO group and hence does not form oxime.

Sample **Problem 5**

Glucose when treated with CH_3OH *in presence of dry* HCl *gas, gives* α- *and* β-*methyl glucosides because it contains*

(*a*) *an aldehydic group* (*b*) —CH_2OH *group*

(*c*) *a ring structure* (*d*) *five* —OH *groups*

Interpret (*c*) Mixture of α- and β-form indicates that one —OH group is different from other which may combine with —CHO group to form intramolecular hemiacetal.

So, this reaction is an evidence for the cyclic structure of glucose in solutions.

Sample **Problem 6**

The optical rotation of the α *form of a pyranose is* +150.7°; *that of* β-*form is* +52.8°. *In solution, an equilibrium mixture of the anomers has an optical rotation of* +80.2°. *The percentage of the* α-*form at equilibrium is*

(*a*) 28% (*b*) 32% (*c*) 68% (*d*) 72%

Interpret (*a*) Let '*a*' and '*b*' be the mole fractions of α and β anomers in equilibrium mixture. Thus,

$$a + b = 1 \quad \text{or} \quad b = (1 - a)$$

$$150.7a + 52.8b = 80.2$$

$$150.7a + 52.8(1 - a) = 80.2$$

$$150.7a + 52.8 - 52.8a = 80.2$$

$$97.9a = 27.4$$

$$a = 0.279 \approx 0.28 = 28\%$$

Hence, $\%$ of α-form = 28%

Fructose

The only important ketohexose is D(–)-fructose (also known as laevulose). In the free state, it is present along with honey and most sweet fruits (berries, melons etc.,), hence named as **fruit sugar.** In the combined state, fructose is present in sucrose and insulin. It is the sweetest monosaccharide.

Methods of Preparation of Fructose

(i) **By hydrolysis of cane sugar with dilute acids.**

$$\underset{\text{cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+,\Delta} \underset{\text{D(+)-glucose}}{C_6H_{12}O_6} + \underset{\text{D(–)-fructose}}{C_6H_{12}O_6}$$

The solution having equal molecules of D-glucose and D-fructose is termed **invert sugar** and the process is known as inversion.

(ii) **By calcium fructosate**

$$C_6H_{11}O_5\text{—O—Ca—OH} + CO_2 \longrightarrow \underset{\text{fructose}}{C_6H_{12}O_6} + CaCO_3$$

(iii) **From insulin**

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow{HCl} nC_6H_{12}O_6$$

(Insulin is a polysaccharide which occurs in dahlia tubers and Jerusalem artichokes).

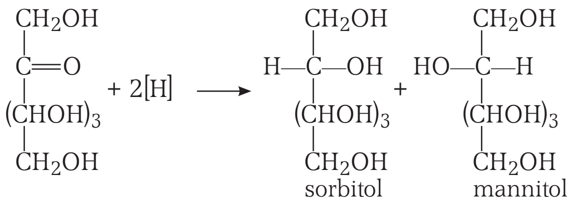
Physical Properties

Fructose is colourless crystalline compound (mp 102°). It is soluble in water and insoluble in benzene and ether. It is less soluble in water than glucose. Like glucose, it also shows mutarotation.

Chemical Properties

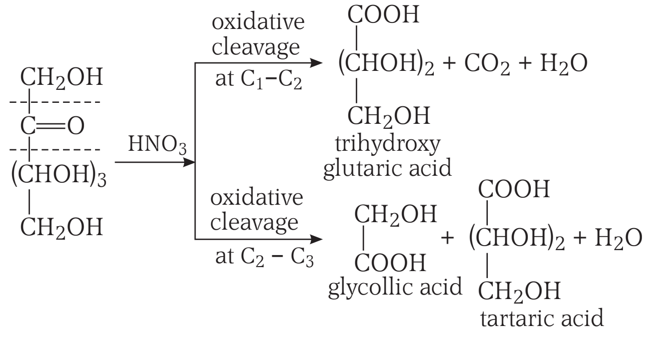
The chemical reactions of fructose are almost similar to those of glucose. The only different behaviour are oxidation and reduction.

(i) **Reduction** On reduction with $NaBH_4$ or $Na\text{–}Hg/H_2O$, fructose forms a mixture of sorbitol and mannitol.



Caution Point *The reduction of glucose with* $NaBH_4$ *forms D-sorbitol while that of fructose forms a mixture of D-sorbitol and D-mannitol* (*they differ in configuration*).

(ii) **Oxidation** Fructose is not oxidised by mild oxidising agent like Br_2 water. However, when oxidised with nitric acid, fructose is converted into a mixture of trihydroxy glutaric, glycollic and tartaric acids.



Since a mixture of acids each containing fewer carbon atoms than fructose is obtained, the carbonyl group in fructose must be a ketonic group.

(iii) **Reducing nature** Unlike ketones, fructose can reduce Fehling's solution and Tollen's reagent. This is probably due to formation of an equilibrium mixture of glucose, mannose and fructose in alkaline solution.

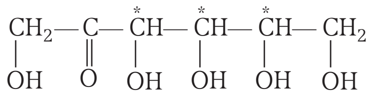
(iv) **Action of conc. HCl**

$$C_6H_{12}O_6 \xrightarrow{HCl} \underset{\text{Laevulinic acid}}{H_3C\cdot CO\cdot CH_2\cdot CH_2\cdot COOH} + \underset{\text{formic acid}}{HCOOH} + H_2O$$

Structure of Fructose

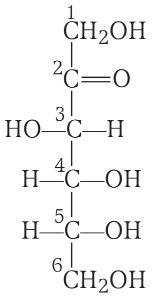
(a) Open Chain Structure of Fructose

The open chain structure of fructose may be represented as below



$$\underset{OH}{CH_2}\text{—}\underset{\|\atop O}{C}\text{—}\underset{OH}{\overset{*}{CH}}\text{—}\underset{OH}{\overset{*}{CH}}\text{—}\underset{OH}{\overset{*}{CH}}\text{—}\underset{OH}{CH_2}$$

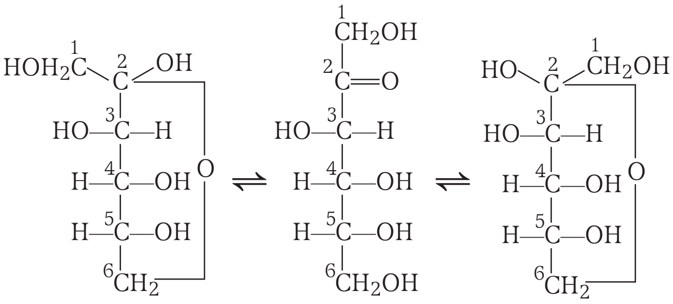
The structure contains three asymmetric carbon atoms and eight optically active forms but only six are known. The configuration of D(–)-fructose is,



D(–)-fructose

(b) Cyclic Structure of Fructose

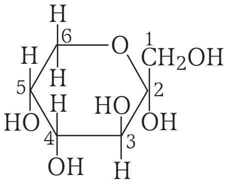
Fructose also has a cyclic structure in aqueous solution, *i.e.*, intramolecular hemiketal. It also exhibit mutarotation.



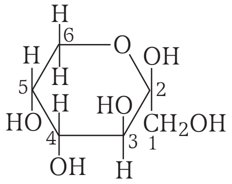
α-D(–)-fructose $[\alpha]_D = -21°$ α-D(–)-fructose $[\alpha]_D = -92°$ β-D(–)-fructose $[\alpha]_D = -133°$

(c) The Haworth Projection Formulae

For the cyclic structure of D(–)-fructose is represented as

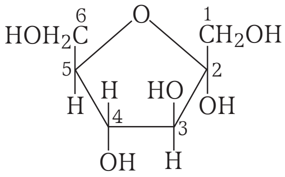


α-D(–)-fructopyranose

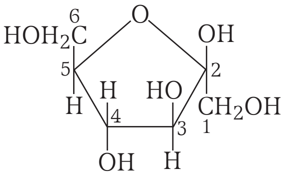


β-D(–)-fructopyranose

However, in the combined state (such as in sucrose) fructose exists in the furanose form.



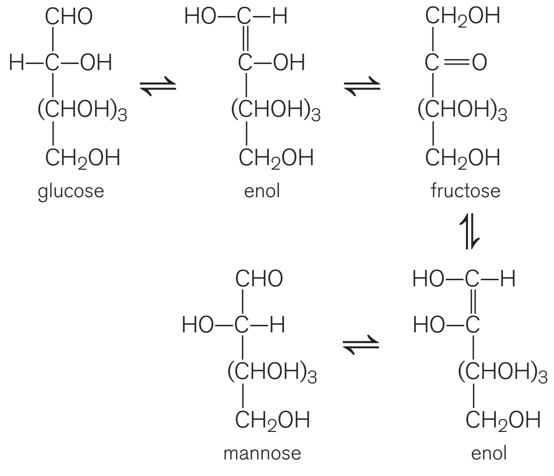
α-D(–) fructofuranose



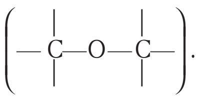
β-D(–) fructofuranose

In solution, fructose exists as an equilibrium mixture of 70% fructopyranose and about 22% fructofuranose as well as small amounts of the three other forms, including the acylic structure [*i.e.,* D(+)-glucose, D(+)-mannose and D(–)-fructose]

Caution Point *Although fructose contains ketonic group, yet it also reduces Tollen's reagent and Fehling's solution. Dilute solution of alkali present in these reagents converts fructose into an equilibrium mixture of glucose, fructose and mannose. Hence, fructose has reducing property.*



Oligosaccharides : General Features

Molecules of these carbohydrates are made up of a small number of monosaccharide units joined together by glycosidic bonds  $\left(-\overset{|}{\underset{|}{C}}-O-\overset{|}{\underset{|}{C}}-\right)$. Glycosidic bonds are *established during the condensation of monosaccharides. The process is called dehydration synthesis.*

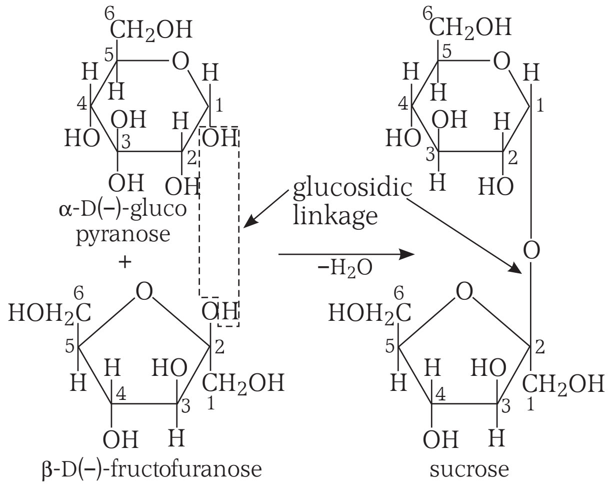
Depending upon the number of monosaccharide molecules condensed to form oligosaccharides, the latter are known as **disaccharides** (*e.g.,* sucrose), **trisaccharides** (*e.g.,* raffinose), **tetrasaccharides** (*e.g.,* stachyrose) etc.

Larger oligosaccharides having branched or unbranched chains often attached to cell membranes.

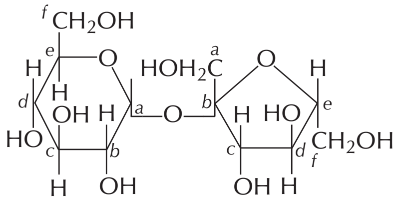
Sucrose ($C_{12}H_{22}O_{11}$)

It is commercial sugar which is also called **cane sugar** because most of it is obtained from sugarcane (16–20%). It also present in sugarbeet (10–15%), pineapple (10–12%), apricot banana, mango and honey.

Preparation It is formed by condensation of one molecule each of glucose and fructose.



Sample Problem 7 *The structure of a disaccharide formed by glucose and fructose is given below. Identify anomeric carbon atoms in monosaccharide units.*



[NCERT Exemplar]

(*a*) *'a' carbon of glucose and 'a' carbon of fructose*
(*b*) *'a' carbon of glucose and 'e' carbon of fructose*
(*c*) *'a' carbon of glucose and 'b' carbon of fructose*
(*d*) *'f' carbon of glucose and 'f' carbon of fructose*

Interpret (*c*) The two cyclic forms of a carbohydrate differ in configuration only of the carbon atom involved in ring formation (hemiacetal carbon). This carbon is called anomeric carbon. Therefore, '*a*' carbon of glucose and '*b*' carbon of fructose is anomeric.

Properties

(i) It is a colourless, odourless, crystalline substance having m.p. 180°C. It is very soluble in water but insoluble in alcohol and ether. It is dextro-rotatory with a specific rotation +66.5°.

(ii) On hydrolysis with dilute acids or invertase or sucrase, it gives an equimolar mixture of D(+)-glucose and D(–)-fructose.

$$\underset{\substack{(+)\text{-sucrose}\\ [a]_D = +66.5^\circ}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{enzyme}]{\text{Acid or}} \underset{\substack{D(+)\text{-glucose}\\ [a]_D = +52.7^\circ}}{C_6H_{12}O_6} + \underset{\substack{D(-)\text{-fructose}\\ [a]_D = -92.4^\circ}}{C_6H_{12}O_6}$$

Since, D(–)-fructose has a greater specific rotation than D(+)-glucose, the resulting mixture is laevorotatory. Because of this, the hydrolysis of cane-sugar is known as **the inversion of cane-sugar** and the mixture is known as **invert sugar.** Due to the presence of fructose, invert sugar is sweeter than sucrose. Invert sugar is used to coat chocolate.

Swetening power of common sugars

Fructose > Invert sugar > Sucrose > Glucose > Maltose > Lactose

(iii) On heating (200°C), sucrose melts and on cooling forms a glassy yellow solid known as **barley sugar.** When heated above its melting point, it loses water and gives a brown substance known as **caramel.** On further heating sucrose gets charred to almost pure carbon (sugar charcoal).

(iv) Sucrose on acetylation gives sucrose octaacetate. This shows the presence of eight —OH groups in sucrose.

(v) Sucrose does not form oxime or osazone. This shows the absence of $>C{=}O$ group.

(vi) Sucrose does not reduces Tollen's reagent and Fehling's solution. This shows the absence of —CHO group in sucrose.

(vii) **Fermentation** In the presence of yeast, it yields ethanol and carbon dioxide.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{ethanol}}{2C_2H_5OH} + CO_2$$

(viii) On reaction with conc. nitric acid sucrose oxidises to oxalic acid.

$$C_{12}H_{22}O_{11} + 8[O] \xrightarrow{\text{Conc. }HNO_3} \underset{\text{oxalic acid}}{6[COOH]_2} + 5H_2O$$

(ix) With conc. H_2SO_4, sucrose loses water to give sugar charcoal (charring of sugar).

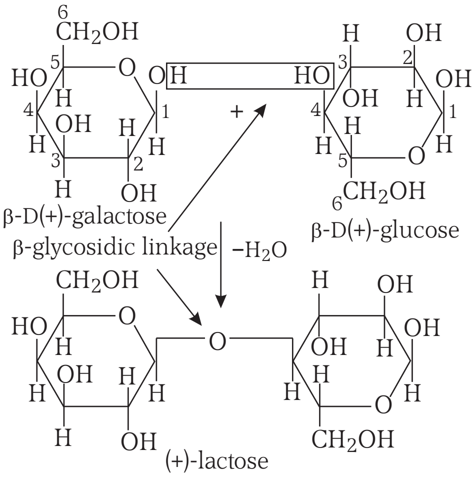
$$C_{12}H_{22}O_{11} + H_2SO_4 \longrightarrow 12C + 11H_2O$$

$$C + 2H_2SO_4 \longrightarrow 2SO_2 + CO_2 + 2H_2O$$

A small of sulphurdioxide is also observed due to reduction of the acid.

Lactose ($C_{12}H_{22}O_{11}$)

It occurs in the milk of all animals (milk-sugar). It is a white crystalline solid (with m.p. 203°C), soluble in water and is dextrorotatory. It is hydrolysed by dilute acid or enzyme lactose, to an equimolar mixture of D(+)-glucose and D(+)-galactose. Lactose is a reducing sugar, forms an oxime and osazone and undergoes mutarotation. It gets hydrolysed by emulsin also, an enzyme which specifically hydrolyses β-1,4-glycosidic linkage.



(+)-lactose

Maltose ($C_{12}H_{22}O_{11}$)

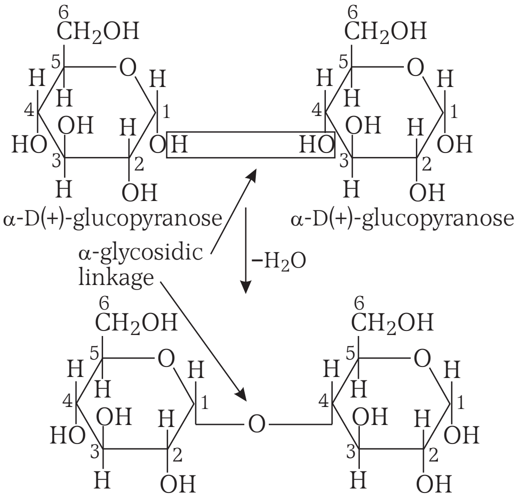
It is obtained by partial hydrolysis of starch by diastase enzyme present in malt, *i.e.,* sprouted barley seeds (hence named **maltose** or **malt sugar**).

$$2(C_6H_{10}O_5)_n + nH_2O \xrightarrow{\text{Diastase}} \underset{\text{maltose}}{nC_{12}H_{22}O_{11}}$$

Properties

(i) Maltose is a white crystalline solid (with m.p. 160°–165°C), soluble in water and dextrorotatory.

(ii) When maltose is hydrolysed with dilute acid or by enzyme maltase, it yields two molecules of D(+)-glucose. Hence, maltose is a condensation product of two α-D-glucose units which are linked by an acetal linkage called α-1,4 glycosidic linkage.



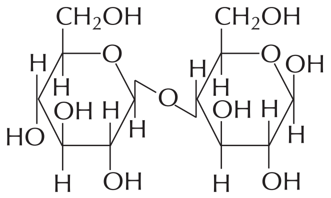
(iii) Maltose is a reducing sugar. It reduces Fehling's solution Tollen's reagent, it forms an oxime and an osazone and undergoes mutarotation. This indicates that at least one aldehyde group is free in it. (Free aldehyde group can be produced at C-1 of second glucose in solution which shows reducing property).

Cellobiose ($C_{12}H_{22}O_{11}$)

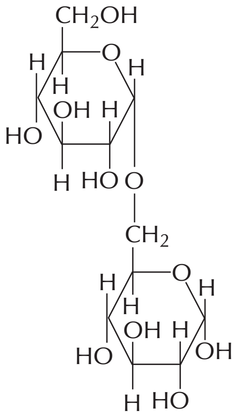
It is obtained by the hydrolysis of cellulose and also contains two D-glucose subunits. These two units are linked together by a β-1,4-glycosidic linkage. Therefore, the only difference in the structures of maltose and cellobiose is the configuration of glucosidic linkage. Like maltose, cellobiose is reducing sugar and undergoes mutarotation.

Sample **Problem 8** *Three structures are given below in which two glucose units are linked. Which of these linkages between glucose units are between* C-1 *and* C-4 *and which linkages are between* C-1 *and* C-6? **[NCERT Exemplar]**

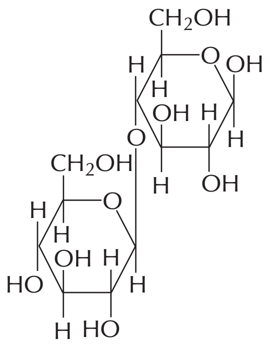
(*A*)



(*B*)



(*C*)



(*a*) *(A) is between* C-1 *and* C-4, *(B) and (C) are between* C-1 *and* C-6

(*b*) *(A) and (B) are between* C-1 *and* C-4. (C) *is between* C-1 *and* C-6

(*c*) *(A) and (C) are between* C-1 *and* C-4, *(B) is between* C-1 *and* C-6

(*d*) *(A) and (C) are between* C-1 *and* C-6, *(B) is between* C-1 *and* C-4

Interpret (*c*) **Structure '*A*'** (structure of maltose) two α-D glucose units are held together by glycosidic linkage between C-1 of one glucose and C–4 of another glucose.

In structure '*B*', glycosidic linkage is in between C-1 of one monosaccharide and C-6 of another monosacccharide.

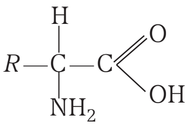
In structure' *C*' , the two monosaccharide units are joined together by glycosidic linkage between C-1 of one unit and C-4 of another unit.

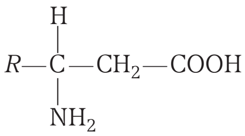
Check Point 1

1. Why do glucose, mannose and fructose form identical osazone?
2. Why is D-glucose used for sweetening cold drinks but not hot ones?
3. Why is sucrose called invert sugar?
4. Aldoses give positive test with Tollen's reagent or Fehling's solution but fail to respond Schiff's and bisulphite tests. Explain.
5. Ketones do not reduce Tollen's reagent or Fehling solution but fructose, however has ketonic group, reduces them. Explain.
6. Which monosaccharides from identical osazone on treatment with an excess of phenyl hydrazine and why?

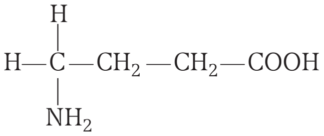
14.2 α-Amino Acids

Bifunctional organic compounds containing carboxylic and amino group either at the same carbon atom or at the nearby carbon atoms are called amino acids. These are the monomers of proteins and properties of a protein mainly depend on the consitituent amino acids. Amino acids can be classified as α, β, γ, δ and so on depending upon the location of the amino group on the carbon chain containing the carboxyl functional group. Some examples are


α-amino acid


$R-\underset{NH_2}{\overset{H}{C}}-CH_2-COOH$

β-amino acid


$H-\underset{NH_2}{\overset{H}{C}}-CH_2-CH_2-COOH$

γ-amino acid

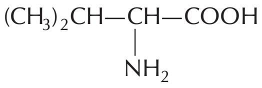
Amino acids are also classified as acidic, basic or neutral depending upon the relative number of amino and carboxyl groups in their molecule. Equal number of amino and carboxyl groups makes it neutral; more number of amino groups than carboxyl groups makes it basic and more carboxyl groups than amino groups makes it acidic.

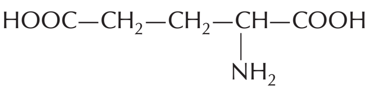
Usually amino acids have primary amino group but proline is a secondary amine.

Natural proteins can be broken down into about 20 different α-amino acids (19α-amino acids and 1α-imino acid). These molecules differ in the nature of the *R*-group attached to the alpha carbon. The *R*–group can be

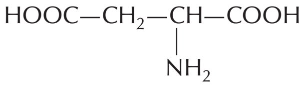
(i) An aliphatic side chain
(ii) A hydroxyl group containing side chain
(iii) A sulphur atom containing side chain
(iv) A side chain containing acidic (carboxylic) group or their amides
(v) A side chain containing basic groups
(vi) A side chain containing aromatic ring

Sample Problem 9 *Amino acids are classified as acidic, basic or neutral depending upon the relative number of amino and carboxyl groups in their molecule. Which of the following are acidic?*

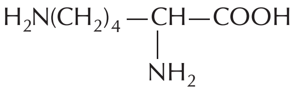
(*a*) 
$(CH_3)_2CH-\underset{NH_2}{CH}-COOH$

(*b*) 
$HOOC-CH_2-CH_2-\underset{NH_2}{CH}-COOH$

(*c*) $H_2N-CH_2-CH_2-CH_2-COOH$

(*d*) 
$HOOC-CH_2-\underset{NH_2}{CH}-COOH$

Interpret (*b,d*) are acidic amino acids because both of them have more number of —COOH groups than that of —NH_2 group.

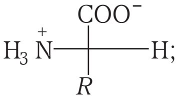
Sample Problem 10 *Lysine,*  $H_2N(CH_2)_4-\underset{NH_2}{CH}-COOH$ *is* **[NCERT Exemplar]**

(*a*) *α-amino acid*
(*b*) *basic amino acid*
(*c*) *amino acid synthesised in body*
(*d*) *β-amino acid*

Interpret (*a,b*) Lysine is α-amino acid because —NH_2 group is attached with α-carbon atom. It is an example of basic amino acid as it has more —NH_2 groups than that of —COOH group.

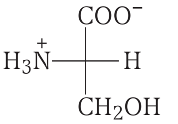
Stereochemistry of the α-Amino Acids

With exception of glycine, all common naturally occurring α-amino acids have an asymmetric α-carbon atom. The chiral amio acids are found within naturally occurring proteins in only one enantiomeric form, which has the following configuration.


; This configuration is S in all cases except for cysteine.

D and L Configuration for α-amino Acids

If refers to the configuration of the α-carbon regardless of the number of asymmetric carbons in the molecule. A D-amino acid has amino group on right and hydrogen on left when —COOH group is up and side chain is down in a Fischer projection of the α-carbon and a L-amino acid has amino group on left. Naturally occurring amino acids have L-configuration.


L-serine or (S) serine

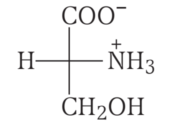
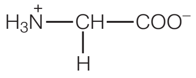
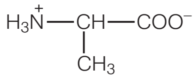
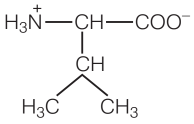
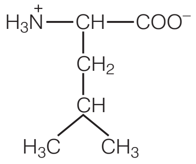
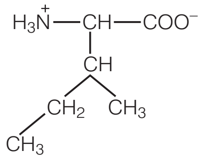
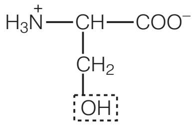
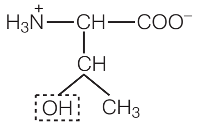
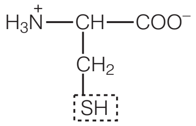
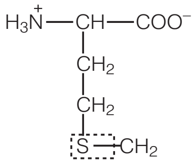
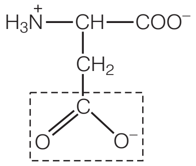
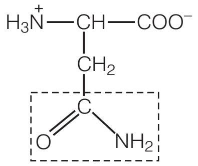
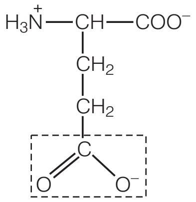
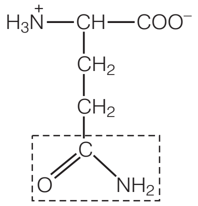
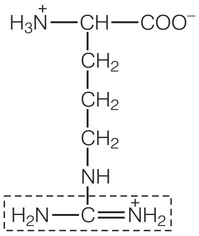
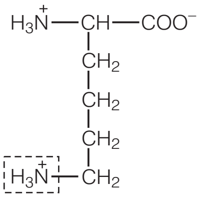
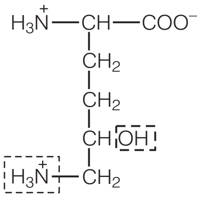
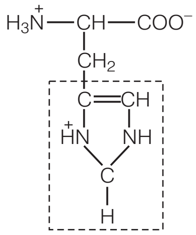

D-serine or (R) serine

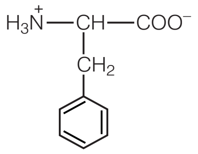
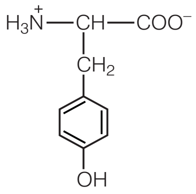
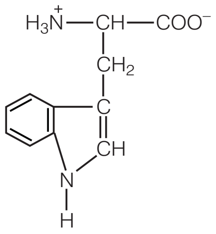
Table 14.1 **Structure of Protein Synthesising Amino Acids**

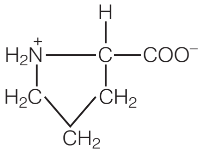
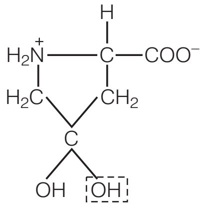
Group I Side Chains with Aliphatic Carbon Chains				
 Glycine (Gly)	 Alanine (Ala)	 Valine (Val)	 Leucine (Leu)	 Isoleucine (Ile)

Group II-Side Chains With –OH Groups		Group III-Side Chains With S Atoms	
 Serine (Ser)	 Threonine (Thr)	 Cysteine (Cys)	 Methionine (Met)

Group IV-Side Chains With Acid Groups or their Amides			
 Aspartate (Asp)	 Asparagine (Asn)	 Glutamate (Glu)	 Glutamine (Gln)

Group V-Side Chains Contain Basic Groups			
 Arginine (Arg)	 Lysine (Lys)	 Hydroxylysine (Hyl)	 Histidine (His)

Group VI-Side Chains Contain Aromatic Rings		
 Phenylalanine (Phe)	 Tyrosine (Tyr)	 Tryptophan (Trp)

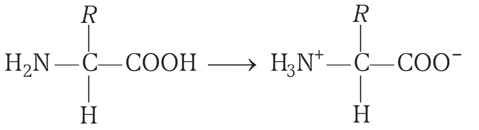
Group VII-Imino Acids	
 Proline (Pro)	 4-hydroxyproline (Hyp)

Essential and Non-Essential Amino Acids

Human body can synthesise 10 out of 20 amino acids found in proteins, these are called **non-essential** or **dispensable amino acids** while the remaining ten, which the human body cannot synthesise, are called **essential** or **indispensable amino acids**. These essential amino acids are required for the growth of the body and their deficiency causes disease like kwashiorkor. The essential amino acids are – Arginine, Valine, Methionine, Leucine, Threonine, Phenylalanine, Histidine, Isolucine, Lysine and Tryptophan.

Zwitter Ion Structure

- Amino acids contain the —COOH group, which is acidic and the —NH_2 group which is basic. In the solid state, an amino acid ordinarily exists as a **Zwitter ion** or as **a bipolar ion,** formed by the transfer of a proton from a —COOH group to an —NH_2 group.



$$H_2N-\underset{\underset{H}{|}}{\overset{\overset{R}{|}}{C}}-COOH \longrightarrow H_3N^+-\underset{\underset{H}{|}}{\overset{\overset{R}{|}}{C}}-COO^-$$

amino acid Zwitter ion form

- Modern researches have proved that the acidic properties of amino acids are due to —NH_3^+ group (which can donate a proton) and basic properties are due to the $-\overset{\overset{O}{\|}}{C}-O^-$ group (which can accept a proton) in a Zwitter ion or 'inner salt'.
- A Zwitter ion behaves like a polar molecule. Within the molecule, there is a (+)ve charge at the nitrogen atom of the amino group and a (–)ve charge at the oxygen atom of the carboxyl group. Overall, the Zwitter ion has no net charge.

Hot Spot 2

ISOELECTRIC Point

Isoelectric point of α-amino acids is also an important topic for JEE Main examination. Generally level of questions based on this topic are from easy to average.

In aqueous solution, Zwitter ions are stable only over a certain pH range. At high H^+ ion concentration (low pH), the $-COO^-$ group picks up a proton and forms a cation (due to the presence of NH_3^+ group) with a (+)ve charge. At low H^+ ion concentration (high pH), the NH_3^+ group loses a proton and forms an anion (due to the presence of $-COO^-$ group) with a (–)ve charge.

$$\underset{\text{cation}}{{}^+NH_3-CH_3COOH} \xleftarrow[\text{Less pH}]{H^+} \underset{\text{Zwitter ion}}{{}^+NH_3-CH_2-COO^-}$$

$$\xrightarrow[\text{More pH}]{} \underset{\text{anion}}{NH_2-CH_2-COO^-}$$

Caution Point *The amino acid can never exist as an uncharged compound at any* pH. *In fairly acidic medium, it exists as cation while in fairly basic medium it exists as an anion. At physiological* pH (≈ 7.3), *an amino acid exists as a dipolar ion called* ***Zwitter ion or inner salt.***

The point (pH range) at which the amino acid molecule has equal positive and negative charges is called the **isoelectric point.** At this point, the amino acids do not migrate in an electric field.

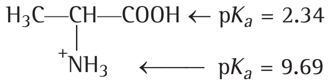
All aminoacids do not have the same isoelectric point. Neutral amino acids have isoelectric point from pH 5.5 to 6.3 (*e.g.,* glycine = 6.1). Acidic amino acids have isoelectric point around 3 (*e.g.,* aspartic acid = 3) and basic amino acids have isoelectric points from pH 7.6 to 10.8 (*e.g.,* Lysine = 9.7)

Amino acids usually shows their lowest solubility in a solution at the isoelectric point, since here, there is a highest concentration of dipolar ion. This property has been used in the separation of different amino acids obtained from the hydrolysis of proteins.

The acidity and basicity constants of amino acids are very low as compared to carboxylic acids and aliphatic amines. The reason being that in α-amino acids, —NH_3^+ and —COO^- groups which acts as acid and base respectively.

α-amino acids have protonated —NH_3^+ group which exerts a strong electron withdrawing inductive effect (–*I* effect) and therefore, increases acid strength. That's why the carboxylic acid groups of the amino acids are so much more acidic (pK_a = 2) than a carboxylic acid such as acetic acid (pK_a = 4.76).

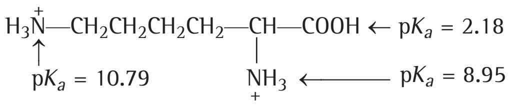
If an amino acid has amino group and one carboxyl group such as alanine, it has two pK_a values. The isoelectric point of this amino acid has the average value of the both pK_a values.



$$H_3C-\underset{\underset{{}^+NH_3\ \longleftarrow\ pK_a = 9.69}{|}}{CH}-COOH \leftarrow pK_a = 2.34$$

$$\text{The isoelectric point, pI} = \frac{2.34 + 9.69}{2} = 6.02$$

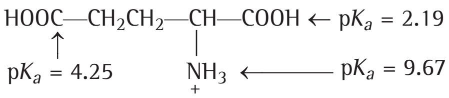
The pI of an amino acid that has an ionisable side chain is the average of the pK_a values of the similarly ionizing group. For example, Lysine :



$$\underset{\uparrow \atop pK_a = 10.79}{\overset{+}{H_3N}}-CH_2CH_2CH_2CH_2-\underset{\underset{+}{NH_3}\ \longleftarrow\ pK_a = 8.95}{\underset{|}{CH}}-COOH \leftarrow pK_a = 2.18$$

$$pI = \frac{8.95 + 10.79}{2} = 9.87$$

Glutamic acid :



$$\underset{\uparrow \atop pK_a = 4.25}{HOOC}-CH_2CH_2-\underset{\underset{+}{NH_3}\ \longleftarrow\ pK_a = 9.67}{\underset{|}{CH}}-COOH \leftarrow pK_a = 2.19$$

$$pI = \frac{2.19 + 4.25}{2} = 3.22$$

Sample Problem 11 *The isoelectric point or* pI *of an amino acid or a protein is*

(a) *the* pH *at which the amino acid or protein has no net charge*

(b) *zero at* pH 7.0

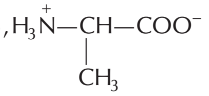
(c) *the* pH *at which the amino or protein is neither hydrophobic nor hydrophilic*

(d) *The measure of the hydropathy of an amino acid or protein.*

Interpret (*a*) At isoelectric point, an amino acid exist only as Zwitter ion giving net charge equal to zero.

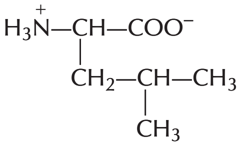
Sample Problem 12 *In which of the following case, the forms of amino acid and* pH *is not correctly matched?*

(*a*) *Alanine* : pH = 3,



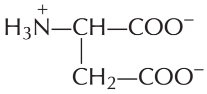
$$\overset{+}{H_3N}-\underset{\underset{CH_3}{|}}{CH}-COO^-$$

(*b*) *Leucine* : pH = 10,



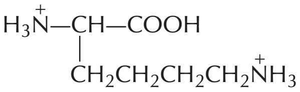
$$\overset{+}{H_3N}-\underset{\underset{CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3}{|}}{CH}-COO^-$$

(*c*) *Aspartic acid* : pH = 9,



$$\overset{+}{H_3N}-\underset{\underset{CH_2-COO^-}{|}}{CH}-COO^-$$

(*d*) *Lysine* : pH = 3,



$$\overset{+}{H_3N}-\underset{\underset{CH_2CH_2CH_2CH_2\overset{+}{N}H_3}{|}}{CH}-COOH$$

Interpret (*a*) Isoelectric point for neutral amino acids ranges from pH 5.5 to 6.3. Acidic amino acids have isoelectric point around 3 while basic amino acids have ranges from pH 7.6 to 10.8. At isoelectric point amino acid exist as Zwitter ion. At low pH it exists as cation and at high pH it is exists as anion. Hence, alanine (pH = 3) will exists as cation.

Sample Problem 13 *Give the* pOH *range for isoelectric point of the amphoteric ion of an amino acid*

(*a*) 5.5 *to* 6.3
(*b*) 2.5 *to* 5.0
(*c*) 7.7 *to* 8.5
(*d*) 9.0 *to* 10.7

Interpret (*c*) The pH at which a particular amino acid does not migrate under the influence of an electric field is called isoelectric point of that amino acid. The pH range for the isoelectric point is from 5.5 to 6.3 or the pOH range for the isoelectric point is from 7.7 to 8.5.

Check Point 2

1. The amino acids in water acts as an ampholyte. Explain.
2. In an electric field, the amino acids migrates towards cathode when pH is below the isoelectric point while it migrates towards anode when pH is higher than isoelectric point. Explain.
3. How does the proline differ from the other α-amino acids in structure?
4. Give reason, "amino acids have relatively higher melting point as compared to corresponding halo acids".
5. The monoamino monocarboxylic acids have two pK values. Explain.
6. Amino acids behave like salts rather than simple amines or carboxylic acids. Explain. **[NCERT Exemplar]**

14.3 Proteins

The term protein is derived from the Greek word 'proteios' meaning of the 'first rank' because the proteins are ranked first amongst the natural polymer essential for the growth and maintenance of life. These are, infact the polymers of amino acids (specifically α-amino acids) and make up to 15% by mass of our body.

The chief sources of proteins are pulses, cheese, milk, egg, peanut, fish, meat etc. The protein content of these sources are

Soyabean (pulse)	= 54%
Meat	= 22%
Egg	= 14%
Wheat	= 12%
Milk	= 4%

Table 14.2 **Examples of Some Proteins and Their Biological Functions**

S.N.	Class of proteins	Example	Function
1.	Structural proteins	Collagen	Connective tissue
2.	Enzumes	DNA polymerase	Replicate and repair DNA
3.	Transport protein	Haemoglobin	Transportation of respiratory gases (O_2 and CO_2)
4.	Contractile protein	Active myosin	Responsible for contraction of muscles
5.	Protective proteins	Antibodies	Complex with foreign proteins
6.	Hormones	Insulin	Regulate glucose metabolism
7.	Toxins	Snake venom	Incapcitate prey

Proteins are important components of most foods. In the digestive system, proteins are broken down into small molecules called **α-amino acids.** These molecules are then reassembled in cells to form other proteins required by the body.

- A pure protein is tasteless, odourless and colourless. Chromoproteins are coloured. Most of proteins are hydrophilic. They do not have sharp melting point.
- All proteins on partial hydrolysis give peptide of varying molecular masses, which on complete hydrolysis gives α-amino acids.

$$\text{Proteins} \xrightarrow{\text{Hydrolysis}} \text{Peptides} \xrightarrow{\text{Hydrolysis}} \alpha\text{-amino-acids}$$

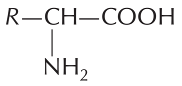
- All the proteins are laevorotatory due to the presence of asymmetric carbon in α-amino acids.

Sample Problem 14 *Amino acids can be classified as α-, β-, γ-, δ-, and so on depending upon the relative position of amino group with respect to carboxyl group. Which type of amino acids form polypeptide chain in proteins?*

[NCERT Exemplar]

(a) *α-amino acids* (b) *β-amino acids*
(c) *γ-amino acids* (d) *δ-amino acids*

Interpret (a) Because on complete hydrolysis, proteins give α-amino acids.

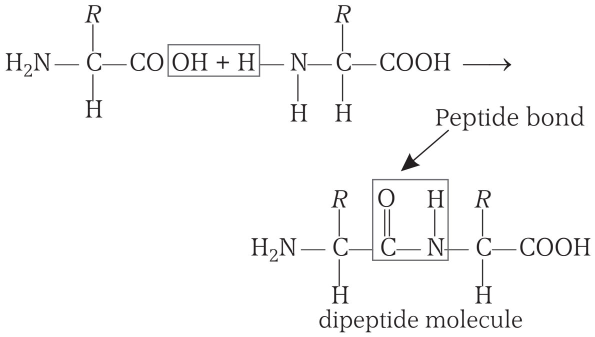


$$R-\underset{\underset{NH_2}{|}}{CH}-COOH$$

Peptide Bond and Protein Structure

Amino acids may be joined together by an amide linkage called **peptide linkage** (—CO—NH—). A water molecule is always eliminated in forming a peptide linkage.

The parts of amino acids in a peptide (after liberation of water molecules) are called **amino acid residues.**



$$H_2N-\underset{\underset{H}{|}}{\overset{\overset{R}{|}}{C}}-CO\boxed{OH + H}-\underset{\underset{H}{|}}{N}-\underset{\underset{H}{|}}{\overset{\overset{R}{|}}{C}}-COOH \longrightarrow$$

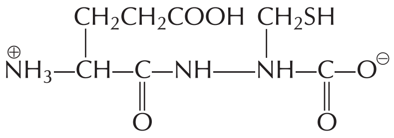
Peptide bond

$$H_2N-\underset{\underset{H}{|}}{\overset{\overset{R}{|}}{C}}-\boxed{\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}}-\underset{\underset{H}{|}}{\overset{\overset{R}{|}}{C}}-COOH$$

dipeptide molecule

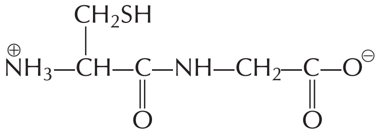
- Peptide are amides formed by the condensation of amino group of one α-amino acid with the carboxyl group of another molecule through peptide linkage, with the elimination of a molecule of water.
- The molecule derived from two amino acids containing a single peptide linkage is called a **dipeptide,** that derived from three amino acids is termed as a **tripeptide.** The peptides having 2-10 amino acid residues are called **oligopeptides** while those with greater than 10 amino acid residues are called **polypeptides**.

Sample Problem 15 *A tripeptide (X) on partial hydrolysis gave two dipeptides Cys-Gly and Gly-Cys i.e.,*



$$\overset{\oplus}{N}H_3-\overset{\overset{CH_2CH_2COOH}{|}}{CH}-\underset{\underset{O}{\|}}{C}-NH-\overset{\overset{CH_2SH}{|}}{NH}-\underset{\underset{O}{\|}}{C}-O^{\ominus}$$

and

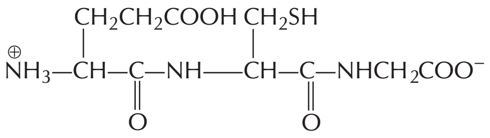


$$\overset{\oplus}{N}H_3-\overset{\overset{CH_2SH}{|}}{CH}-\underset{\underset{O}{\|}}{C}-NH-CH_2-\underset{\underset{O}{\|}}{C}-O^{\ominus}$$

Identify tripeptide.

(a) *Gly-Cys-Gly* (b) *Gly-Gly-Cys*
(c) *Cys-Gly-Glu* (d) *Glu-Cys-Gly*

Interpret (d) Since the tripeptide on hydrolysis give two dipeptides, Glu-Cys and Cys-Gly, hence cystein must be in between glutamic acid and glycine.



$$\overset{\oplus}{N}H_3-\overset{\overset{CH_2CH_2COOH}{|}}{CH}-\underset{\underset{O}{\|}}{C}-NH-\overset{\overset{CH_2SH}{|}}{CH}-\underset{\underset{O}{\|}}{C}-NHCH_2COO^-$$

Glu-Cys-Gly

- **Polypeptide** with molecular weight greater than 10,000 u is termed as a **protein**. Proteins generally have more than 70 amino acid residues, but a polypeptide with fewer α-amino acids may also be called a **protein** if it has a well defined conformation characteristic of a protein such as insulin (contains 51 amino-acids).

- Polypeptides are amphoteric in nature because of the presene of terminal ammonium and carboxylate ions as well as the ionised side chains of amino acid residues. Therefore, like α-amino acids, they neutrlise both acids as well as bases and possess isoelectric point. At isoelectric points, polypeptides have least solubility and hence can be separated.

Composition of Proteins

An approximate composition of proteins is as follows :

Carbon = 50 – 53%
Oxygen = 23 – 25%
Nitrogen = 16 – 17%
Hydrogen = 6 – 7%
Sulphur = 1%

Other elements such as phosphorus in nucleoproteins, iron in haemoglobin and iodine in thyroid are also present.

Classification of Proteins

Proteins can be classfied on the basis of their chemical composition and functions or on the basis of their physical properties.

(I) **Based on the molecular structure and the function they perform,** proteins can be further classified as

(i) **Fibrous proteins** These are long and thread like molecules and tend to lie side by side to form fibres. They are held together by intermolecular H-bonding and hence insoluble in water *e.g.,* keratin (in hair, skin, nails, horn and wool), fibroin (in silk) and myosin (in muscle).

(ii) **Globular proteins** Molecules of globular proteins are folded with spheroidal shapes. The folding takes place in such a way that the lipophilic parts are turned inward and hydrophilic parts tend to move towards the surface, Hydrogen bonding is chiefly intramolecular. Hence, they are soluble in water, acids, bases and salts *e.g.,* albumin (in eggs), haemoglobin (in blood), all enzymes and most hormones (insulin).

(II) **On the basis of their physical properties,** proteins can be classified as

(a) **Simple proteins** They give only amino acids on hydrolysis, *e.g.,* albumin, globulins.

(b) **Conjugated proteins** These contain a non-protein part (prosthetic group). The prosthetic group in a protein controls its biological functions. The common prosthetic group in the proteins are tabulated below

Table 14.3 **Examples of Some Conjugated Proteins**

S.N.	Name of protein	Prosthetic group
1.	Glyco-protein	Sugars (carbohydrates)
2.	Nucleo-protein	Nucleic acid
3.	Lipo-protein	Lipid
4.	Phospho-proteins	Phosphoric acid
5.	Chromo-protein	Pigments having metals Cu, Fe (haemoglobin)

(c) **Derived proteins** These are obtained by the hydrolysis of higher proteins with acids, alkalies or enzymes. *e.g.*, peptones, proteases and denatured proteins.

Structure of Proteins

The structure of protein is studied under different levels as primary structure, secondary structure, tertiary structure and quaternary structure.

(a) Primary Structure

The number and sequence of amino acids in the polypeptide chain constitute the primary structure. It shows how the atoms in protein molecule are joined to one another through covalent bonds to form chains. **Fredrick Sanger,** for the first time determined the amino acid sequence of a protein (*i.e.,* insulin) and for this work he was awarded by the Nobel Prize (in 1958). The nature and the sequence of the amino acids determines the three dimensional structure and properties of proteins.

Determination of sequence of amino acids in a peptide chain It can be determined either by analyzing the products of partial hydrolysis or by end group analysis.

(i) **Partial hydrolysis** In partial hydrolysis method, dilute acids or enzymes are used to break the polypeptide chain into small fragments. By knowing the structures of these small fragments, the sequence of amino acids in a polypeptide chain is determine. For example, partial hydrolysis of a tetra peptide containing Ala, Gly, Phe and Val yields a tripeptide Gly–Phe–Val and a dipeptide Ala–Gly.

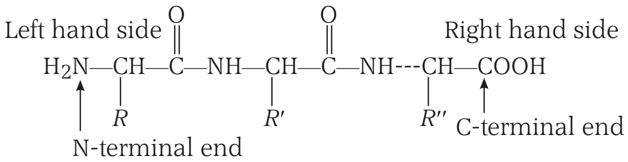
$$\text{Tetrapeptide} \xrightarrow{\text{Hydrolysis}} \text{Gly–Phe–Val} + \text{Ala–Gly}$$

Since, dipeptide shows that Ala is linked to Gly, the amino acids in the tetrapeptide are linked in the following sequence.

$$\text{Ala}\underset{1.}{\mid}\text{Gly}\underset{2.}{\mid}\text{Phe—Val}$$

Cleavage at 1. gives tripeptide and at 2. gives dipeptide.

(ii) **Terminal residue analysis or End group analysis** Peptide structures are written in such a way that the amino group is at the left and carboxy group is at the right. Hence, the amino end is called the N-terminal and carboxy end is called C-terminal. Amino groups of all amino acids except N-terminal amino acid and carboxy group of all amino acids except C-terminal amino acid are involved in amide bond formation. In other words, amino group is free at the N-terminal end and carboxy group is free at the C-terminal end.



$$H_2N-\underset{R}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-NH-\underset{R'}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-NH\text{---}\underset{R''}{\underset{|}{CH}}-COOH$$

The primary structure of proteins dissolved in water is not disrupted by heating above 80°C. The difference in chemical and biological properties of various proteins and peptides arise due to the difference in their primary structure. *e.g.,* in haemoglobin (blood protein) which carries oxygen, there are 574 amino acid units in a definite sequence but the replacement of only one α-amino acid results in defective haemoglobin. This is the cause of a disease, called **sickle cell anaemia.** In the patients suffering from this disease, the defective haemoglobin precepitates causing the cells to sickle shaped and sometimes even makes them burst leading ultimately to death. Normal haemoglobin has–Val–His–Len–Thr–Pro–Glu–Lys. On the other hand, sickle cell haemoglobin structure.

Val–his–Len–Thr–Pro–Val–Glu–Lys structure.

(b) Secondary Structure

Most of the long polypeptide chain are folded or coiled to produce specific three-dimensional structures. These are called **secondary structure** and give idea about shape of the conformation of the protein molecule. Depending upon the size of *R* groups, three major types of secondary structure (α-helix, β-conformation, β-pleated sheet and triple-helix) have been identified.

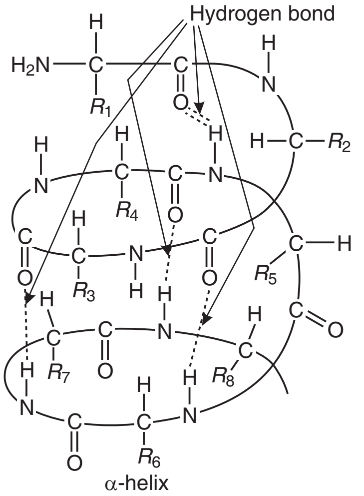


Fig. 14.1 α-helix structure of proteins

- Imagine, you can coil a polypeptide chain around an invisible rod. This results in a structure called a **helix.** The most common form of coiling is the right handed **α-helix.** In α-helix, the size of *R* groups is quite large and H-bonds are formed between the $>$C=O of one amino acid and the ($>$N—H) of the fourth amino acid residue in the chain. Only right handed α- helix exists in nature, since it is more stable than left handed helix. In this form, there are 3.6 amino acid residues per complete turn. The rise along the central axis is 1.5 Å per residue.
- The structure is stabilized by intramolecular hydrogen bonds between an amide hydrogen ($>$N—H group) and the carbonyl oxygen ($>$C=O group) of the fourth amino acid residue away in the peptide chain.

$$>C{=}O\text{---}H{-}N<$$

- Although the hydrogen bond is fairly weak, their large number stabilizes the structure. The imino acid, **proline** along with amino acids **glycine, serine** do not fit into the normal α-helix. They disrupt the α-helical structure and cause **sharp bends** in the direction of the chain. They are called **helix-breakers.** α-helix is found in both fibrous and globular proteins. Fibrous proteins such as α-keratin in hair, nail, wool, skin, beaks, claws and myosin in muscle have α-helix structure. Globular proteins also contain segments of α-helix, because of the α-helical structure, human hair fibres are stretchable and elastic to some extent. When hair is stretched, the H-bonds are broken but when the stretching force is removed, the H-bonds are reformed.

Sample **Problem 16** *Proteins are found to have two different types of secondary structures viz α-helix and β-pleated sheet structure. α-helix structure of protein is stabilised by*

[NCERT **Exemplar]**

(*a*) *peptide bonds*
(*b*) *van der Waals' forces*
(*c*) *hydrogen bonds*
(*d*) *dipole-dipole interaction*

Interpret (*c*) In α-helix, hydrogen bonds are present between —NH group of one amino acid residue to the $>$C=O group of another amino acid residue.

- **β-conformation** (β-pleated sheet) results from hydrogen bonding between two peptide chains. In this conformation, the polypeptide chains lie side by side in a *zig-zag* manner with alternate —*R* groups on the same side situated at fixed distances apart. The chains may be parallel or antiparallel. In a parallel chain β-pleated sheet, the N-atoms point in the same direction, while in the antiparallel chain β-pleated sheet, alternate chains are oriented in the same direction. The antiparallel structure permits maximum hydrogen bonding. The β-conformation is found in fibrous proteins.

- Keratin protein (present in hair) has parallel β-pleated sheet structure while the silk protein, fibroin has anti-parallel β-pleated sheet structure.

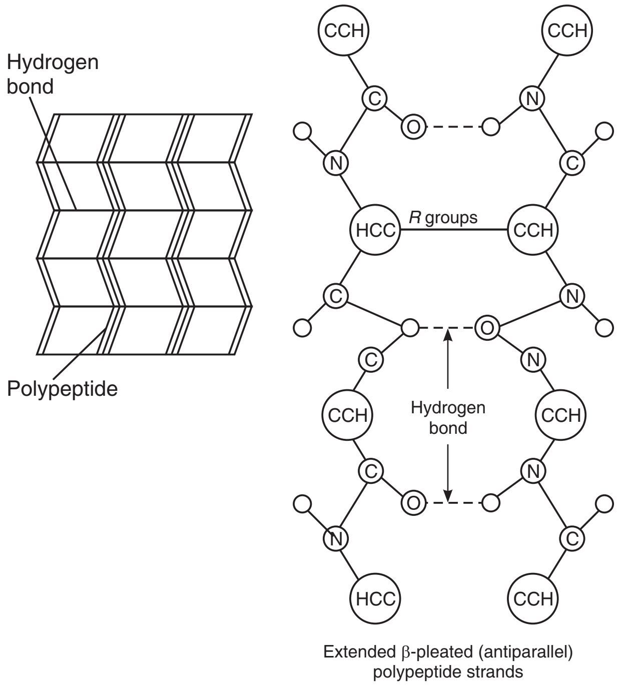


Fig. 14.2 β-pleated structure

- Three loosely coiled helical polypeptide chains can wind around each other to form a stiff cable. This rod like structure is called a **triple helix.** It is very strong and relatively rigid. The triple helix is found mainly in collagen, the major structural protein of skin, bones, teeth, tendons and cartilage. It can be seen that the triple helix structure is more extended and stabilised by hydrogen bonds between the chains, while in the α-helix, it is between the amino acid residues in the same chain.

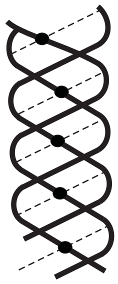


Fig. 14.3 Triple helix

- A protein may have the different secondary structures throughout its length. Some parts may have α-helix structure, while other may have β-pleated sheet structure. Some parts of the chain may even have no secondary strcutrue at all. These structureless parts are called **random coils** and the arrangement is called **random coil arrangement.** This type of structure is flexible, changing and statistically random. Synthetic polylysine exists as a random coil.

(c) **Tertiary structure** The tertiary structure of a protein is its three dimensional shape that arises from further foldings of its polypeptide chains, foldings superimposed on the coils of the α -helixes. This folding brings together **active amino acids,** which are otherwise scattered along the chain, and may form a distinctive **cavity** or **cleft** in which the substrate is bound. At normal pH and temperature, each protein will take up a tertiary structure that is energetically most stable. In proteins consisting of a single polypeptide chain, the tertiary structure determines the overall shape of the molecule. So, proteins are called **fibrous proteins** when they form thin, long threads and **globular proteins,** if very compact.

- The tertiary structure is specific to a given amino acid sequence and is called the native shape of the protein. Thus, primary structure of a protein dictates its tertiary structure.

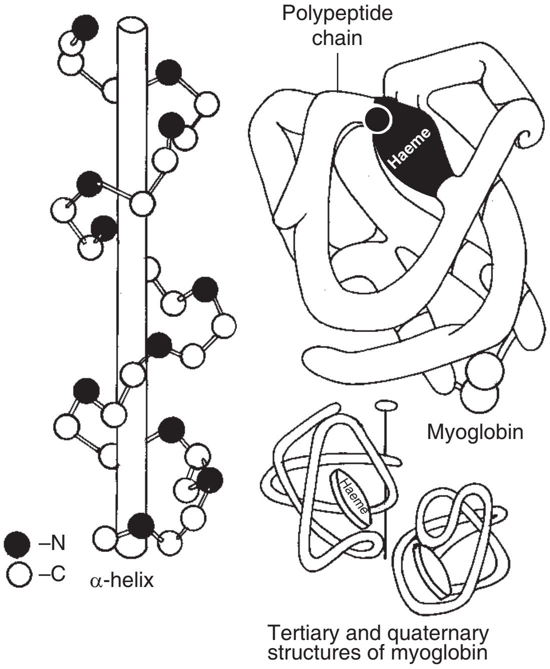


Fig. 14.4 Structure of proteins

(d) Quaternary Structure

It is shown by proteins containing more than one polypeptide chain. Two or more polypeptide chains may associate to give rise to the quaternary structure. These are held together by non-covalent forces such as hydrogen bonds, electrostatic interactions and van der Waals' interactions.

If the protein consists of identical units it is said to have a **homogeneous quaternary structure**, *e.g.,* the isozymes H_4 and M_4 of **lactic dehydrogenase** (LDH) and the enzyme phosphorylase. If the units are dissimilar, the protein is said to have a **heterogeneous quaternary structure,** *e.g.,* haemoglobin which consists of two α chains and two β chains.

Denaturation of Proteins

A protein that is in a biologically inactive form is said to be in a denatured state. The conformational change that produces this state is called **denaturation of proteins.** Denatured proteins usually forms large aggregates that are precipitated from solution. This process is called **coagulation. During denaturation no peptide bonds are broken,** *i.e.,* chemical composition or primary structure remains unaffected.

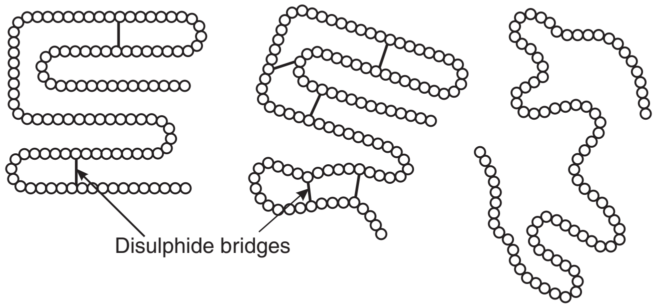


Fig. 14.5 Denaturation of proteins

The relatively weak, non-covalent interactions are disrupted in the denaturation of a protein.

The following can bring about the denaturation of proteins

(a) **Heat** When you fry or boil an egg, you bring about a denaturation of egg proteins. The reason why bacteria are destroyed at high temperatures that exist in an autoclave is that their proteins are denatured.

(b) **Exposure to organic solvents** Organic solvents such as ethanol and rubbing alcohol can denature proteins. Alcohol is rubbed on the skin, before an injection to kill surface bacteria by denaturing bacteria proteins, thus preventing infection.

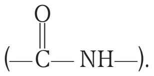
(c) **Exposure to acid and bases** Strong acids and bases can denature proteins by disrupting salt bridges and hydrogen bonds. Prolonged treatment with strong acids will bring about hydrolysis of peptide bonds of a protein.

(d) **Exposure to salts of heavy metal ions** Cation of metals such as Hg^{2+}, Ag^{+} and Pb^{2+} interfere with the disulphide bonds and salt bridges that stabilize the protein structure and bring about denaturation. Hence, mercury and lead are poisonous to the human system as they denature proteins in the body. (The first aid treatment for a person who has ingested a heavy metal is to give a large dose of egg whites or milk, both of which are rich in proteins. The proteins in them form complexes with the heavy metals in the stomach, temporarily preventing absorption of the metals into the blood. The patient should later be given an emetic to get rid of the poison.)

Test for Proteins

With the help of following tests, presence of proteins can be checked.

(i) **Biuret test** Protein is gently warmed with 10% solution of NaOH and then a drop of dil. $CuSO_4$ solution is added. Formation of reddish-violet colour indicates the presence of peptide linkage



$(-\overset{\overset{O}{\|}}{C}-NH-)$.

This test is also given by the compound biuret, obtained by urea on heating.

(ii) **Xanthoprotic test** Certain proteins give yellow colour with conc. HNO_3. This yellow colour is same which is formed on skin when skin comes on contact with conc. HNO_3.

(iii) **Millon's test** When Millon's reagent (a solution of mercurous and mercuric nitrates in nitric acid containing some nitrous acid) is added to a protein solution, a white precipitate is obtained. On heating it turns to red precipitate or colour.

(iv) **Ninhydrin test** When a protein is boiled with a dilute solution of ninhydrin, a violet colour is obtained.

This test is given by all proteins.

(v) **Nitroprusside test** When sodium nitroprusside is added to proteins containing —SH group, a violet colour is obtained.

Sample **Problem 17** *Proteins when heated with conc.* HNO_3 *give a yellow colour. This is*

(a) *Hoppe's test*
(b) *acid-base test*
(c) *Biuret's test*
(d) *Xanthoprotic test*

Interpret (*d*) Protein + conc. $HNO_3 \xrightarrow{\Delta}$ yellow colour

This test is called Xanthoprotic test. It is given by those proteins which consists of α-amino acid containing benzene ring, *e.g.,* tyrosine.

Check Point 3

1. Why do polypeptide have amphoteric nature? **[NCERT Exemplar]**
2. Coagulation of egg white on boiling is an example of denaturation of proteins. Explain it in terms of structural changes. **[NCERT Exemplar]**
3. Explain the terms primary and secondary structure of proteins. What is the difference between α-helix and β-pleated sheet structure of proteins? **[NCERT Exemplar]**
4. Why are bacteria destroyed at high temperature?
5. Why is alcohol rubbed on the skin, before an injection?

14.4 Enzymes

Kuhne (1878) coined the term enzyme. **Buchner** (1897, 1903) isolated enzmes (including zymase from yeast for the first time). **Sunner** found that enzymes are protinaceous. He crystallised the first enzyme, urease from jack bean.

An enzyme is a specialised protein produced within an organism which is capable of catalysing a specific chemical reaction. Since the enzymes act as catalyst, they are sometimes referred to as **biocatalysts.** A catalyst alters the rate of a chemical reaction, usually without undergoing any change itself. In this respect an enzyme differs from a normal catalyst. The enzyme may participate in a reaction by combining with the substrate. Ultimately, however, it is set free.

Some examples of enzymes along with the reaction, they catalyse are as follows

Table 14.4 **Enzymes**

S.N.	Enzymes	Reaction catalyse
1.	Amylase	Starch to *n* glucose
2.	Maltase	Maltose to (2) glucose
3.	Lactase	Lactose to glucose + galactose
4.	Invertase	Sucrose to glucose + fructose
5.	Pepsin	Proteins to amino acids
6.	Trypsin	Polypeptides to α-amino acids
7.	Urease	Urea to ammonia + CO_2
8.	Nuclease	DNA, RNA to nucleotides
9.	Carbonic anhydrase	H_2CO_3 to $H_2O + CO_2$
10.	DNA polymerase	Deoxyribonucleotide triphosphate to DNA
11.	RNA polymerase	Ribonucleotide triphosphate to RNA

Nomenclature and Classification of Enzymes

Enzymes are generally named by adding **-ase** to the root indicating the substrate on which the enzyme acts. This system was provided by **Duclau x** (1883). Thus, **fumarase** catalyses the conversion of fumaric acid to malic acid.

- The **International Union of Biochemistry report of 1962** (revised in 1964) contains a scheme for the classification of enzymes. *Enzymes have been divided into following six groups, viz.*

(a) Oxidoreductases

They include a large number of enzymes (221 are listed). They bring about the main energy yielding reactions of living tissue. Oxidoreductases include **oxidases** and **dehydrogenases.** They act by transferring electrons and hydrogen ions.

(b) Transferases

They are concerned with the transfer of a group of atoms from one molecule to another. Oxidoreductases and transferases together represent over half the enzymes known.

(c) Hydrolases

Complex molecules undergo cleavage, and the elements of H_2O are added across the bond cleaved by the action of hydrolases.

(d) Lyases

They may work in two ways. A group of atoms may be removed from the substrate leaving double bonds, or groups may be added to double bonds without hydrolysis, oxidation or reduction. The enzymes act on the following bonds : C—C, C—O, C—N, C—S and C—*X*.

(e) Isomerases

They catalyse reactions which bring about intramolecular rearrangement of atoms in substrates.

(f) Ligases (Synthetases)

They catalyse reactions in which the pyrophosphate bond of ATP is broken down and linkage takes place between two molecules. These enzymes form the following bonds : C—O, C—S, C—N and C—C.

Table 14.5 **Types of Reactions Shown by Enzymes**

S.N.	Enzymes	Reactions
1.	Oxidoreductases	Oxidation-reduction reactions
2.	Transferases	Group transfer reactions
3.	Hydrolases	Hydrolytic reactions (addition of H_2O)
4.	Lyases	Addition or loss of groups to double bonds
5.	Isomerases	Isomeration reactions
6.	Ligases	Synthesis by condensation of two groups requiring ATP

- In another system of classification, the name of the enzyme is derived from its substrate *e.g.,* carbohydrases, proteases, dehydrogenases, oxidases, decarboxylases, hydrases, isomerases, transferases, amidases and esterases.

Mechanism of Enzyme Action

There is a very close structural relationship between the molecular surface of an enzyme and its substrates. Enzyme are protein molecules with definite surface geometry. The functional groups of the enzyme are exactly complementary to those of the substrate. Only particular types of substrate molecules will fit with a given enzyme molecule for example, substrates A and B will fit into the enzyme E but not substrate C, this is referred to as a **lock-and-key** mechanism. Thus, reactions involving A and B will be speeded up but not reactions involving C.

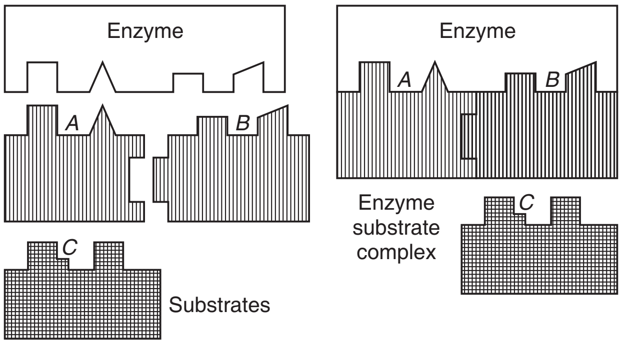


Fig. 14.6 Diagram illustrating how only particular substrates react with an enzyme

The **enzyme** enters into a chemical combination with the **substrate** to form an **enzyme-substrate complex** (Michaelis-Menton hypothesis).

$$E + S \longrightarrow ES$$

The enzyme-substrate complex then breaks down to give the products of reaction. The enzyme is released and can be used over and over again.

$$ES \longrightarrow E + \text{products}$$

Features of Enzymes

(a) Specificity

Enzymes show striking specificity. They catalyse specific reactions of specific substrates. Some enzymes are so specific that they catalyse only one type of substrate molecule. The specificity may extend to only one isomer of a substrate. *e.g.,* The enzyme chymotrypsin catalyses the hydrolysis of acetyl-L-phenyl- alanine methyl ester, but is inert to the D isomer.

(b) Required in Small Amount

Only one enzyme can catalyse a large number of substrate molecules. In other words, enzymes are required in very small amounts.

(c) Activation Energy

Enzymes alter the speed of a chemical reaction. In increasing the speed, they lower the energy of activation of a reaction, thus enabling it to occur at ordinary physiological temperatures. When reactions proceed from one direction to another they have to overcome an energy barrier called the **activation energy.**

Normally only a small part of the total number of molecules in a compound contain enough energy to react. Application of heat enables a larger proportion of molecules to overcome the activation energy barrier. However, living systems are relatively isothermal, *i.e.*, they do not have large temperature differences. They, therefore, employ enzymes to activate the molecules of the reacting compounds. When the enzyme combines with the substrate to form the enzyme-substrate complex, the energy level of the substrate is raised, and it reacts faster. Enzymes increase the speed of a chemical reaction thousands of times by bringing about mutual contact of reacting compound. The coming together of these compounds is no longer a matter of chance, but becomes a certainty.

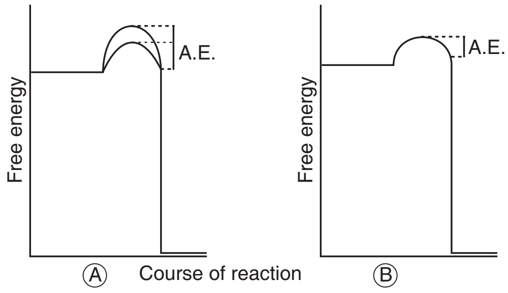


Fig. 14.7 Change in activation energy (A.E.) (A) Reaction without enzyme, (B) Reaction with enzyme.

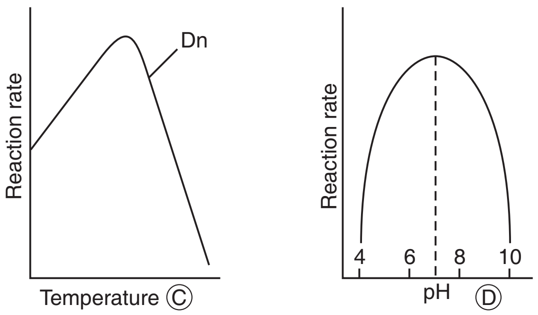


Fig. 14.8 (C) Effect of temperature on the rate of enzymatic reaction. Dn represents the point where thermal denaturation of the enzyme beings (44–45°C). (D) Effect of pH on the rate of enzyme reaction. The dashed line indicates optimum pH.

Enzymes, as we call them biological catalyst work in the same manner as a catalyst does, *i.e.,* by lowering the energy of activation of chemical reaction.

Factors Affecting Enzyme Activity

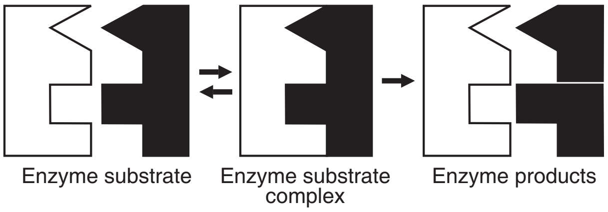
(a) **Effect of temperature** Enzyme action is greatly affected by temperature. If the temperature is increased by 10°C, the rate of most chemical reactions is doubled. However, at 40–60°C, there is loss of enzyme activity because denaturation of proteins occurs at this temperature.

(b) **pH** At optimum pH, the activity of enzyme is maximum. For most **enzymes,** the effective pH range is 4–9. Below and beyond these limits, denaturation of enzymes takes place. The optimum pH for pepsin is 2.0 and for trypsin is 8.0.

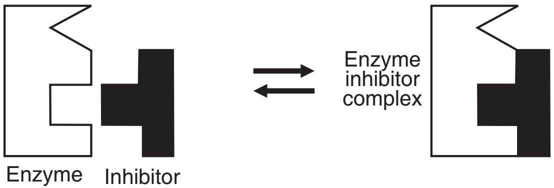
(c) **Ions** Enzyme activity is affected by H^+ ion concentration and other ionic concentrations. Some enzymes require a loosely bound cation such as Mg^{2+}.

(d) **Concentration** Enzyme concentration affect the rate of a reaction. If the substrate concentration is increased, the rate of enzyme reaction also rises. Beyond a certain point, however, the enzyme becomes saturated with substrate molecules. Further increase in reaction velocity occurs only if the enzyme concentration is increased. For example, during starvation the supply of the substrate (glucose) decreases and glycolysis is depressed. Conversely increase in glucose concentration accelerates the rate of reaction upto the point when enzyme is saturated with glucose.

(e) **Inhibitiors** Certain compounds (*e.g.,* drugs, poisons) combine with an enzyme but do not serve as substrates. They thus block catalysis by the enzyme and function as **inhibitors.** The inhibitors usually closely resemble the substrate in structure. The enzyme and the inhibitor form an enzyme-inhibitor complex which is inactive.



(a) Enzyme action



(b) Inhibition

Fig. 14.9 Mechanism of enzyme action inhibition.

- Inhibition may be **competitive** or **non-competitive.** In competitive inhibition both inhibitor and substrate molecules compete for binding with the enzyme. If the inhibitor is in sufficiently high concentration, it displaces the substrate molecules. For example, sulphanilamide is a competitive inhibitor for a bacterial enzyme that incorporates *p*-amino benzoic acid into folic acid. Competitive inhibition can be reversed by increasing the concentration of the substrate. In **non-competitive inhibition**, the inhibitors (poisons) react with the various functional groups of the enzyme. They inhibit the *normal reactions catalysed by the enzyme and result in death. Non-competitive inhibition cannot be reversed by increasing the concentration of the substrate*.

Check Point 4

1. Some enzymes are named after the reaction, where they are used what name is given to class of enzymes which catalyse the oxidation of one substrate with simultaneous reduction of another substrate. **[NCERT** Exemplar]
2. Enzymes are called biological catalyst, why? Also tell, how do enzymes differ from usual catalysts?
3. At high temperature enzymes loss their activity, explain why?

14.5 Vitamins

These are essential dietary factors required by an organism in minute quantities. Vitamins are not utilized in cell building or as energy source but they act as catalysts (coenzymes) in biological processes. In general, the fresh natural foods contain all necessary vitamins in appropriate amount, but human beings (and sometimes other animals) take food which is prepared by some processes result in loss or deficiency of some vitamins in food. Remember vitamins are not synthesised in the body and hence should be supplied in diet. Their deficiency causes specific diseases (avitaminosis).

Classification of Vitamins

These are classified into two groups

(a) **Fat soluble vitamins** These are vitamin A, D, E and K.

(b) **Water soluble vitamins** These are vitamin B and vitamin C. Water soluble vitamins must be supplied regularly in diet because they are excreted in urine and cannot be stored in our body (except B_{12}).

Caution Point *Excess of vitamins specially fat soluble vitamins is also harmful and vitamin pills should not be taken without the advice of doctor. Fat soluble vitamins are stored in liver and adipose tissues (fat storing tissues).*

- Vitamins catalyze biological reactions in very low concentration, therefore the daily requirement of any vitamin for any individual is extremely small.
- The sources and diseases caused by the deficiency of different vitamins are tabulated below

Table 14.6 **Vitamins : Sources and Deficiency Diseases**

Name of vitamin	Sources	Deficiency disease
Vitamin A (Retinol or Axerophthol, $C_{20}H_{30}O$)	Fish liver oil	Xerophthalamia (hardening of cornea)
Vitamin B_1 (Thiamine or Aneurin, $C_{12}H_{18}N_4SOCl_2$)	Green vegetables, milk	Beri-Beri (disease of nervous system)
Vitamin B_2 (Riboflavin or Lactoflavin, $C_{17}H_{20}N_4O_6$)	Vegetables, milk, liver, egg white, kidney	Dark red tongue dermatitis, cheilosis
Vitamin B_3 (Pantothenic acid, $C_9H_{17}O_5N$)	All food, more in yeast, liver, kidneys tomatoes	Dermatities in cocks, retarded body and mental growth
Vitamin B_5 (Nicotinic acid or Niacin, (C_5H_4N—COOH)	Fresh meat, liver, fish, cereals, milk, pulses	Pellagra, dermatities
Vitamin B_6 (Pyridoxine or adermin, $C_8H_{11}O_3N$)	Grams, molasses, egg yolk meat	Savere dermatitis, convulsions
Vitamin H (Biotin, $C_{10}H_{16}N_2O_3S$)	Yeast, liver, kidney milk	Dermatitis, loss of hair and paralysis
Vitamin B_{12} (Cyanocobalamine, $C_{63}H_{88}O_4$ $N_{14}PCo$)	Liver of ox, sheep, pig, fish etc.	Pernicious anaemia
Vitamin C (Ascorbic acid, $C_6H_8O_6$)	Citrus fruits, green vegetables	Scurvy
Vitamin K (K_1 and K_2) (Phylloquinone, $C_{13}H_{46}O_2$)	Cereals, leafy vegetables	Hemorrhagic conditions, increased blood clotting time
Vitamin D (Ergocalciferol, $C_{28}H_{44}O$)	Synthesized in skin cells in the presence of sunlight, liver, egg yolk, meat and milk	Rickets with osteomalacia, soft and fragile teeth
Vitamin E (Tocopherol, $C_{29}H_{50}O_2$)	Wheat germ oil, cotton seed oil, soyabean oil	Sterility (impotency), muscular weakness.
Coenzyme Q_{10}	Chloroplast (green plants), mitochondria (of animals)	Low order of immunity of body against many diseases.

Caution Point *Provitamins are the biologically inactive compounds which have almost similar structure as vitamins and can be converted into active vitamins.*

Sample **Problem 18** *Which one of the following vitamin is responsible for the coagulation of blood?* **[NCERT]**

(a) *Vitamin A* (b) *Vitamin C*
(c) *Vitamin K* (d) *Vitamin E*

Interpret (c) Vitamin K is responsible for the coagulation of blood.

Check Point 5

1. Why does vitamin B not store in human body?
2. Why must vitamin C be supplied regularly in diet?

[NCERT Exemplar]

14.6 Nucleic Acids

Nucleic acids are present in all living organisms, whether plants, animals or virus. They are generally associated with proteins (in eukaryotes) to form **nucleoproteins.** Nucleic acids are responsible in the biosynthesis of proteins and for the transmission of heredity characters. The genetic information coded in nucleic acids helps to know the structure of all proteins including enzymes and all metabolic activities of living organisms.

Classification of Nucleic Acids

There are two types of nucleic acids, **deoxyribose nucleic acid** (DNA) and **ribose nucleic acid** (RNA). DNA is found predominantly in the nucleus, while RNA is predominant in the cytoplasm. DNA is the genetic material of most organisms, including many viruses. Some viruses, however, have RNA as their genetic material.

- Some important discoveries about nucleic acids are

  1869 - **Meischer** isolated nucleic acids, which he called **nuclein.**

  1899 - **Altmann** used the term **nucleic acid** to replace nuclein.

  1912 - **Feulgen** discovered a staining reaction (now called the Feulgen reaction), specific for DNA.

  1944 - **Avery, MacLeod** and **McCarty** presented first evidence that DNA is the genetic material.

  1953 - **Watson** and **Crick** presented the now famous double helix model of DNA.

Deoxyribose Nucleic Acid (DNA)

It is present in the cells of all plants, animals, prokaryotes and in a number of viruses. In prokaryotes (*e.g., Escherichia coil* , a bacterium), the genetic material consists of a single giant molecule of DNA without any associated proteins. DNA is present mainly in the chromosomes. It has also been reported in cytoplasmic organcells like mitochondria and chloroplasts. The DNA of most plants and animals and many viruses (polyoma virus, small-pox virus, bacteriophages T_2, T_4 and T_6) is double stranded. In bacteria and in higher plants and animals both DNA and RNA are present. Viruses usually contain either DNA or RNA.

Structure of DNA

The widely accepted molecular model of DNA is the **double helix structure,** proposed by **Watson** and **Crick** (1953). The DNA molecule consists of two helically twisted strands connected together by **steps.** Each strand consists of alternating molecules of deoxyribose (a pentose sugar) and phosphate groups. Each step is made up of a double ring purine base and a single ring pyrimidine base. The purine and pyrimidine bases are connected to deoxyribose sugar molecules. The two strands are interwined in a clockwise direction, *i.e.,* in a right hand helix, and run in opposite directions. The strand completes a turn each 34Å. Each nucleotide occupies 3.4Å. Thus, there are 10 nucleotides per turn. Each successive nucleotide turns 36 degrees in the horizontal plane. The width of the DNA molecule is 20Å. The twisting of the strands results in the formation of **deep** and **shallow** spiral grooves.

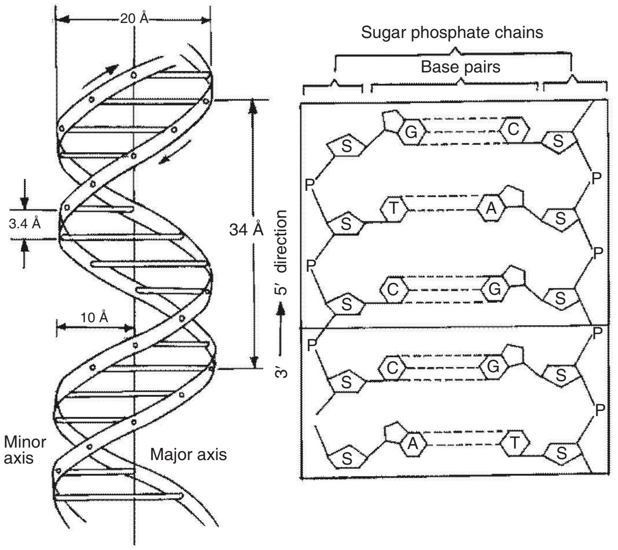


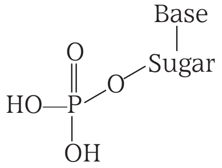
Fig. 14.10 Double helix structure of DNA

Chemical Composition of DNA

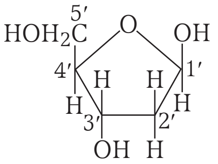
The DNA molecule is a polymer consisting of several thousand pairs of nucleotide monomers. Each nucleotide consists of the pentose sugar, deoxyribose, a phosphate group and nitrogenous base which may be either a purine or pyrimidine. Deoxyribose and a nitrogenous base together form a **nucleoside.** A nucleoside and a phosphate together form a **nucleotide.**

Nucleoside = deoxyribose + nitrogenous base
Nucleotide = deoxyribose + nitrogenous base + phosphate
= nucleoside + phosphate

Thus, nucleotide may be represented, as,

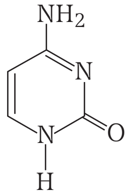


(i) **Deoxyribose** is a pentose sugar with five carbon atoms. Four of the five carbon atoms plus a single atom of oxygen form a five-membered ring. The fifth carbon atom is outside the ring and forms a part of a —CH_2 group. The four atoms of the ring are numbered 1′, 2′, 3′ and 4'. The carbon atom of —CH_2 is numbered 5′. There are three —OH groups in position 1′, 3′ and 5′. Hydrogen atoms are attached to carbon atoms 1′, 2′, 3′ and 4′.
All the sugars in one strand are directed to one end *i.e.,* the strand has polarity. The sugars of the two strands are directed in opposite direction (antiparallel strands).

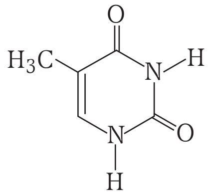


2-deoxyribose sugar

(ii) **Nitrogenous bases** are of two types, *viz,* pyrimidines and purines. The pyrimidines are single ring compounds, with nitrogen in position 1 and 3 of a 6-membered benzene ring. The two most common pyrimidines of DNA are **cytosine** (C) and **thymine** (T). The purines are double ring compounds. A purine molecule consists of a 5-membered imidazole ring joined to a pyrimidine ring at positions 4 and 5. The two most common purines of DNA are **adenine** (A) and **guanine** (G). The structure of these bases are follows :

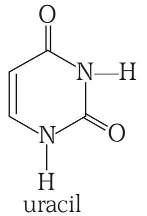


cytosine (*C*)

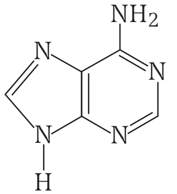


thymine (*T*)

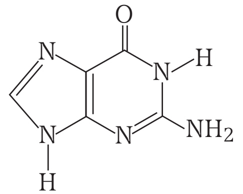
Pyrimidines



uracil
(a pyrimidine base present in RNA)



adenine (*A*)



guanine (*G*)

purines

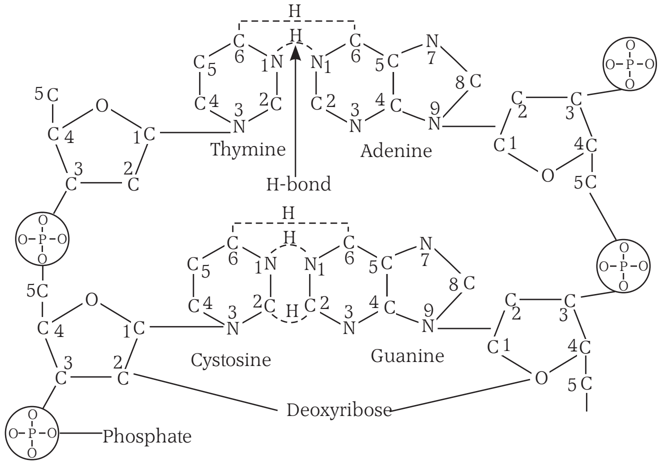
Sample **Problem 19** *Which of the following are purine bases?* **[NCERT** Exemplar**]**

(a) *Guanine* (b) *Adenine*
(c) *Thymine* (d) *Uracil*

Interpret (*a,b*) Purines are double ring compounds. Guanine and adenine are purines.

- **Base pairing** Each **'step'** on the DNA ladder is made up of a purine and a pyrimidine pair, *i.e.,* of a double ring and a single ring.
- Two purines would occupy too much space, while two pyrimidines would occupy too little. Because of the purine-pyrimidine pairing, the total number of purines in a double-stranded DNA molecule is equal to the total number of pyrimidines. Thus, A/T = 1 and G/C = 1 or A + G = C + T (Chargaff's rule).

(iii) **Phosphate** In the DNA strand, the phosphate groups alternate with deoxyribose. Each phosphate group is joined to carbon atom 3 of one deoxyribose and to carbon atom 5 of another. Thus, each strand has a 3 end and a 5 end. The two strands are oriented in opposite direction. The 3 end of one strand corresponds to the 5 end of the other. Consequently the oxygen atoms of deoxyribose point in opposite directions.



Caution Point *A unit formed by the attachment of a base to* 1 *position of sugar is called* ***nucleoside.*** *When nucleoside is linked with phosphoric acid at* 5 *position of sugar moiety, a* ***nucleotide*** *is formed. Nucleotides are joined together by* ***phosphodiester linkage*** *between* 5 *and* 3 *carbon atoms of the pentose sugar.*

Sample **Problem 20** *What products would be formed when a nucleotide from DNA containing thymine is hydrolysed?* **[NCERT]**

(a) *A deoxyribose molecule*
(b) *Phosphoric acid*
(c) *Thymine, a pyrimidine base*
(d) *All of the above*

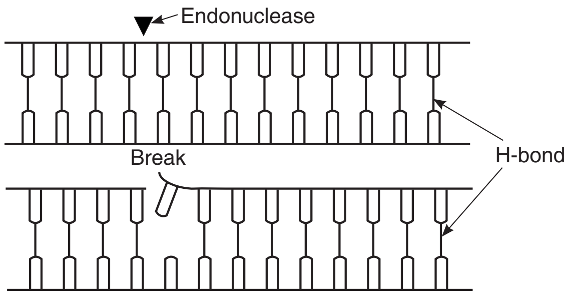
Interpret (*d*) When a nucleotide from DNA is hydrolysed, it will give a deoxyribose sugar molecules, phosphoric acid and a pyrimidine base (thymine in this case) or a purine base.

Replication of DNA

The formation of new DNA from older one is called replication.

Its outlines are as

1. Replication is a **semi-conservative process** in which each of the two double helices formed from the parent double strand have one old and one new strand. Repair replication is non-conservative.
2. DNA replication requires a DNA template, a primer, deoxyribonucleoside triphosphates (dATP, dGTP, dTTP and dCTP), Mg^{2+}, DNA unwinding protein, super helix relaxing protein, a modified RNA polymerase to synthesize the RNA primer, the products of DNAA, DNAB, DNAC-D, DNAE and DNAG genes and polynucleotide ligase, a joining enzyme.
3. Replication starts at a specific point called the origin.
4. According to one model replication starts with a 'nick' or incision made by an **incision enzyme** (endonuclease).



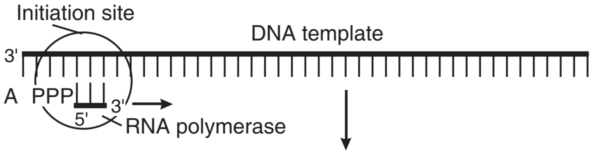
Enzyme (endonuclease) action starts with incision

Fig. 14.11 Replication of DNA

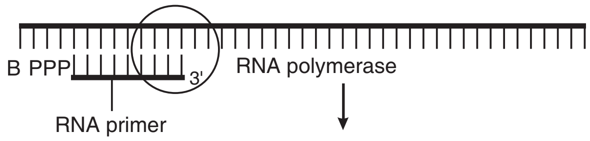
5. The two strands of the DNA double helix unwind with the help of a DNA unwinding protein (also called the DNA binding protein) which binds to single DNA strands.
6. The unwinding of the strands imposes strain which is relieved by the action of a super helix relaxing protein or swiveling protein.
7. Initiation of DNA synthesis requires an RNA primer. The primer is synthesized by the DNA template close to the origin of replication. The synthesis is catalysed by a special form of RNA polymerase.
8. Deoxyribose nucleotides are now added to the 3' end of the RNA primer and the main DNA strand is synthesized on the DNA template. This strands is complementary to the DNA strand and is synthesized

by DNA polymerase III. The roles of polymerases in DNA replication are

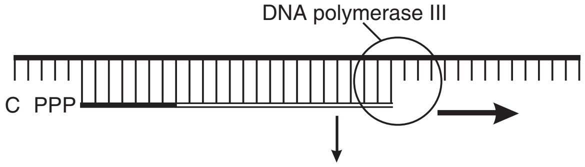
(i) Complementary RNA primer initiated on the DNA template at the initiation point by a form of RNA polymerase'.



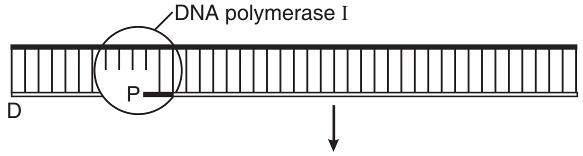
(ii) RNA primer grows in $5' \rightarrow 3'$ direction. RNA polymerase ultimately dissociates from the DNA template.



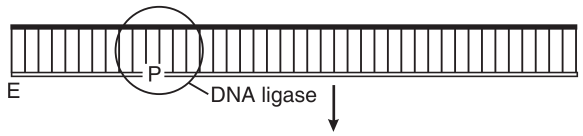
(iii) DNA nucleotides added at the 3' end of the RNA primer and a complementary DNA strand synthesized by DNA polymerase III.



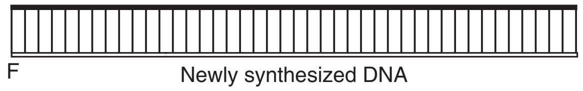
(iv) RNA primer degraded and simultaneously replaced by a DNA polymerase I.



(v) RNA primer completely degraded and DNA segment further extended. The segment is now joined to the main DNA strand by ligase.



(vi) The DNA template strand (black) with the newly synthesized DNA strand (white).



9. The enzyme DNA polymerase I now degrades the RNA primer and simultaneously catalyses the synthesis of a short DNA segment to replace the primer. This segment is then joined to the main DNA strand by a DNA ligase.
10. Replication takes place discontinuously and short pieces called Okazaki fragments are synthesized. One strand may synthesize a continuous strand and the other Okazaki fragments, or both strands may synthesize Okazaki fragments. Both new strands are synthesized in the $5' \rightarrow 3'$ direction. Thus, one strand is synthesized forwards (leading strand) and the other backwards (lagging strand).
11. The Okazaki pieces are joined by polynucleotide ligase, a joining enzyme, to form continuous strand.
12. Replication may be in one direction (unidirectional) from the point of origin or in both directions (bidirectional).

Ribose Nucleic Acid (RNA)

It is the genetic material of mainly viruses. It can be single stranded or double stranded.

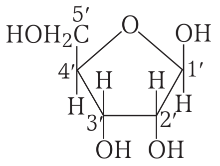
Chemical Composition of RNA

RNA, like DNA is also a polymer of nucleotide which in turn obtained from nucleoside, chemical which when combines with phosphate. Here the point of difference is that the sugar present in nucleoside is ribose sugar instead of deoxyribose sugar.

Nucleoside = ribose + nitrogenous base

Nucleotide = ribose + nitrogenous base + phosphate

(i) **Ribose** The pentose sugar of RNA has an identical structure with deoxyribose sugar except that there is an —OH group instead of H on carbon atom 2′.



ribose sugar

(ii) **Nitrogenous base** here also are of two types : pyrimidines and purines. Purine bases are same as that in DNA but pyrimidine bases are cytosine (C) and uracil (U). (In RNA uracil replaces thymine).

(iii) **Phosphate** same as DNA.

Caution Point *There are viruses, called retroviruses, in which information flows from RNA to DNA. The virus that causes AIDS is a retrovirus.*

Types of RNA

$$\text{RNA}\begin{cases} m\text{-RNA} \xrightarrow{\text{Formed}} \text{During cleavage} \\ r\text{-RNA} \xrightarrow{\text{Formed}} \text{At the end of cleavage} \\ t\text{-RNA} \xrightarrow{\text{Formed}} \text{During gastrulation} \end{cases}$$

(i) ***m*-RNA** makes **3–5%** of total cellular RNA. The name messenger RNA was proposed by Jacob and Monad (1961). Some points related to structure and functioning of *m*-RNA are as follows

(a) Structurely the *m*-RNA contains a cap at its 5' end. The cap controls the rate of protein synthesis.

(b) The cap is followed by non coding region 1 which is usually 10–100 nitrogenous bases long and is rich in adenine and uracil bases.

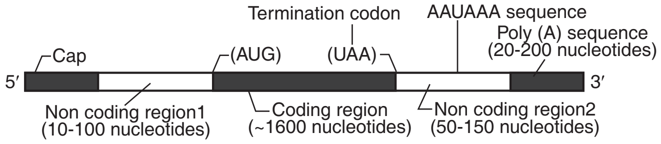


Fig. 14.12 Structure of *m*-RNA

(c) The *m*-RNA of prokaryotes is considered as metabolically unstable as it does not stays so longer in their body, it normally destroyed while concerning metabolic process is going on. The *m*-RNA of eukaryotes on the other hand is considered as metabolically stable as it normally waits for the completion of process concerned.

(d) The *m*-RNA comes out with proteins into the cytoplasm and normally swim as spherical balls along with the same untill these are required. These RNA + protein spherical balls are called informosomes.

(ii) *r*-RNA makes 80% of total cellular RNA. This RNA is the basic constituent of ribosomes. It is developed from r-DNA in the case of prokaryotes while in the case of eukaryotes, it is developed from the nucleolar organizer region of chromosome. Some points related to rRNA are as follows

(a) The *r*-RNA may be seen in the form of a compact rod or a coil or in the form of extended regions. The structure actually depends upon various factors like ionic strength, temperature and pH etc.

(b) The *r*-RNA is found to be stable for atleast 2 generations.

(c) The various *r*-RNAs present in different units of ribosome are as follows :

Prokaryotes (70S)

$30\text{S} \longrightarrow 16\text{S}\, r\text{-RNA};\ 50\text{S} \longrightarrow 23\text{S and } 5\text{S}\, r\text{-RNA}$

Eukaryotes (80S)

$40\text{S} \longrightarrow 18\text{S}\, r\text{-RNA};\ 60\text{S} \longrightarrow 28\text{-}29\text{S}, 5.85\text{S}, 5\text{S}\, r\text{-RNA}$

Chloroplast and Mitochondria (55S)

$30\text{S} \longrightarrow 12\text{-}13\text{S}\, r\text{-RNA};\ \mathbf{40S} \longrightarrow 16\text{-}17\text{S}\, r\text{-RNA} + 5\text{S}$

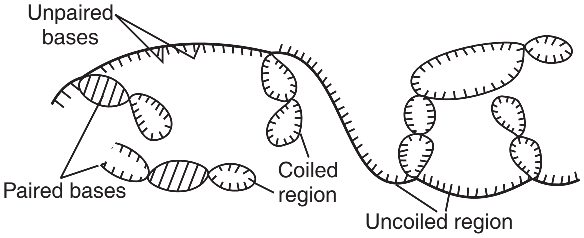


Fig. 14.13 Structure of *r*-RNA

(iii) *t*-RNA makes 10–20% of total cellular RNA with sedimentation coefficient of 3.8S. This RNA contains 73–93 nucleotides with in the structure given below.

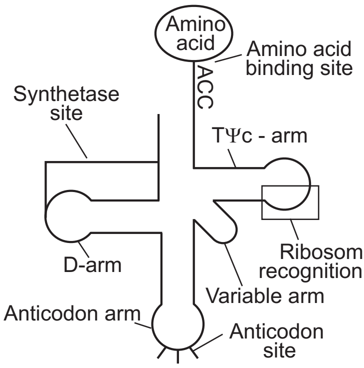


Fig. 14.14 Structure of *t*-RNA

The above structure is called Clover Leaf Model and was fully worked out by Holley *et al*. of yeast alanine *t*-RNA.

- The function of *t*-RNAs is to align the required amino acids according to the nucleotide sequence of *m*-RNA.

  The *t*-RNA can be of **monomeric** (arising from one gene) or **multimeric** (arising from many genes) type.

Differences between DNA and RNA

1. DNA is the usual genetic material while RNA is the genetic material of some viruses.
2. DNA is usually double stranded (single stranded in some viruses like $\phi \times 174$), while RNA is usually single stranded (some viruses like reovirus contain double stranded RNA).
3. DNA have deoxy ribose sugar as the pentose sugar while RNA have ribose sugar.
4. The nitrogenous bases of DNA are adenine, guanine, cytosine and thymine while RNA has uracil in the place of thymine.
5. Base pairing is seen throughout the molecule in DNA while it is region specific or absent in the case of RNA.
6. DNA is only of one type while RNA is of three types namely messenger RNA (*m*-RNA), ribosomal RNA (*r*-RNA) and transfer RNA (*t*-RNA).
7. Most of the DNA is found in nucleus and some of it is also found in cytoplasm while RNA is found in cytoplasm only.
8. DNA on replication forms DNA and on transcription forms RNA while usually the RNA does not replicate or transcribe.
9. Genetic messages are usually encoded in DNA while RNA translates the encoded messages from DNA and thus helps in protein formation.
10. There are few uncommon bases found in DNA while these bases are more found in RNA.

The Genetic Code

Nucleic acids control heredity on molecular level. The double helix of DNA is reponsible for the hereditary information of the organisms. The information is stored as the sequence of bases along the polynucleotide chain. DNA preserve the hereditary informations and use it.

It does these things through two properties

(i) DNA molecules can duplicate themselves (replication)

(ii) DNA molecules can control the synthesis of proteins in an exact and specific way. Synthesis of a polypeptide chain is controlled by a particular **gene.** The gene, which is almost always a segment of a DNA strand, transcribes an *m*-RNA which thus acts as an intermediate in conveying information from the sequence of amino acids in the polynucleotide chain. Each amino acid is specified by a sequence of three bases known as **codon** of *m*-RNA. Each *t*-RNA molecules has a sequence of three bases known as **anticodon,** which reads a codon of *m*-RNA. *t*-RNA molecules thus serve as adaptors in protein synthesis by reading of *m*-RNA codons in a sequence.

The relationship between the sequence of bases in DNA/RNA and the sequence of amino acids in a polypeptide chain is called the **genetic code.** The code indicates which codons specify which amino acids.

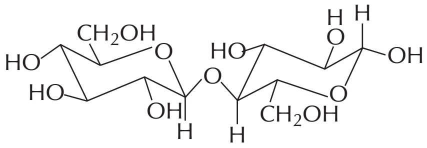
Check Point 6

1. What is the difference between ribose and deoxyribose sugar?
2. The two strands of DNA are easily separated during replication. Why?
3. When RNA is hydrolysed, there is no relationship among the quantities of different bases obtained. What does this fact suggest about the structures of RNA? **[NCERT]**
4. Which moieties of nucleosides are involved in the formation of phosphodiester linkages present in dinucleotides? Which acid is involved in the formation of this linkage? **[NCERT Exemplar]**

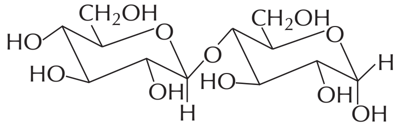
WORKED OUT Examples

Example 1 *Which of the following disaccharides is a non-reducing sugar?*

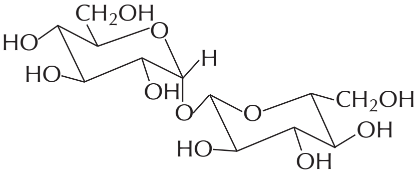
(*a*)



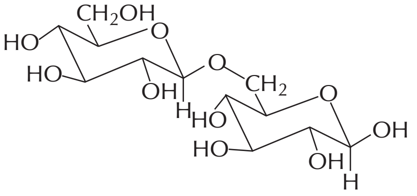
(*b*)



(*c*)



(*d*)



Solution (*c*) Because it does not contain free aldehyde or ketone group or in other words it has a stable acetal structure which cannot be opened into a free carbonyl group.

Example 2 *D-fructose is used for sweetening cold drinks but not hot ones because*

(*a*) *it is not a true carbohydrate*
(*b*) *on heating it converts into pyranose form*
(*c*) *on heating it converts into furanose form*
(*d*) *on heating it gets decomposed of D-fructose*

Solution (*c*) The sweeter form of D-fructose is fructopyranose. The high temperature causes a shift in the pyranose $\rightleftharpoons$ furanose equilibrium towards the less sweet furanose.

Example 3 *Given,* $[\alpha]_D = +52.7°$ *for D-glucose and* $[\alpha]_D = -92.40$ *for D-fructose. The specific rotation of invert sugar is*

(*a*) $-39.7°$ (*b*) -145.1 (*c*) $-19.9°$ (*d*) $-72.55°$

Solution (*c*) The specific rotation of invert sugar is one half of the sum of those of individual monosaccharides.

$$\therefore \text{ Specific rotation of invert sugar} = \frac{1}{2}\,[+52.7° + (-92.4°)]$$
$$= -19.9°.$$

Example 4 $A \xrightarrow{\text{HOH/H}^+}$ *glucose* + *fructose*

$B \xrightarrow{\text{HOH/H}^+}$ *glucose* + *glucose*

$C \xrightarrow{\text{HOH/H}^+}$ *glucose* + *galactose*

the disaccharides A, B and C respectively are

(*a*) *lactose, sucrose, maltose*
(*b*) *sucrose, maltose, lactose*
(*c*) *sucrose, lactose, maltose*
(*d*) *maltose, sucrose, lactose*

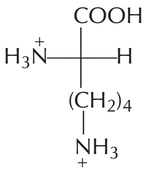
Solution (*b*) $\underset{\text{(invert sugar)}}{\text{Sucrose}} \xrightarrow{\text{HOH/H}^+} \text{glucose} + \text{fructose}$

$\text{Maltose} \xrightarrow{\text{HOH/H}^+} 2\ \text{glucose}$

$\text{Lactose} \xrightarrow{\text{HOH/H}^+} \text{glucose} + \text{galactose}$

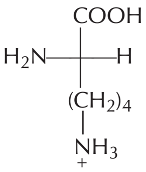
Example 5 *Which of the following is the major solute species in a solution of lysine at pH* = 10.5 *(pI* = 9.6*)* ?

(*a*)



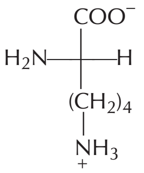
$$\begin{array}{c}\mathrm{COOH}\\ \mathrm{H_3\overset{+}{N}}\text{—}\!\!\!|\!\!\!\text{—}\mathrm{H}\\ \mathrm{(CH_2)_4}\\ |\\ \mathrm{\underset{+}{N}H_3}\end{array}$$

(*b*)



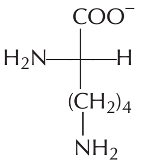
$$\begin{array}{c}\mathrm{COOH}\\ \mathrm{H_2N}\text{—}\!\!\!|\!\!\!\text{—}\mathrm{H}\\ \mathrm{(CH_2)_4}\\ |\\ \mathrm{\underset{+}{N}H_3}\end{array}$$

(*c*)



$$\begin{array}{c}\mathrm{COO^-}\\ \mathrm{H_2N}\text{—}\!\!\!|\!\!\!\text{—}\mathrm{H}\\ \mathrm{(CH_2)_4}\\ |\\ \mathrm{\underset{+}{N}H_3}\end{array}$$

(*d*)



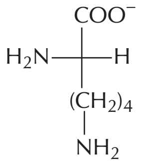
$$\begin{array}{c}\mathrm{COO^-}\\ \mathrm{H_2N}\text{—}\!\!\!|\!\!\!\text{—}\mathrm{H}\\ \mathrm{(CH_2)_4}\\ |\\ \mathrm{NH_2}\end{array}$$

Solution (*d*) $\because$ Here, pH = 10.5 and pI = 9.6

$$\text{pH} > \text{pI}$$

∴ Anionic form dominates

i.e.,



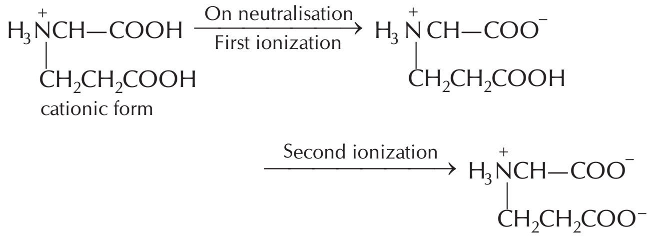
$$H_2N-\overset{COO^-}{\underset{(CH_2)_4-NH_2}{C}}-H$$

is present in solution.

Example 6 *Glutamic acid,* $H_2NCH(CH_2CH_2COOH)\cdot COOH$ *has* $pK_{a_1}, (\alpha - COOH) = 2.2, pK_{a_2}(\alpha - \overset{+}{N}H_3) = 9.8$ *and* pK_{a_3} *(R group* $COOH) = 4.3$. *The isoelectric point of glutamic acid is*

(a) 3.2
(b) 6
(c) 7.05
(d) 8.3

Solution (*a*)



$$\underset{\text{cationic form}}{H_3\overset{+}{N}\underset{CH_2CH_2COOH}{CH}-COOH} \xrightarrow[\text{First ionization}]{\text{On neutralisation}} H_3\overset{+}{N}\underset{CH_2CH_2COOH}{CH}-COO^- \xrightarrow{\text{Second ionization}} H_3\overset{+}{N}\underset{CH_2CH_2COO^-}{CH}-COO^-$$

So, $$pI = \frac{pK_{a_1} + pK_{a_3}}{2} = \frac{2.2 + 4.3}{2} = 3.25$$

Example 7 *For which of the following amino acid, van-Styke estimation method is not applicable?*

(a) *Alanine*
(b) *Aspartic acid*
(c) *Senine*
(d) *Proline*

Solution (*d*) Proline has a 2° amino group. Hence, it is not estimated by this method.

Example 8 *A hexapeptide has the composition Ala, Gly, Phe, Val. Both the N-terminal and C-terminal units are Val. Cleavage of the hexapeptide by chemotrypsin gives two different tripeptides, both having Val as the N-terminal group. Among the products of random hydrolysis is a Ala-Val dipeptide fragment. What is the primary structure of the hexapeptide?*

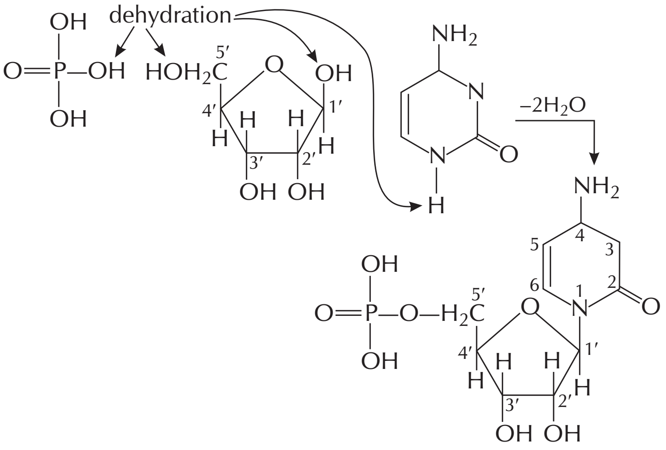
(a) Val-Gly-Phe-Val-Ala-Val
(b) Val-Ala-Phe-Val-Gly-Val
(c) Val-Gly-Ala-Val-Phe-Val
(d) Val-Phe-Val-Ala-Gly-Val

Solution (*a*) Val-Gly-Phe-Val-Ala-Val Random hydrolysis gives Ala-val dipeptide fragment which indicates the connected presence of Ala and Val.

Example 9 *In both DNA and RNA, heterocyclic base and phosphate ester linkages are at*

(a) C_1' *and* C_5' *respectively of the sugar molecule*
(b) C_5' *and* C_1' *respectively of the sugar molecule*
(c) C_2' *and* C_5' *respectively of the sugar molecule*
(d) C_5' *and* C_2' *respectively of the sugar molecule*

Solution (*b*) Synthesis of RNA/DNA from phosphoric acid ribose and cylosine is given below. Thus, ester linkages are at C_5' and C_1' of sugar molecule.



Example 10 *An electric current is passed through an aqueous solution of a mixture of alanine (isoelectric point* 6.0), *glutamic acid* (3.2) *and arginine* (10.7) *buffered at* pH 6. *What is the fate of the three acids?*

(a) *Glutamic acid migrates to anode at* pH 6. *Arginine present as a cation and migrates to the cathode. Alanine in a dipolar ion remains uniformly distributed in solution*
(b) *Glutamic acid migrates to cathode and others remain uniformly distributed in solution*
(c) *All these remain uniformly distributed in solution*
(d) *All three move to cathode*

Solution (*d*) At pH = 6, glutamic acid exists as a dianionic species and migrates to anode while arginine exists as cationic species and moves to cathode. Alanine does not migrate to any electrode at its isoelectric point.

Start Practice for JEE Main

Round I (Topically Divided Problems)

Carbohydrates

1. Glycogen is a branched chain polymer of α-D-glucose units in which chain is formed by $C_1—C_4$ glycosidic linkage whereas branching occurs by the formation of $C_1—C_6$ glycosidic linkage. Structure of glycogen is similar to **[NCERT Exemplar]**

(a) amylose (b) amylopectin
(c) cellulose (d) glycogen

2. Which of the following polymer is stored in the liver of animals? **[NCERT Exemplar]**

(a) Amylose (b) Cellulose
(c) Amylopectin (d) Glycogen

3. Which is not a hexose?

(a) Glucose (b) Ribose
(c) Fructose (d) Galactose

4. What is not true for carbohydrates?

(a) General formula is $C_nH_{2n}O_n$
(b) Glucose is the most common monomer of carbohydrates
(c) Fructose is the sweetest of all sugars
(d) Do not conjugate with lipids

5. Identify the product '*C*' in the following series of reactions

$$\text{Glucose} \xrightarrow{\text{HCN}} A \xrightarrow{H_2O} B \xrightarrow{\text{HI}} C$$

(a) heptanoic acid (b) hexanoic acid
(c) α-methyl caproic acid (d) None of these

6. Milk changes after digestion into

(a) glucose (b) lactose
(c) fructose (d) glucogen

7. A solution of D-glucose in water rotates the plane of polarised light

(a) to the left (b) to the right
(c) to either side (d) None of these

8. Which of the following reagent is used to identify fructose?

(a) Neutral $FeCl_3$ (b) $CHCl_3$/alc. KOH
(c) Ammoniacal $AgNO_3$ (d) Iodine

9. Which of the following pairs give positive Tollen's test?

(a) Glucose, sucrose
(b) Glucose, fructose
(c) Hexanal, acetophenone
(d) Fructose, sucrose

10. The two forms of D-glucopyranose obtained from the solution of D-glucose are called

(a) isomer (b) anomer
(c) epimer (d) enantiomer

11. Consider the following reagents

I. Br_2 water II. Tollen's reagent
III. Fehling's solution

Which can be used to make distinction between an aldose and a ketose?

(a) I, II and III (b) II and III
(c) I only (d) II only

12. Although D-galactose rotates plane-polarised light, its oxidation product, galactaric acid, due to HNO_3, does not. It is due to

(a) galactaric acid is racemic mixture of D- and L-isomer
(b) galactaric acid is a *meso* compound
(c) Both are correct
(d) None of the above is correct

13. If α-D-glucopyranose is reacted with acetic anhydride at 373 K, the major product is the β-isomer of the pentaacetate. It is attributed to

(a) isomerisation of α-D into β-D-glucose at 373 K
(b) opening of glucopyranose ring
(c) Both the statements are correct
(d) None of the statement is correct

14. Sucrose (cane sugar) is a disaccharide. One molecule of sucrose on hydrolysis gives …… . **[NCERT Exemplar]**
(a) 2 molecules of glucose
(b) 2 molecules of glucose + 1 molecule of fructose
(c) 1 molecule of glucose + 1 molecule of fructose
(d) 2 molecules of fructose

15. Which of the following statements is not true about glucose?
(a) It is an aldohexose
(b) On heating with HI it forms *n*-hexane
(c) It is present in furanose form
(d) It does not give 2,4-DNP test

16. An organic compound consumes 4 moles of periodic acid to form following compounds, per mole of the starting compounds HCHO, 3HCOOH and CHOCOOH. The organic compound is
(a) glucose (b) fructose
(c) gluconic acid (d) sorbitol

17. An optically active compound *A*, gave an $[\alpha]_D^{25} = 30°$, while a mixture of *A* and its enantiomer *B*, gave $[\alpha]_D^{25} = +15°$. The ratio of *A* to *B* in the mixture is
(a) 1 to 3 (b) 3 to 1
(c) 1 to 2 (d) 2 to 1

Amino Acids

18. Which of the following is involved in the formation of heme?
(a) Lysine (b) Glysine
(c) Tryosin (d) Arginine

19. Which one of the following is involved in the formation of nicotinamide and indole-3-acetic acid?
(a) Lysine (b) Tryptophan
(c) Tyrosine (d) Glutamic acid

20. At intermediate pH values of about 6.0, an amino acid behaves as a dipolar ion or Zwitter ion. On decreasing and increasing the pH values, the amino acid becomes
(a) basic and acidic respectively
(b) acidic and basic respectively
(c) remains in the state of a neutral molecule
(d) loses its optical activity with the exception of glycine

21. Which of the following is not an essential amino acid for man?
(a) Tyrosine (b) Leucine
(c) Lysine (d) Valine

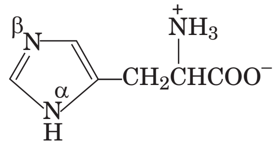
22. Which of the following has an imino ($>$NH) group instead of amino group (—NH_2) ?
(a) Proline (b) Isoleucine
(c) Tryptophan (d) Serine

23. Which of the following is not an α-amino acid?
(a) Cysteine (b) Proline
(c) Trypsin (d) Serine

24. In an amino acid, the carboxyl group ionises at $pK_{a_1} = 2.34$ and ammonium ion at $pK_{a_2} = 9.6$. The isoelectric point of the amino acid is at pH
(a) 5.97 (b) 2.34
(c) 9.60 (d) 6.97

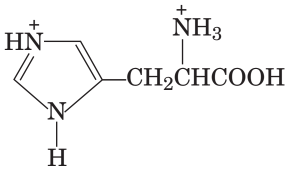
25. Which of the following statement(s) is/are true?
(i) All amino acids contain one chiral centre
(ii) Some amino acids contain one, while some contain more chiral centre or even no chiral centre
(iii) All amino acids found in protein have L-configuration
(iv) All amino acids found in proteins have 1° amino group
(a) (ii), (iii) and (iv)
(b) (ii) and (iii)
(c) (i), (iii) and (iv)
(d) (i) and (iv)

26. Which of the nitrogen of histidine is first protonated?

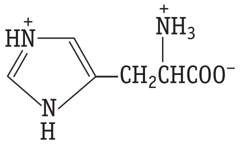


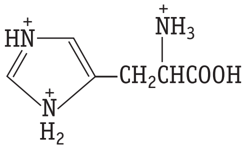
(a) α (b) β
(c) Both (a) and (b) (d) None of these

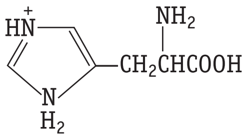
27. Histidine, a heterocyclic amino acid has following structure at pH < 1.82

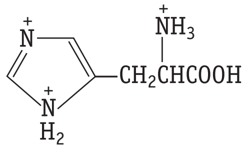


At pH > 1.82, it should have which structure?

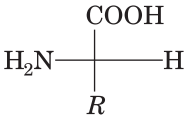
(a)


(b)


(c)


(d)


28. Which amino acid have more than one stereogenic centre?
(a) Aspartic acid (b) Lysine
(c) Arginine (d) Histidine

29. When 
$H_2N-\overset{COOH}{\underset{R}{C}}-H$ is acylated using Ac_2O
- (a) its configuration is retained
- (b) its configuration is inverted
- (c) it becomes unstable
- (d) no reaction takes place

30. In an electric field, if an amino acid migrate towards cathode, the pH of the solution is said to be
- (a) less than pI
- (b) more than pI
- (c) equal to pI
- (d) 7

Proteins

31. Which one is a fibrous protein?
- (a) Globulin
- (b) Collagen
- (c) Hordein
- (d) Glutin

32. Casein contained in milk as a
- (a) carbohydrate
- (b) lipid
- (c) protein
- (d) important molecule

33. Which one is not a protein?
- (a) Actin
- (b) Collagen
- (c) Albumin
- (d) Haematin

34. Aleurone grains are
- (a) starch
- (b) glycogen
- (c) lipid
- (d) protein

35. Initiation of polypeptide chain is through
- (a) lysine
- (b) glycine
- (c) leucine
- (d) methionine

36. Which of the following is not a function of proteins?
- (a) Nail formation
- (b) Skin formation
- (c) Muscle formation
- (d) Providing energy for metabolism

37. Which one of the following is not a protein?
- (a) Wool
- (b) Nail
- (c) Hair
- (d) DNA

38. A tripeptide is composed equally of L-valine, L-tyrosine and L-alanine (one molecule of each). How many isomeric tripeptide of this kind may exist?
- (a) 3
- (b) 4
- (c) 6
- (d) 8

39. Primary structure of protein is based upon the
- (a) hydrogen bonding
- (b) van der Waals' forces
- (c) ionic bonding
- (d) covalent bonding

40. Each polypeptide in a protein has aminoacids linked with each other in a specific sequence. This sequence of amino acids is said to be …… . **[NCERT Exemplar]**
- (a) primary structure of proteins
- (b) secondary structure of proteins
- (c) tertiary structure of proteins
- (d) quaternary structure of proteins

41. Denaturation of proteins leads to loss of its biological activity by
- (a) formation of amino acids
- (b) loss of primary structure
- (c) loss of both primary and secondary structure
- (d) loss of both secondary and tertiary structure

Enzymes

42. The enzyme which facilitates internal rearrangement in 3-phosphoglyceric acid to form 2-phosphoglyceric acid is
- (a) aldolase
- (b) triose phosphate isomerase
- (c) phosphoglycero mutase
- (d) pyruvate kinase

43. The enzymes which have control site in addition to active site are called
- (a) holozymes
- (b) coenzymes
- (c) apoenzymes
- (d) allosteric enzymes

44. Enzymes, in the living systems
- (a) provide energy
- (b) provide immunity
- (c) transport oxygen
- (d) catalyse biochemical processes

45. Which enzyme is present in saliva?
- (a) Urease
- (c) Maltase
- (c) Lactase
- (d) Amylase

46. Which of the following is present in animals like cow, buffaloes etc., to digest compound like paper cloth etc?
- (a) Urease
- (b) Cellulase
- (c) Silicones
- (d) Sucrase

47. The enzyme pepsin hydrolysis
- (a) proteins to amino acids
- (b) fats to fatty acids
- (c) glucose to ethyl alcohol
- (d) polysaccharides to monosaccharides

Vitamins

48. Which of the following B group vitamins can be stored in our body? **[NCERT Exemplar]**
- (a) Vitamin B_1
- (b) Vitamin B_2
- (c) Vitamin B_6
- (d) Vitamin B_{12}

49. Which of the following biomolecules contains non-transition metal ion?
(a) Vitamin B_{12} (b) Chlorophyll
(c) Haemoglobin (d) Insulin

50. Which of the following compounds is known as the antisterility factor?
(a) α-tocopherol (b) Retinol
(c) Calciferol (d) Pyridoxine

51. Vitamin B_6 is known as
(a) pyridoxin (b) thiamine
(c) tocopherol (d) riboflavin

52. The best source of vitamin A is
(a) wheat (b) beans
(c) carrots (d) oranges

53. The deficiency of vitamin B_1 causes
(a) beri-bei (b) dermatitis
(c) scurvy (d) rickets

54. The metal present in vitamin B_{12} is
(a) iron (b) manganese
(c) cobalt (d) mercury

Nucleic Acids

55. Maximum amount of RNA is found in
(a) nucleolus (b) chloroplast
(c) ribosomes (d) cytoplasm

56. When adenine is attached to ribose sugar, it is called adenosine. To make a nucleotide from it, it would require
(a) oxygenation
(b) addition of a base
(c) addition of phosphate
(d) hydrogenation

57. DNA template sequence of CTGATAGC is transcribed over *m*-RNA as
(a) GUCTUTCG (b) GACUAUCG
(c) GAUTATUG (d) UACTATCU

58. Which is capable of self replication?
(a) Enzymes (b) DNA polymerase
(c) DNA ligase (d) DNA

59. Genetic code determines
(a) sequence of amino acids in a peptide chain
(b) sequence of variable amino acids in a protein chain
(c) structure of human cells
(d) morphology of traits

60. Double stranded DNA virus with 20000 base pairs has nucleotides
(a) 20000 (b) 10000
(c) 666 (d) 40000

61. A DNA nucleotide chain has AGCTTCGA sequence. The nucleotide sequence of other chain would be
(a) TCGAAGCT (b) GCTAAGCT
(c) TAGCATAT (d) GATCCTAG

62. Ligase is an enzyme required for
(a) renaturation of DNA (b) proof-reading
(c) joining DNA bits (d) breaking of DNA

63. Nucleotide pairs present in one turn of DNA helix are
(a) 4 (b) 10
(c) 8 (d) 9

64. DNA and RNA contain four bases each. Which of the following bases is not present in RNA?
[NCERT Exemplar]
(a) Adenine (b) Thymine
(c) Uracil (d) Cytosine

65. Antibiotic inhibiting translation in eukaryotes is
(a) tetracyclin (b) penicillin
(c) puromycin (d) chloromycetin

66. Which one is not a constituent of nucleic acid?
(a) Uracil (b) Guanidine
(c) Phosphoric acid (d) Ribose sugar

67. In biological systems, the RNA molecules direct the synthesis of specific proteins which are characteristics of each kinds of organisms. This process is known as
(a) transcription (b) mutation
(c) replication (d) translation

68. Charagaff's rule states that in an organism
(a) amount of adenine (A) is equal to that of thymine (T) and amount of guanine (G) is equal to that of cytocine (C)
(b) amont of adenine (A) is equal to that of guanine (G) and the amount of thymine (T) is equal to that of guanine (G)
(c) amount of adenine (A) is equal to that of cytocine (C) and the amount of thymine (T) is equal to that of guanine (G)
(d) amount of all bases are equal

69. In DNA, the complementary bases are,
(a) adenine and thymine; guanine and cytocine
(b) uracil and adenine; cytocine and guanine
(c) adenine and guanine; thymine and cytocine
(d) adenine and thymine; guanine and uracil

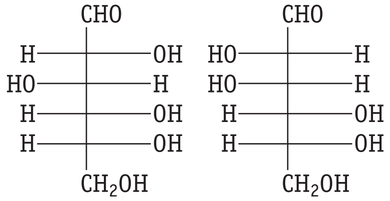
70. The hydrogen bonding for the bases pairs of DNA are between
(a) amide carbonyl and —NH_2 only
(b) amide N—H and cyclic amine nitrogen only
(c) alcohols and carbonyls only
(d) Both (a) and (b)

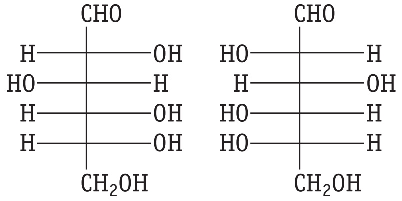
Round II (Mixed Bag)

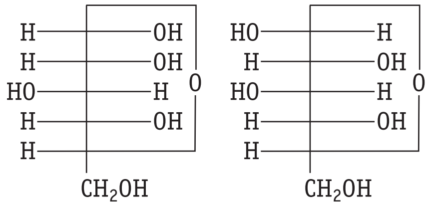
Only One Correct Option

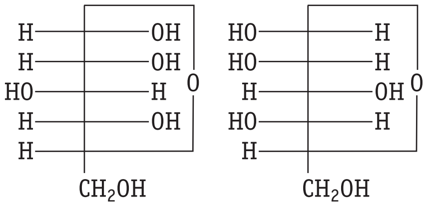
1. A compound gives negative test with ninhydrin and positive test with Benedict's solution. The compound is
(a) a protein (b) an amino acid
(c) a lipid (d) a monosaccharide

2. Which of the following pairs represents anomers? **[NCERT Exemplar]**

(a)


(b)


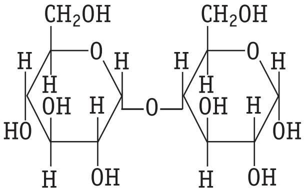
(c)


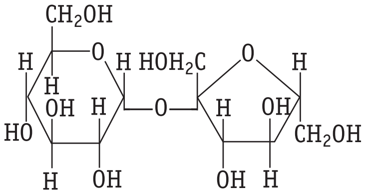
(d)


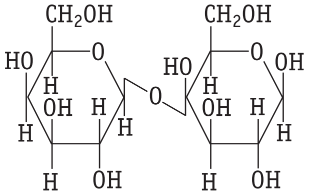
3. The charring of sugar when it is treated with conc. H_2SO_4 is due to
(a) oxidation
(b) reduction
(c) dehydration
(d) hydrolysis

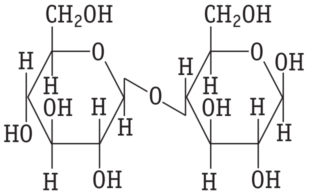
4. Pick out the one which does not belong to the family of enzyme
(a) pepsin (b) cellulose
(c) ptyalin (d) lipase

5. In disaccharides, if the reducing groups of monosaccharides *i.e.*, aldehydic or ketonic groups are bonded, these are non-reducing sugars. Which of the following disaccharide is a non-reducing sugar? **[NCERT Exemplar]**

(a)


(b)


(c)


(d)


6. Complete hydrolysis of cellulose gives
(a) D-fructose
(b) D-ribose
(c) D-glucose
(d) L-glucose

7. The reason for double helical structure of DNA is operation of
(a) van der Waals' forces
(b) dipole-dipole interaction
(c) hydrogen bonding
(d) electrostatic attractions

8. The prosthetic group of haemoglobin is
(a) porphin (b) globulin
(c) haem (b) gelatin

9. Isoelectric point is a
- (a) specific temperature
- (b) suitable concentration of amino acid
- (c) hydrogen ion concentration that does not allow migration of amino acid under electric field
- (d) melting point of an amino acid under the influence of electric field

10. The number of disulphide linkages present in insulin are
- (a) 1
- (b) 2
- (c) 3
- (d) 4

11. From the following statements

I. Albumin is a simple protein.
II. Amino acid alanine contains an acidic side chain.
III. Insulin is a hormone.
IV. Muscles contain the protein keratin.

Choose the wrong statements.
- (a) I, II
- (b) III, IV
- (c) I, III
- (d) II, IV

12. The correct statement in respect of protein haemoglobin is that it
- (a) acts as an oxygen carrier in the blood
- (b) forms antibodies and offers resistance to diseases
- (c) functions as a catalyst for biological reactions
- (d) maintains blood sugar level

13. Identify the correct statement regarding enzymes.
- (a) Enzymes are specific biological catalysts that can normally function at very high temperatures ($T \sim 1000$ K)
- (b) Enzymes are normally heterogeneous catalysts that are very specific in their action
- (c) Enzymes are specific biological catalysts that cannot be poisoned
- (d) Enzymes are specific biological catalysts that possess well defined active sites

14. The highest calorific value is found in
- (a) proteins
- (b) fats
- (c) vitamins
- (d) carbohydrates

15. Which of the following acids is a vitamin? **[NCERT** Exemplar**]**
- (a) Aspartic acid
- (b) Adipic acid
- (c) Ascorbic acid
- (d) Saccharic acid

16. Dinucleotide is obtained by joining two nucleotides together by phosphodiester linkage. Between which carbon atoms of pentose sugars of nucleotides are these linkages present? **[NCERT** Exemplar**]**
- (a) 5′ and 3′
- (b) 5′ and 5′
- (c) 1′ and 5′
- (d) 3′ and 3′

17. An example of a protein which acts as a hormone is
- (a) casein
- (b) oxytocin
- (c) trypsin
- (d) keratin

18. Insulin production and its action in human body are responsible for the level of diabetes. This compound belongs to which of the following categories?
- (a) A co-enzyme
- (b) A hormone
- (c) An enzyme
- (d) An antibiotic

19. When glucose reacts with bromine water the main product is
- (a) acetic acid
- (b) saccharic acid
- (c) glyceraldehyde
- (d) gluconic acid

20. Nucleic acids are polymers of **[NCERT** Exemplar**]**
- (a) nucleosides
- (b) sugars
- (c) bases
- (d) nucleotides

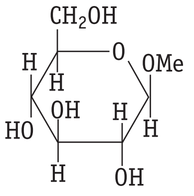
21. Night-blindness may be caused by the deficiency of vitamin
- (a) A
- (b) B
- (c) D
- (d) C

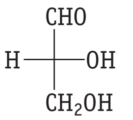
22. The number of amino acids in insulin is
- (a) 21
- (b) 574
- (c) 51
- (d) 5733

23. Amylopectin is a polymer of
- (a) α-D glucose
- (b) α-D fructose
- (c) lactose
- (d) amylose

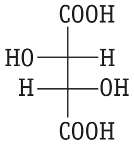
More than One Correct Option

24. Which of the following carbohydrates are D-isomers?

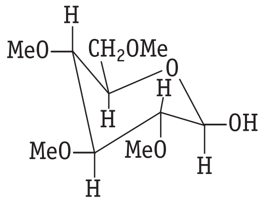
(a)


(b)


$$\begin{array}{c} CHO \\ H-\!\!\!-\!\!\!\!\!\!\mid\!\!\!\!\!\!-\!\!\!-OH \\ CH_2OH \end{array}$$

(c)


$$\begin{array}{c} COOH \\ HO-\!\!\!\!\!\mid\!\!\!\!\!-H \\ H-\!\!\!\!\!\mid\!\!\!\!\!-OH \\ COOH \end{array}$$

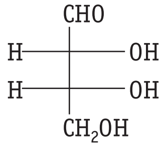
(d)


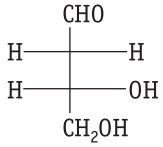
25. Which of the following monosaccharides are present as five membered cyclic structure (furanose structure)? **[NCERT** Exemplar**]**
- (a) Ribose
- (b) Glucose
- (c) Fructose
- (d) Galactose

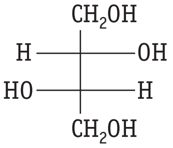
26. The product of the reaction

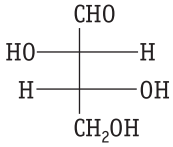
D-glyceraldehyde $\xrightarrow[\text{HCl}]{\text{Me}_2\text{CO}} \xrightarrow{\text{H}_2\text{C}{=}\text{CHMgCl}} \xrightarrow{\text{O}_3}$

is/are?

(a) 

(b) 

(c) 

(d) 

27. Which of the following carbohydrates are branched polymer of glucose? **[NCERT Exemplar]**

(a) Amylose (b) Amylopectin

(c) Cellulose (d) Glycogen

28. A mixture of two amino acids having pI 9.60 and 5.40 can be separated

(a) by adjusting the pH of the solution a 9.60

(b) by adjusting the pH of the solution at 5.40

(c) by adjusting the pH of the solution at 7.0

(d) by adjusting the pH of the solution at 14.0

29. Proteins can be classified into two types on the basis of their molecular shape *i.e.*, fibrous proteins and globular proteins. Examples of globular proteins are **[NCERT Exemplar]**

(a) Insulin (b) Keratin

(c) Albumin (d) Myosin

30. In fibrous proteins, polypeptide chains are held together by .... **[NCERT Exemplar]**

(a) van der Waals' forces

(b) disulphide linkage

(c) electrostatic forces of attractions

(d) hydrogen bonds

31. Which of the following terms are correct about enzyme? **[NCERT Exemplar]**

(a) Proteins (b) Dinucleotides

(c) Nucleic acids (d) Biocatalysts

Assertion and Reason

Directions (Q. Nos. 32 to 36) *Each of these questions contains two statements : Statement* I (*Assertion*) *and Statement* II (*Reason*). *Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes* (*a*), (*b*), (*c*), (*d*) *given below :*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I.

(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I.

(c) Statement I is true; Statement II is false.

(d) Statement I is false; Statement II is true.

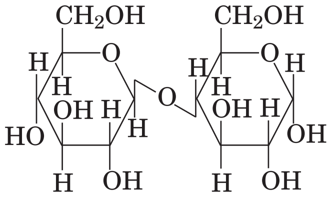
32. **Statement I** D(+)-glucose is dextrorotatary in nature.

Statement II 'D' represents its dextrorotatory nature. **[NCERT Exemplar]**

33. **Statement I** Vitamin D can be stored in our body.

Statement II Vitamin D is fat soluble vitamin. **[NCERT Exemplar]**

34. **Statement I** β-glucodisic linkage is present in maltose.



Statement II Maltose is composed of two glucose units in which C-1 of one glucose unit is linked to C-4 of another glucose unit. **[NCERT Exemplar]**

35. **Statement I** In presence of enzyme, substrate molecule can be attacked by the reagent effectively.

Statement II Active sites of enzymes hold the substrate molecule in a suitable position. **[NCERT Exemplar]**

36. **Statement I** All naturally occurring α-aminoacids except glycine are optically active.

Statement II Most naturally occurring amino acids have L-configuration. **[NCERT Exemplar]**

Comprehension Based Questions

Directions (Q. Nos. 37 to 39) Monosaccharides have —CHO (or $\gt C{=}O$) and —OH groups, so they undergo usual oxidation and reduction. Further, monosaccharides form osazone when treated with excess of phenylhydrazine (3 equivalents). In osazone formation, only the first two carbon atoms are involved. Thus, monosaccharides having identical configuration on rest of C atoms except first two will form same osazone, as in the case with glucose and fructose, *A*, *B* and *C* are three hexoses and form osazone *D*. Compounds *A* to *D* behave as below

(i) $D \xrightarrow{\text{HCl}} \xrightarrow[\text{CH}_3\text{COOH}]{\text{Zn}}$ D-fructose

(ii) $A \xrightarrow{\text{Ni, H}_2} \xrightarrow{\text{HNO}_3} \xrightarrow[\text{H}_3\text{O}^+]{\text{Na–Hg}} B + C$

(iii) $B \xrightarrow{HNO_3}$ optically active glyceric acid

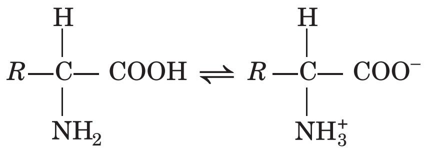
(iv) $C \xrightarrow{HNO_3}$ optically active glyceric acid

37. Compound A should be
(a) D-glucose (b) D-fructose
(c) L-glucose (d) L-fructose

38. Compound B should be
(a) D-glucose (b) D-mannose
(c) L-glucose (d) L-mannose

39. Compound C should be
(a) D-mannose (b) D-glucose
(c) L-glucose (d) L-mannose

Directions (Q. Nos. 40 to 42) Amino acids contain an —NH_2 as well as a —COOH group. In many non-polar solvents, they exist in their neutral form, but in aqueous solution, they exist as dipolar ions (Zwitter ions).

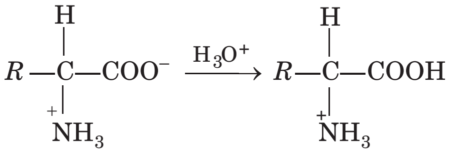


$$R-\underset{NH_2}{\overset{H}{C}}-COOH \rightleftharpoons R-\underset{NH_3^+}{\overset{H}{C}}-COO^-$$

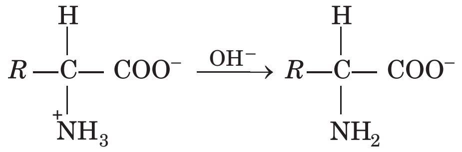
neutral Zwitter ion

This explains their several characteristics properties, like composition on heating, solubility in water, large dipole moment.

If the pH is lowered significantly, say to pH 1 or 2, then carboxylate ion will be protonated, likewise at a very high pH, the free amino group is exposed by deprotonation of ammonium ion.



$$R-\underset{\overset{+}{N}H_3}{\overset{H}{C}}-COO^- \xrightarrow{H_3O^+} R-\underset{\overset{+}{N}H_3}{\overset{H}{C}}-COOH$$

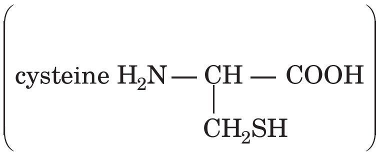


$$R-\underset{\overset{+}{N}H_3}{\overset{H}{C}}-COO^- \xrightarrow{OH^-} R-\underset{NH_2}{\overset{H}{C}}-COO^-$$

There is a pH corresponding to each amino acid where it remains neutral and neither moves towards cathode nor anode when the electric field is applied. This pH of the solution is referred to as isoelectric point. For example, the isoelectric point of alanine is 6.01, that of isoleucine is 6.02 and so on.

Hence, the ionic form of the amino or carboxylic group is the effect of pH on the functional group in the side chain of amino acid. The side chain of many amino acids contain a functional group that can also be protonated or deprotonated.

40. For the thiol group of cysteine at pH 8.2, of pK_a is 8.3, the concentration ratio of RS^- *vs* RSH (cysteine $H_2N-CH(CH_2SH)-COOH$) is



$$\left(\text{cysteine } H_2N-\underset{CH_2SH}{CH}-COOH\right) \text{ is}$$

(a) 0.8 (b) 0.6
(c) 0.9 (d) 0.2

41. In cysteine at $pK_a = 8.3, pH = 8.2$. If total amounts of RSH and RS^- is equal to 100%, then the side-chain of cysteine will exist in the protonated thio form to the extent of
(a) 26% (b) 36%
(c) 46% (d) 56%

42. If pK_a of carboxyl (2.34) and ammonia (9.69) groups, for alanine, the pH would be
(a) 12.03 (b) 7.35
(c) 6.02 (d) 11.33

Previous Years' Questions

43. Which of the following compounds can be detected by Molisch's test? **[AIEEE 2012]**
(a) Nitro compounds
(b) Sugars
(c) Amines
(d) Primary alcohols

44. The change in the optical rotation of freshly prepared solution of glucose is known as **[AIEEE 2011]**
(a) tautomerism
(b) racemization
(c) specific roation
(d) mutarotation

45. The presence or absence of hydroxy group on which carbon atom of sugar differentiates RNA and DNA **[AIEEE 2011]**
(a) 1st (b) 2nd
(c) 3rd (d) 4th

46. Biuret test is not given by **[AIEEE 2010]**
(a) carbohydrates
(b) polypeptides
(c) urea
(d) proteins

47. The two functional groups present in a typical carbohydrate are [AIEEE 2009]

(a) —OH and —COOH

(b) —CHO and —COOH

(c) $>C{=}O$ and —OH

(d) —OH and —CHO

48. The secondary structure of a protein refers to [AIEEE 2007]

(a) α-helical structure

(b) hydrophobic interactions

(c) sequence of α-amino acids

(d) fixed configuration of polypeptide back bone

Answers

Round I

1. (b)	**2.** (d)	**3.** (b)	**4.** (b)	**5.** (c)	**6.** (a)	**7.** (b)	**8.** (c)	**9.** (b)	**10.** (b)
11. (c)	**12.** (b)	**13.** (a)	**14.** (c)	**15.** (c)	**16.** (c)	**17.** (b)	**18.** (b)	**19.** (b)	**20.** (b)
21. (a)	**22.** (a)	**23.** (c)	**24.** (a)	**25.** (b)	**26.** (b)	**27.** (a)	**28.** (c)	**29.** (a)	**30.** (a)
31. (b)	**32.** (c)	**33.** (d)	**34.** (d)	**35.** (d)	**36.** (d)	**37.** (d)	**38.** (c)	**39.** (d)	**40.** (a)
41. (d)	**42.** (c)	**43.** (d)	**44.** (d)	**45.** (d)	**46.** (b)	**47.** (a)	**48.** (d)	**49.** (b)	**50.** (a)
51. (a)	**52.** (c)	**53.** (a)	**54.** (c)	**55.** (a)	**56.** (c)	**57.** (b)	**58.** (d)	**59.** (a)	**60.** (d)
61. (a)	**62.** (c)	**63.** (b)	**64.** (c)	**65.** (c)	**66.** (b)	**67.** (d)	**68.** (a)	**69.** (a)	**70.** (d)

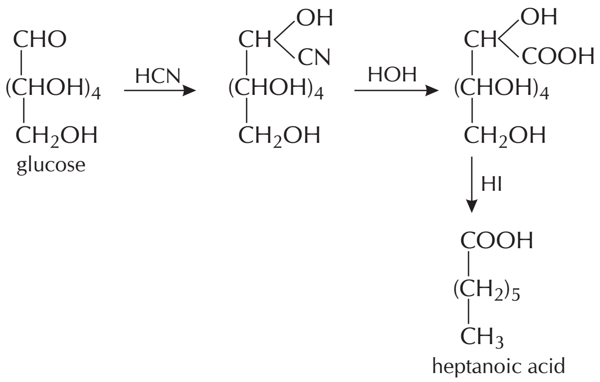
Round II

1. (d)	**2.** (c)	**3.** (c)	**4.** (b)	**5.** (b)	**6.** (c)	**7.** (c)	**8.** (c)	**9.** (c)	**10.** (b)
11. (d)	**12.** (a)	**13.** (d)	**14.** (b)	**15.** (c)	**16.** (a)	**17.** (b)	**18.** (b)	**19.** (d)	**20.** (d)
21. (a)	**22.** (c)	**23.** (a)	**24.** (a,b,c,d)	**25.** (a,c)	**26.** (a,d)	**27.** (b,d)	**28.** (a,b)	**29.** (a,c)	**30.** (b,d)
31. (a,d)	**32.** (c)	**33.** (a)	**34.** (d)	**35.** (a)	**36.** (b)	**37.** (d)	**38.** (a)	**39.** (a)	**40.** (a)
41. (d)	**42.** (c)	**43.** (b)	**44.** (d)	**45.** (b)	**46.** (a)	**47.** (d)	**48.** (a)		

the Guidance

Round I

5.



6. Milk contains lactose which on hydrolysis gives glucose and galactose.

7. Natural glucose is dextrorotatory and thus glucose is also known as dextrose.

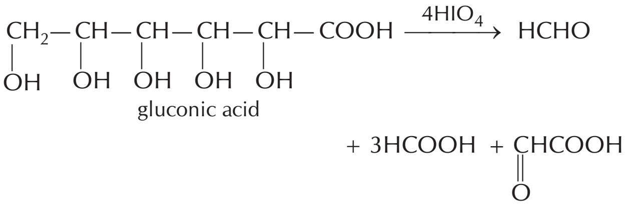
8. Fructose is oxidised by ammoniacal $AgNO_3$.

9. Aldehydes and α-hydroxy ketones give positive Tollen's test. Glucose is a polyhydroxy aldehyde and fructose is an α-hydroxy ketone.

10. α-D(+)-glucopyranose and β-D(+)-glucopyranose are anomers (a pair of stereoisomers which differ in configuration only around first carbon atom).

15. Glucose is present in pyranose form.

16.



$$\underset{OH}{\underset{|}{CH_2}}-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-COOH \xrightarrow{4HIO_4} HCHO + 3HCOOH + \underset{\underset{O}{\|}}{C}HCOOH$$

gluconic acid

17. $\frac{15}{30} \times 100 = 50$

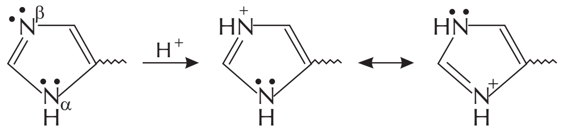
Thus, the mixture is 50% optically pure. Hence, the amount of

$$A = 50 + 25 = 75$$
$$B = 0 + 25 = 25 \therefore A : B = 3 : 1$$

18. The heme ring system is synthesized from glycine and succinyl —CoA.

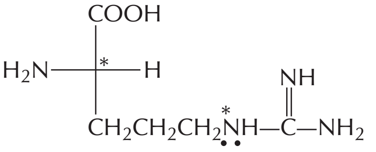
25. pH (at isoelectric point) $= \frac{2.34 + 9.6}{2} = 5.97$

26. Protonation of β-N leads to imidazolium ion, which is stabilized by two equivalent resonating structures.



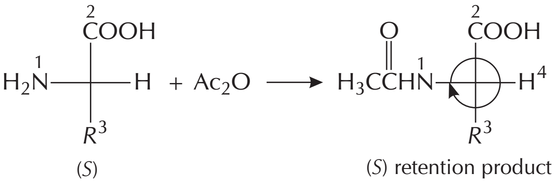
equivalent resonating structure

27. On increasing the pH by adding an alkali; H^+ will be lost from —COOH.

28.


$$H_2N-\underset{CH_2CH_2CH_2\overset{*}{N}H-\overset{\overset{NH}{\parallel}}{C}-NH_2}{\overset{COOH}{\overset{|}{\underset{|}{\overset{*}{C}}}}}-H$$

arginine

29.


30. Cations move towards cathode and when pH < pI, thus cationic form dominates.

35. The first codon of *m*-RNA will be always AUG. This codon specifies the amino-acid methionine. So, the first amino-acid in a polypeptide chain will be always methionine.

38. Val. Uyr. Ala Tyr. ala. val
Val. Ala. Tyr Ala. Tyr. Val
Tyr. Val. Ala Ala. Val. Tyr

42. The internal rearrangement of 3-phosphoglyceric acid into 2-phosphoglyceric acid takes place in the presence of enzyme phosphoglycero mutase.

65. The antibiotic puromycin inhibits protein synthesis by causing nascent polypeptide chains to be released before their synthesis is completed.

Round II

1. Protein gives blue-violet colour with ninhydrin while carbohydrate give negative test with ninhydrin. Carbohydrates give brown red ppt. with Benedict's solution. Hence, compound is a monosaccharide.

2. Cyclic hemiacetal forms of monosaccharides which differ only in the configuration of the hydroxyl group at C-1 are anomers.

3. Charring of sugar when it is treated with conc. H_2SO_4 is due to dehydration. All water molecule is removed from the sugar.

$$C_{12}H_{22}O_{11} + \text{Conc. } H_2SO_4 \longrightarrow 12C + 11H_2O$$

4. Pepsin, ptyalin and lipase are enzyme while cellulose is not the enzyme. It is a polysaccharide.

5. Sucrose is a non-reducing sugar because reducing groups of glucose and fructose are involved in glycosidic linkage formation.

6. Cellulose is a polysaccharide, composed of D-glucose units which are joined by β-glucosidic linkages. On complete hydrolysis cellulose produces D-glucose.

$$\underset{\text{cellulose}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{H^+} \underset{\text{D-glucose}}{nC_6H_{12}O_6}$$

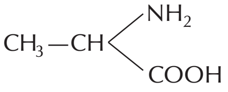
7. The two polynucleotide chains or strands of DNA are joined by hydrogen bonding between the nitrogenous base molecules of their nucleotide monomers.

8. The prosthetic group of haemoglobin is haem (Fe^{2+}).

9. Isoelectric point is a pH at which Zwitter ions do not migrate towards any of the electrode. Amino acids are also Zwitter ions hence, they do not migrate under electric field at isoelectric point.

10. Insulin is composed of two peptide chains referred as the chain *A* and *B*. *A* chain of 21 residues and *B* chain of 30 residues are crosslinked by two disulphide bridges.

11. Amino acid, alanine contains side chain of methyl group, *i.e.*,



$$CH_3-CH\begin{matrix} NH_2 \\ COOH \end{matrix}$$

Muscles contain myoglobin protein.

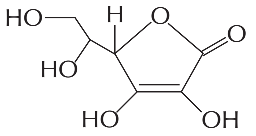
12. Haemoglobin act as an oxygen carrier in the blood because four Fe^{2+} ions of haemoglobin can bind with 4 molecules of O_2 and form oxyhaemoglobin.

$$Hb + O_2 \longrightarrow \text{Oxyhaemoglobin}$$

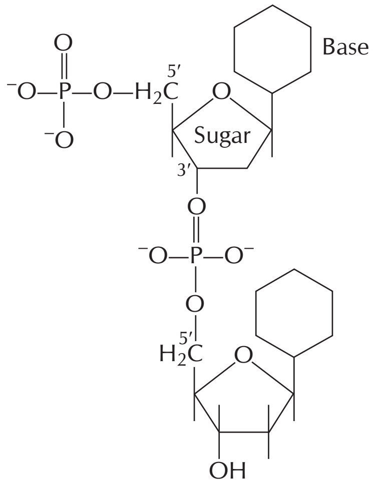
13. Enzymes have well defined active sites and their action are specific in nature. They are called biological catalysts and work at optimum temperature between 25 to 40°C.

14. 1 g fat provide 37 kJ of energy on oxidation while 1 g carbohydrate on oxidation gives 17 kJ of energy. Hence, fat has highest calorific value.

15. Ascorbic acid is vitamin C. Its structure is



16. Nucleotides are joined together by phosphodiester linkage between 5′ and 3′ carbon atoms of pentose sugar.



17. Oxytocin hormone plays an important role in child birth and milk ejection. It is secreted by posterior pitutary gland.

18. Insulin is proteinaceous hormone. It is secreted by pancreas and controls the metabolism of glucose and maintains glucose level in the blood.

19. When glucose reacts with Br_2 water, gluconic acid is obtained as main product.

20. Nucleic acids are polymers of nucleotides. They play an important role in all living cells.

21. Night blindness is caused by the deficiency of vitamin A or retinol.

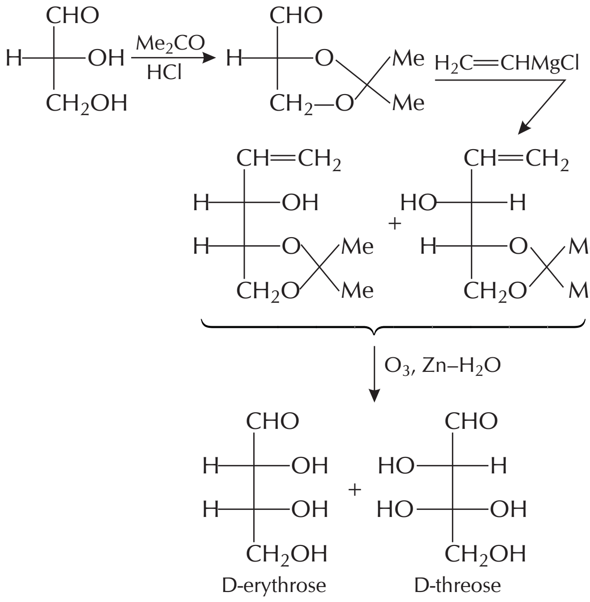
22. Insulin is an important peptide hormone. Its structure was determined by Sangar. It has two polypeptide chains with 21 and 30 amino acids. Hence, total amino acids are 51.

23. Amylopectin is a polymer of α-D-glucose. It consists of branched chains of α-D-glucose involving about 1000 or more units per molecule.

24. The compound whose numerically largest numbered (as per IUPAC convention) asymmetric carbon has configuration similar to D-glyceraldehyde has D-configuration.

25. Ribose and fructose have furanose structure.

26.



27. Amylopectin is insoluble in water, it is branched chain polymer of α-D glucose units in which chain is formed by C-1 and C-4 glycosidic linkage whereas branching occurs by C-1 and C-6 glycosidic linkage.

Structure of glycogen is similar to amylopectin and it also highly branched.

28. Every amino acid exists exclusively as dipolar ion when the pH of the solution is equal to its isoelectric point (pI), hence at this pH it does not migrate to either electrode, while at other pH, an amino acid migrates either to cathode or to anode depending upon its pH. Thus, at pH 9.60, amino acid with pI 5.40 will exist as an anion and migrate to anode while that with pI 9.60 will not migrate to any electrode. Similarly, at pH 5.40, amino acid with pI 9.60 will exist as cation and migrate to either electrode.

29. Albumins and insulin are common examples of globular proteins. In this structure, chains of polypeptides coil around to give a sperical shape.

30. In fibrous proteins, polypeptide chains are held together by hydrogen and disulphide bonds.

31. Almost all enzymes are globular proteins. These are biocatalysts because they speed up the reactions in biosystems.

32. D and L are the relative configurations given to carbohydrates in order to distinguish between the two different stereoisomers. If the —OH group attached to the bottom most asymmetric carbon (the carbon that second from the bottom) is on the right, then the compound is a D-sugar and its mirror image is L-sugar.

⊕ sign indicates that compound is dextrorotatory.

33. Vitamin D is a fat soluble vitamin so it can be stored in our body.

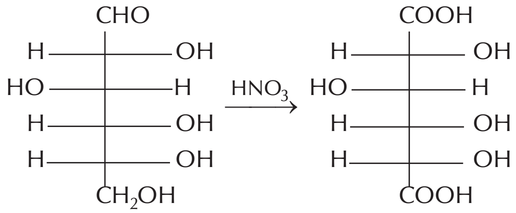
34. In maltose, α-1, 4′-glycosidic linkage is present because the oxygen atom involved in the glycosidic linkage is in the α-position.

35. Statement II is the correct explanation of statement I.

36. All naturally occurring α-amino acids except glycine are optically active because α-carbon atom is asymmetric.

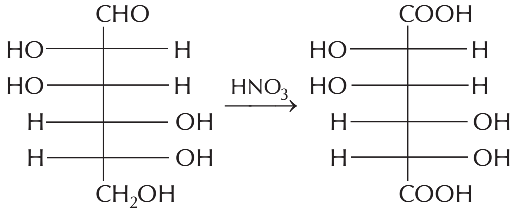
37. The (ii) series of reactions points out for the presence of a ketonic group in *A*, hence *A* must be D-fructose.

38. *B* on oxidation gives an optically active glyceric acid thus *B* should have following structure



D-glucose   optically active

39. C on oxidation gives an optically inactive glyceric acid, which is indicative of following structure for C.



D-mannose   optically active

40. For the equilibrium, $RSH \rightleftharpoons RS^- + H^+$

Henderson-Hasselbalch equation,

$$\text{pH} = \text{p}K_a + \log\frac{[\text{salt}]}{[\text{acid}]}$$

$$\therefore \quad 8.2 = 8.3 + \log\frac{[RS^-]}{[RSH]}$$

$$\text{or} \quad \frac{[RS^-]}{[RSH]} = 0.8$$

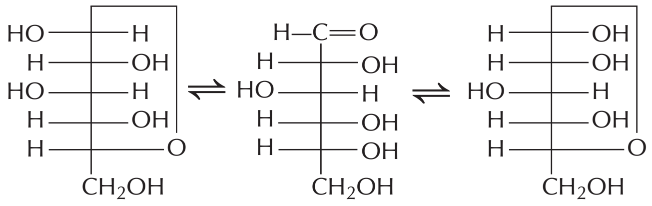
41. From the above calculations, $\dfrac{[RSH]}{[RS^-]} = \dfrac{1}{0.8} = 1.25$

$$\frac{[RSH]}{[RS^-] + [RSH]} \times 100 = 56\%$$

42. $\text{pH} = \dfrac{2.34 + 9.69}{2} = 6.015$

43. Molisch's test is for carbohydrates (*e.g.,* sugar). Add two drops of alcoholic solution of α-naphthol to the carbohydrate solution under study. Add conc. H_2SO_4 slowly by the side of the test tube. A violet ring is formed at the junction of two liquids if carbohydrate is present.

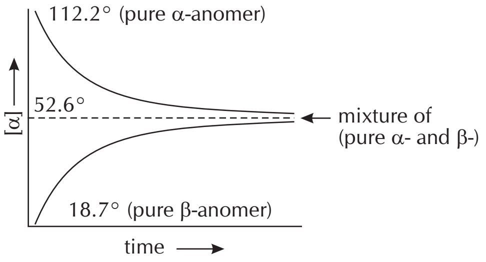
44. A spontaneous change in the specific rotation of a solution of an optically active compound is called mutarotation. Hemiacetal forms of α and β-D-glucose are stable in solid stable but in aqueous solution, there is opening of the cyclic structure which gives solution of constant specific rotation.



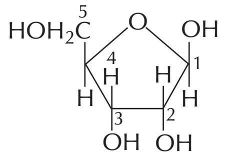
β-
Specific roatation
[α] = + 18.7°

D-glucose
+52.6°

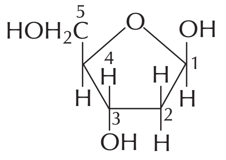
α-
+112.2°



45. Oxytocin is a hormone.

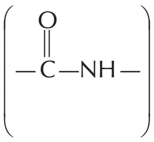


β-D-ribose used in
RNA
(at 2 carbon atom, —OH
group is present)



β-D-deoxyribose used in
DNA
(at 2 carbon atom, —OH
group is missing)

46. Biuret test is characteristically given by the compound having



$\left(-\overset{\overset{\displaystyle O}{\|}}{C}-NH-\right)$ functional group.

47. Carbohydrate are optically active polyhydroxy aldehyde or polyhydroxy ketones.

$>$C=O, —OH are functional groups of typical ketose.

—CHO, —OH functional groups of typical aldose.

48. Secondary structure involves α-helical and β-pleated sheet like structure.

15 Chemistry in Everyday Life

JEE Main MILESTONE

- Chemicals in Medicines
- Chemicals in Food
- Cleansing Agents

15.1 Chemicals in Medicines

Usually there are three systems for curing diseases. These are Unani system, Ayurvedic system and Allopathic system. In all of these three systems, the substances used to cure diseases, are chemical compounds. These compounds may be of natural or synthetic origin and are called **medicines** or **drugs.** Therefore, "the chemical substances either of natural or synthetic origin, used for treating diseases and reducing suffering from pain are called **medicines** or **drugs."** The average molecular mass of drug is ~ 100 u to 500 u.

Caution Point *All medicines are drug but all drugs are not medicines.*

Chemistry plays a vital role in every aspect of our life. Many substances which are used in daily life, are chemical compounds, e.g., soaps, detergents, household bleach, toothpaste etc., all are made up of chemicals.

The branch of science which deals with the treatment of diseases using suitable chemical compounds is called **chemotherapy.** On this basis, the various drugs used for curing diseases are also known as **chemotherapeutic agents**.

While designing a drug the following factors must be considered

(i) The target of drug
(ii) Drug metabolism
(iii) Physiological function of the drug target
(iv) Mechanism of drug action

Actually, when the biological response of a drug is therapeutic and useful, it is termed as **medicine** and used for diagnosis, prevention and treatment of diseases. If medicines are taken in higher doses than the recommended, these are potential poisons.

The factors on the basis of which medicines (drugs) can be classified are structure of drug, drug target, drug action and pharmacological effect of drug. Out of these, the classification based on pharmacological effect of drug is useful for doctors because it provides them the whole range of drugs available for the treatment of a particular type of problem.

Drug-Target Interaction

Macromolecules of biological origin such as proteins, carbohydrates, lipids, enzymes and nucleic acids are called drug targets because drug interact with these macromolecules.

(a) Enzymes as Drug Targets

Enzymes have active sites that bind the substrate for effective and quick chemical reaction. The functional groups present at the active site of enzyme interact with functional groups of substrate *via* ionic bonding, hydrogen bonding, van der Waals' interactions or dipole-dipole interaction. Some drugs interfere with this interaction by blocking the binding site of enzyme and prevent the binding of actual substrate with enzyme. This inhibits the catalytic activity of the enzyme so, these are called **enzyme inhibitors.** Drugs which block the active site of an enzyme are of two types Competitive inhibitors and non-competitive inhibitors.

Competitive inhibitors are those drugs which compete with substrate for the attachment on active sites of enzymes.

Non-competitive inhibitor are those drugs which changes the active site of enzyme after binding at **allosteric site.** Sites different from active site of the enzyme where a molecule (drug molecule) can bind and affect the active site are called allosteric site.

Caution Point *If the formation between an enzyme and an inhibitor is a strong bond, then the enzyme is blocked permanently. The body then synthesises the new enzyme.*

(b) Receptors as Drug Targets

Receptor proteins are embedded in the cell membrane. The active site of the receptor opens on the outside region of the cell membrane. **Chemical messengers** communicate the messages between two neurons and between neurons to muscles. Receptor receives chemical messenger at its binding site (or active site). Shape of the receptor site changes which results in the transfer of message into the cell.

- Receptor regains shape after removal of chemical messenger.

Antagonistic drugs are those that bind to the receptor site and inhibit its natural function. **Agonistic drugs** are those that mimic the natural messenger by switching on the receptor.

Sample **Problem 1** *Which one of the following is not a drug target?* **[NCERT Exemplar]**

(a) *Vitamins* (b) *Proteins*
(c) *Carbohydrates* (d) *Nucleic acids*

Interpret (a) Nucleic acids, proteins, carbohydrates, lipids and enzymes are drug targets because drugs interact with these macromolecules, but vitamins are not drug targets.

Therapeutic Action of Different Classes of Drugs

Antipyretics

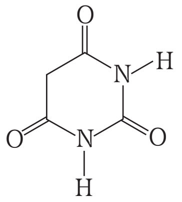
The chemical substances which are used to bring down body temperature during high fever are called antipyretics. *e.g.*, paracetamol, aspirin, phenacetin (4-ethoxy acetanilide), analgin, novalgin etc. Out of these, paracetamol is the most popular antipyretics.

Caution Point *Paracetamol, aspirin, novalgin and phenacetin act as antipyretics as well as analgesics.*

Tranquillizers

The chemical compounds which are used for the treatment of stress, mild and severe mental diseases are known as tranquillizers. They induce the sense of fitness and relieve stress and fatigue. Therefore, these drugs are also known as **psychotherapeutic drugs.** They form an essential part of sleeping pills.

Tranquillizers act on central nervous system and are habit forming in nature. They make the patient passive and help to control their emotional distress or depression. Moreover, they simply help the individuals to work with full capacities that they already have. Derivatives of barbituric acid, *i.e.*, barbiturates such as amytal, veronal, nembutal, seconal and luminal are the examples of hypnotic tranquillizers (sleep producing) whereas equanil, valium, serotonin, chlorodiazepoxide, meprobamate are examples of non-hypnotic tranquillizers. An alkaloid resperine, extracted from the plant "*Rauwolfia serpentina*" is also a tranquillizer which lowers the blood pressure and slows down the pulse rate.



barbituric acid

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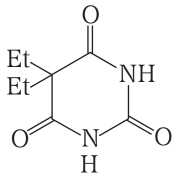
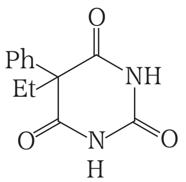
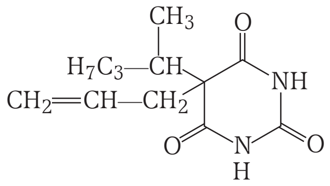


veronal (barbital)

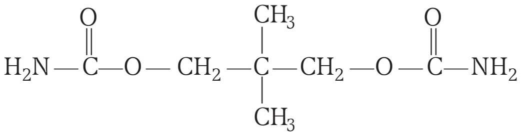


luminal

;

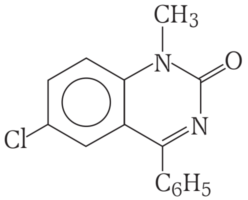


seconal

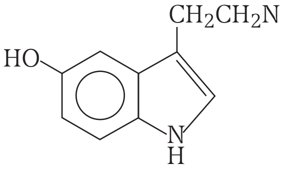


$H_2N-\overset{\overset{O}{\|}}{C}-O-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-O-\overset{\overset{O}{\|}}{C}-NH_2$

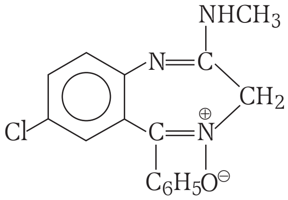
equanil



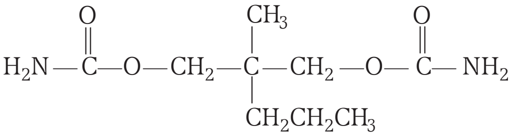
valium



serotonin



chlorodiazepoxide



$H_2N-\overset{\overset{O}{\|}}{C}-O-CH_2-\underset{\underset{CH_2CH_2CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-O-\overset{\overset{O}{\|}}{C}-NH_2$

meprobamate

Caution Point *Tranquillizers and analgesics are neurologically active drugs.*

Tranquillizers may be of the following types

(a) **Sedatives** These act as depressant and suppress the activities of central nervous system. These are given to mentally agitated and violent patients. Sedatives give a feeling of calmness, relaxation or drowsiness in the body, *e.g*., valium, barbiturates, diazepam etc.

(b) **Antidepressants** These drugs are given to persons with shattered confidence. These drugs act on central nervous system and produce a feeling of well being and confidence in the person of depressed mood. That's why these are also termed as mood booster drugs. *e.g*., Iproniazid, phenelzine, equanil, vitalin, benzedrine, tofranil, methedrine, cocaine etc.

(c) **Hypnotics** These are used to reduce mental tension and anxiety, *e.g*., chloretone, luminal, seconal etc.

(d) **Psychedic drugs** They produce hallucination, disturb vision and hearing and cause false feeling of happiness. An example of powerful psychedlic drug is LSD (lysergic acid diethylamide). Other example of such drugs is mescaline.

Sample **Problem 7** *Which of the following statements are correct about barbiturates?* **[NCERT Exemplar]**

(a) *Hypnotics or sleep producing agents*

(b) *These are tranquillizers*

(c) *Non-narcotic analgesics*

(d) *Pain reducing without disturbing the nervous system*

Interpret (*a, b*) Barbiturates constitute an important class of tranquillizers. These are hypnotic *i.e.,* sleep producing agents.

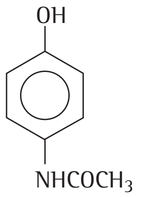
Hot Spot 1

ANALGESICS

Analgesics specially non-narcotic analgesics is the most important topic of this chapter. Generally questions are asked on paracetamol and aspirin from this topic.

The medicines which are used to reduce pain are known as analgesics. In simple words, we can say, analgesic is the medical name for pain killers. These can be further of two types :

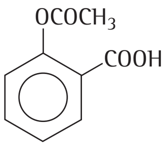
(a) **Non-narcotic** (or non-addictive) **analgesics** The non-habit forming chemicals which are used to reduce mild to moderate pain such as headache, toothache, muscle and joint pain etc., are called non-narcotic analgesics. Because of their non-habit forming nature, they are also termed as non-addictive. These drugs do not produce sleep and unconsciousness. Some examples of non-narcotic analgesics are naproxen, diclofenac sodium or potassium, ibuprofen, paracetamol, ketoprofen, mefenamic acid etc.



paracetamol
(4-acetamidophenol)

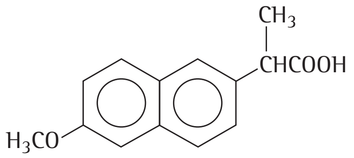
Some non-narcotic analgesics have anti-inflammatory properties, *i. e.*, they inhibit the synthesis of prostaglandins which leads to inflammation in a tissue and causes pain. Due to which these are known as non-steroidal anti-inflammatory drugs (NSAIDS).

Examples of such drugs (medicines) with their structure are given below :

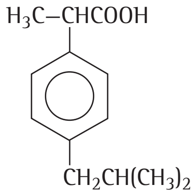


acetyl salicylic acid
or 2-acetoxy benzoic acid
(aspirin)

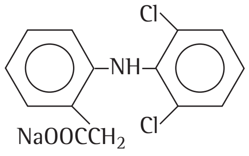
;



naproxen



ibuprofen



dichlorofenac sodium

Aspirin is the most common analgesic alongwith antipyretic (temperature lowering), anti-inflammatory and anti-blood clotting properties (due to its anti-blood clotting action, it is widely used to prevent heart attack). Moreover aspirin is also used to check pregnancy related problems, viral inflammation in AIDS patients and cancer.

Aspirin is supposed to be toxic to the liver. In some cases, it causes bleeding from the wall of stomach and gastric irritation. Infact, in empty stomach aspirin gets hydrolysed into salicylic acid which is responsible for these problems. Therefore, it is advised that aspirin should not be taken into empty stomach. However, calcium and sodium salts of aspirin are more soluble and less harmful.

Sample **Problem 4** *The* pH *value of gastric juice in human stomach is about* 1.8 *and in the small intestine it is about* 7.8. *The* pK_a *value of aspirin is* 3.5. *Aspirin will be*

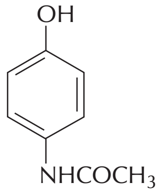
(*a*) *completely ionised in the small intestine and in the stomach*
(*b*) *ionised in the small intestine and almost unionised in the stomach*
(*c*) *unionised in the small intestine and in the stomach*
(*d*) *ionised in the stomach and almost unionised in the small intestine*

Interpret (*b*) Aspirin is a moderate acid (pK_a = 3.5), hence is almost unionised in stomach due to strong acidic medium of it (because of HCl). It is due to common ion effect. While in small intestine, the medium is alkaline, hence aspirin will be sufficiently ionised in small intestine.

Sample **Problem 5** *The functional groups present in paracetamol are*

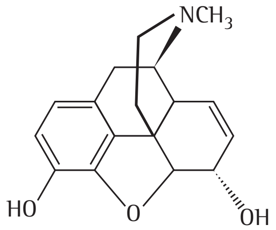
(*a*) —OH, —$NHCONH_3$ (*b*) —OH, —COOH
(*c*) —OH, —COO*R* (*d*) —NH_2, —OH

Interpret (*a*) The structure of paracetamol is

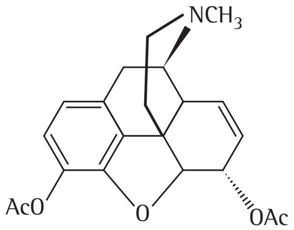


Thus, it have —OH and —$NHCOCH_3$ groups.

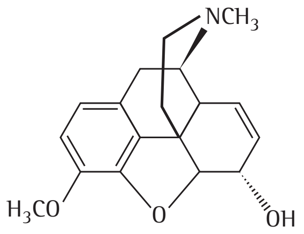
(b) **Narcotic** (or addictive) **analgesics** The pain relieving drugs which produce sleep and unconsciousness are called narcotic analgescis. Unlike non-naroctic analgesics, these are habit forming. These are more effective than non-narcotic drugs. These are mostly opium derivatives and used only in severe pain, ***e.g.,*** morphine, codeine, meperidine, heroin (or morphine diacetate obtained by acetylation of morphine) etc.



morphine



heroin

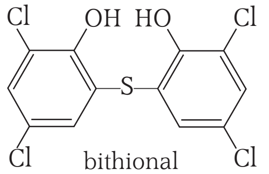


codeine

These drugs when used in small dose, relieve pain and produce sleep but their large dose, causes laziness, convulsions and ultimately death.

Antiseptics and Disinfectants

The chemicals which either prevent the growth of microorganisms or kill them but are not harmful to the living tissues, are known as antiseptics. Being harmless to living tissues, antiseptics can be safely applied on wounds, ulcers, cuts and diseased skin surfaces. These drugs also reduce odours caused by bacterial decomposition on the body or in the mouth. These are, therefore, mixed with body deodorants, face powders and breath purifiers, *e. g.*, bithional, an antiseptic, is mixed to medicated soaps to impart antiseptic properties.



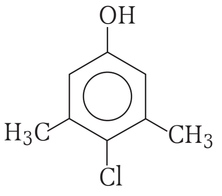
bithional

The chemical substances which also kill the microorganisms but are not safe to apply over living tissues, are called **disinfectants.** Disinfectants play an important role in water treatment and in public health sanitation. They are actually used for inanimate objects such as floors, toilets, instruments etc.

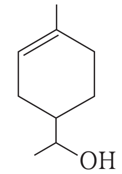
Many times, the same substance can act as an antiseptic as well as disinfectant on the basis of its concentration, *e. g.*, 0.2% solution of phenol is an antiseptic whereas its 1% solution acts as disinfectant. Similarly, low concentration of SO_2 is used to sterilize squash for preservation but its high concentration is used as disinfectant for living rooms.

Other examples of antiseptics and disinfectants are as follows

(i) Dettol is one of the most commonly used antiseptics. It is a mixture of chloroxylenol and α-terpineol. It is chloroxylenol which is responsible for its antiseptic and disinfectant properties.



chloroxylenol



α-terpineol

(ii) 0.2 to 0.4 ppm (parts per million) concentration of chlorine is used for making water fit for drinking.

(iii) Savlon in non-aqueous solution is used as an antiseptic.

(iv) Amyl metacresol (5-methyl-2-pentylphenol) is an antiseptic which is used as a mouthwash or gargles in infections of the mouth and throat.

(v) Iodine and iodoform both are powerful antiseptics. Iodine is employed as tincture, *i.e.*, a solution of 2–3% iodine in alcohol and water while iodoform is used as powder for wounds.

(vi) A dilute aqueous solution of boric acid is used as a weak antiseptic for eyes. Boric acid is also used as antiseptic in baby talcum powders.

(vii) Hydrogen peroxide, salol (phenyl salicylate) and mercurochrom are also used as antiseptics.

(viii) A soapy solution of cresol, called lysol, is used as disinfectant.

(ix) Some organic dyes such as gention violet, methylene blue have antiseptic property and are used for dressing wounds and for treating various skin diseases.

Antimicrobials

The chemicals which are used to cure infections caused by microbes (microorganisms) either by killing or destroying them, are known as antimicrobials. Microbes are extremely small organisms that can be seen through microscope only, *e.g.*, bacteria, viruses etc. The microbes which produce diseases/infections are known as **pathogens**.

Human body possesses an efficient natural defence mechanism for fighting against potential pathogenic microbes. Certain body secretions such as nasal secretion, saliva, lactic acid (in sweat) and hydrochloric acid (in stomach), kill the pathogens and also inhibit their growth.

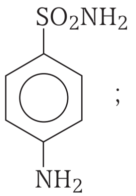
However, when the natural defence mechanism is not working properly or fails, the pathogens attack on the living tissues and lead to infection or disease. There are three possible ways by which these microbial diseases can be controlled.

These are

1. By using bacteriostatic drug which inhibits or arrests the growth of microbes.
2. By using bactericidal drug which kills the microbes.
3. By increasing immunity and resistance to infection of the body.

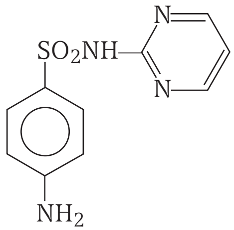
Most of the microbial diseases are cured by using antibiotics and sulpha drugs. The examples of antibiotics are tetracycline, penicillin, chloramphenicol and the examples of sulpha drugs are sulphanilamide (*p*-amino benzene sulphonamide) and its derivative such as sulphadiazine, sulphadimidine, sulphadimethoxine, sulphadoxine, sulphasomidine, sulphaguanidine etc.

In fact sulpha drugs are a group of drugs which are derivatives of sulphanilamide and have great antimicrobial capacity, thus these are used widely against diseases such as dyptheria, dysentry, tuberculosis etc., caused by cocci, a type of bacteria. In structure, these drugs are analgoues of *p*-amino benzoic acid as shown below.

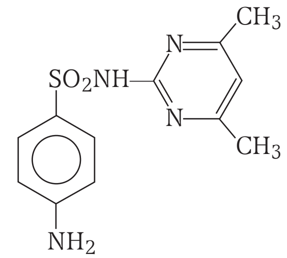


sulphanilamide
(p-amino benzene
sulphonamide)

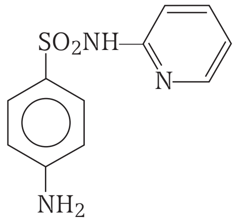
;



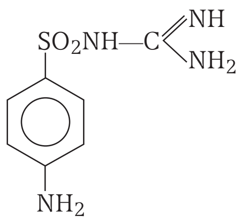
sulphadiazine



sulphadimidine



sulphapyridine



sulphaguanidine

Sulphonamides in combination with trimethoprim are used for the treatment of urinary tract infection.

Mode of Action of Sulpha Drugs

Sulpha drugs inhibit the growth of those bacteria which need *p*-amino benzoic acid for the synthesis of folic acid. Sulphanilamide acts as an inhibitor for those enzymatic steps which are involved in the synthesis of folic acid by the bacteria.

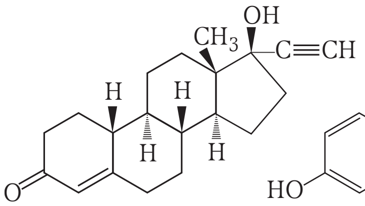
This results in the death of bacteria because synthesis of folic acid is essential for bacteria. Humans do not synthesize their own folic acid, they get it from dietry sources, so they are unaffected by sulpha drugs.

Antifertility Drugs

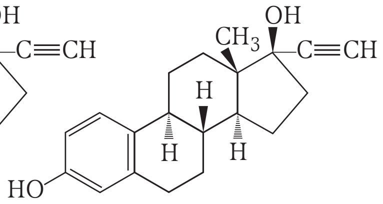
The chemicals which are used to check pregnancy in woman are known as antifertility drugs. These are also known as **birth control pills** or **oral contraceptives**. The basic aim of these drugs is to prevent conception or fertilization.

Chemically, antifertility drugs belong to the class of natural products, known as steroids. Steroids are the active ingredients of antifertility drugs. These check the pregnancy by controlling female menstrual cycle and ovulation.

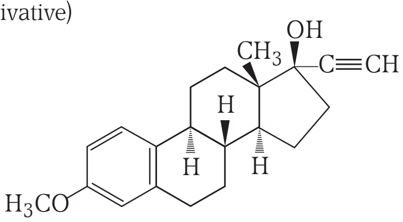
These, essentially, contain a mixture of synthetic estrogen and progesterone derivatives which are more potent than the natural hormones. The common progesterone, used are ethynodial, norethindrone, noresthistereone, lynestrenol etc., and estrogens used are ethynylestradiol, mestranol etc., *e.g.,* a brand name enovid *E* contains a mixture of norethindrone (a progesterone derivative) and mestranol (a synthetic estrogen).



norethindrone
(a progesterone
derivative)

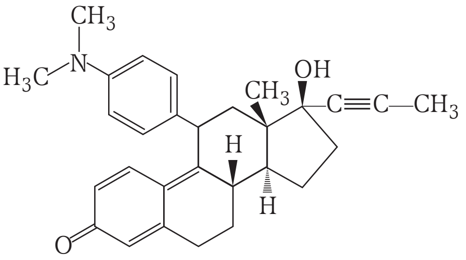


ethynylestradiol
(an estrogen)



mestranol
(ethynylstradiol monomethyl ether)
(an estrogen)

Ormeloxifene (centchroman, saheli) is also an effective antifertility drug. Mifepristone is a synthetic steroid that checks the effect of progesterone and is used as a "morning after pill".



mifepristone (a synthetic steroid)

Adverse Effects These contraceptives may cause disruption of normal menstrual cycle (prolonged or excessive bleeding) and increase in weight. In some cases, prolonged infertility has been reported after the use of these contraceptives.

Antibiotics

The chemicals which are obtained from microorganisms such as bacteria, fungi, moulds etc., and used to inhibit the growth or even kill the microorganisms are called antibiotics. However, this definition has been modified with the development of synthetic methods. An antibiotic now refers to a chemical which in low concentration inhibits the growth or kills microorganisms by intervening in their metabolic processes.

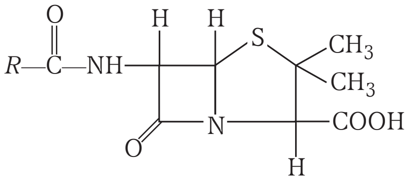
Since, antibiotics are the products of microbial growth, this therapy has been likened to "setting one thief against another".

Antibiotics can be either bactericidal or bacteriostatic. **Bactericidal drugs** (*bacteri* = microorganisms, *cidal* = kill)

kill the microorganisms. Penicillin, aminoglycosides, ofloxacin etc., are the examples of bactericidal antibiotics. **Bacteriostatic drugs** (*bacteri* = microorganisms, *satic* = inhibit) inhibit or arrest the growth of microorganisms. Commonly used bacteriostatic antibiotics are tetracycline, erthyromycin etc.

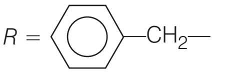
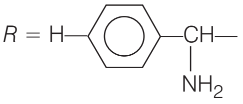
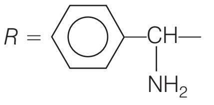
The full range of microorganisms affected by an antibiotic is called its **spectrum**. An antibiotic may be narrow spectrum or broad spectrum. A **broad spectrum antibiotic** is effective against a large number of harmful organisms whereas **narrow spectrum antibiotics** affect only certain classes of microorganisms. Ofloxacin, aminoglycosides, tetracycline, chloramphenicol etc., are the examples of broad spectrum antibiotics while penicillin is an example of narrow spectrum antibiotics.

First discovered antibiotic is penicillin which is discovered by A. Fleming in 1929. He obtained it from *penicillium notatum*. General formula of penicillin is $C_9H_{11}O_4SN_2R$. With the substitution of different *R* groups, about six natural penicillins have been isolated so far. The general structure of penicillin and its derivatives are given below :



General structure of penicillin

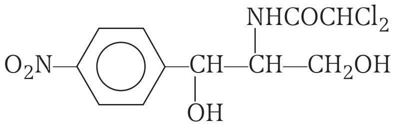
Table 15.1 **Different Penicillines**

S.N.	*R* group	Name
1.	*R* = 	Penicillin G or benzyl penicillin
2.	$R = CH_3CH_2CH{=}CH{-}CH_2$	Penicillin F
3.	$R = CH_3{-}(CH_2)_6{-}$	Penicillin K
4.	*R* = 	Ampicillin*
5.	*R* = 	Amoxycillin*

*Ampicillin and amoxycillin are semi-synthetic modifications of penicillin.

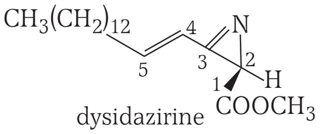
Penicillin is a narrow spectrum antibiotic and used for curing sore throat, gonorrhoea, rheumatic fever etc. Some persons have allergy to it hence, it is essential to test the sensitivity (allergy) of the patient by giving a test dose.

Chloramphenicol, tetracycline and chloromycetin all are broad spectrum antibiotics and used for the treatment of typhoid, acute fever, pneumonia, dysentery, whooping cough and certain urinary infections. Chloramphenicol is readily absorbed from the gastro-intestinal tract and hence, it can be given orally.



chloramphenicol

Streptomycin which is also an antibiotic is highly effective for curing tuberculosis. It is also used for the treatment of meningitis and pneumonia. Dysidazirine, an antibiotic, is supposed to be toxic towards certain strains of cancer cells.



dysidazirine

Sample Problem 10 *Chloramphenicol is a*

(a) *broad spectrum bacteriostatic antibiotic*
(b) *broad spectrum bactericidal antibiotic*
(c) *narrow spectrum bacteriostatic antibiotic*
(d) *narrow spectrum bactericidal antibiotic*

Interpret (a) Chloramphenicol have static (inhibitory) effect on microbes. It is effective against a number of diseases such as fever, typhoid, dysentery, certain form of urinary infections, meningitis and pneumonia. So, it is a broad spectrum bacteriostatic antibiotic.

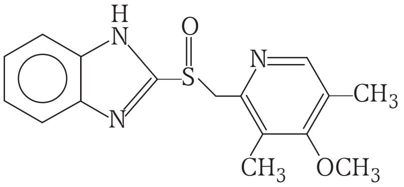
Antacids

Wall of stomach secrets acids to make the stomach acidic and for the digestion of food. When the acid is secreted in excess, it leads to indigestion, heart burn or gastric ulcers. The chemicals which are used to neutralise the excess acid present in the gastric juice and to raise the pH of stomach up to an appropriate level are called antacids.

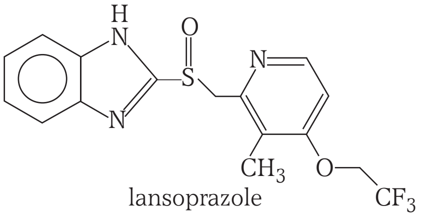
Since acids are neutralised by bases, weak bases such as sodium bicarbonate ($NaHCO_3$), magnesium hydroxide [$Mg(OH)_2$], magnesium carbonate ($MgCO_3$), magnesium trisilicate, aluminium hydroxide etc., are used as antacids.

Generally, antacids in liquid form are more effective than that in the form of tablets because these have great surface area available for interaction and neutralisation of acid.

Calcium salts can also be used as antacids but they are not so effective. Recently omeprazole and lansoprazole have been synthesised to give quick relief from acid gastritis.

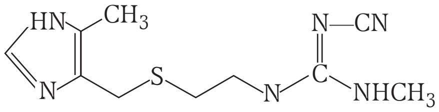


omeprazole

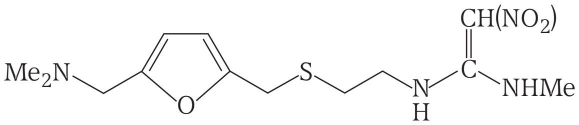


lansoprazole

Histamine also stimulates the secretion of pepsin and hydrochloric acid. To prevent hyperacidity, produced by histamine, cimetidine (tegamet) and ranitidine (zantac) are used as antacid.



cimetidine



ranitidine

Cimetidine and ranitidine both prevent the interaction of histamine with the receptors of stomach wall, which results in the release of lesser amount of acid.

Caution Point *Milk acts as a weak antacid and thus, possesses a protective action against acidity.*

Sample **Problem 13** *Which one of the following statement is incorrect?*

(a) *Cimetidine and ranitidine are better antacids than* $NaHCO_3$, $Mg(OH)_2$ *and* $Al(OH)_3$.

(b) *Cimetidine and ranitidine neutralize the excess acid produced in the stomach.*

(c) *Cimetidine and ranitidine both prevent the interaction of histamine with the receptors of stomach wall.*

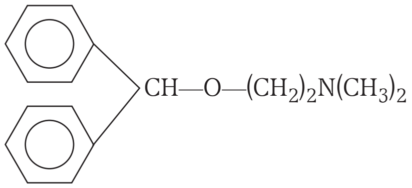
(d) *Cimetidine and ranitidine are also known as tegamet and zantac respectively.*

Interpret (*b*) Cimetidine and ranitidine both prevent the interaction of histamine with the receptors of the stomach wall as histamine stimulates the secretion of acid.

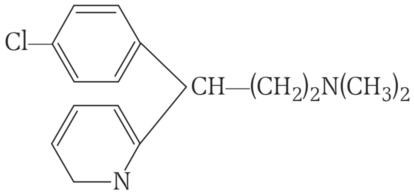
Antihistamines

These are infact anti-allergic drugs. Since, allergy is caused due to secretion of histamine (by mast cells) in the body, these drugs combat the effect of histamines. In other words, "the chemicals which diminish or abolish the effect of histamine and hence, prevent the allergic reactions such as hay fever, mild asthma, nasal discharge etc., are known as antihistamins. These drugs are also useful for conjunctivitis (*i.e.*, inflammation of conjunctiva of eye) and rhinitis (*i.e.*, inflammation of nasal mucosa).

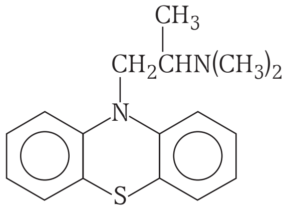
The common examples of antihistamines are diphenylhydramine (common name benadryl), pheniramine maleate (avil), chlorpheniramine maleate (zeet), promethzine etc.



diphenylhydramine (benadryl)



chlorpheniramine



promethazine

Anaesthetics

The chemicals which produce general or local insensibility to pains and other sensations are called anaesthetics. Here, the word 'local' means 'in a limited area'. Some anaesthetics act after inhaling its vapours, *e.g.*, diethyl ether, nitrous oxide, cylopropane etc., while others are administered orally or injected into the body, *e.g.*, morphine and pathedine.

Cocaine, novocine (procaine), xylocaines and ethyl chloride are some examples of local anaesthetics. These are used for tooth extraction or small surgical operations.

Check Point 1

1. What is the difference between a medicine and a drug?
2. What is the mode of action of antimicrobial drugs? **[NCERT Exemplar]**
3. Why is it advised that aspirin should not be taken into empty stomach?
4. Antacids in their liquid form are more effective as compared that in their tablet form. Explain, why?
5. Why are certain drugs called enzyme inhibitors? **[NCERT Exemplar]**
6. Which analgesics are called opiates? **[NCERT Exemplar]**

15.2 Chemicals in Food

All those chemicals which are added to food for its preservation and enhancing its appeal are called food additives. These include antioxidants, artificial sweeteners, preservatives, edible colours, flour improvers etc. With the exception of preservatives, antioxidants and artificial sweetener, the remaining classes mentioned above have no nutritive value.

Preservatives

During the storage and distribution of food, several undesirable changes occur in flavour, colour, texture and appetitic appeal. To avoid these changes some chemicals are added to food. These chemicals are known as preservatives. In other words, the chemicals which are used to protect food from microbes actions, *i.e.*, which arrest the process of fermentation, acidification and any other decomposition of food are known as food preservatives. Some important examples of food preservatives are given below

(i) **Carboxylates** such as sodium benzoate (C_6H_5COONa) are commonly used to preserve food. Sodium benzoate is used as preservative in soft drinks and acidic foods. It is metabolised by conversion to hippuric acid ($C_6H_5CONHCH_2COOH$) which is ultimately excereted with urine. Sodium and calcium propionates are used as preservatives in breads and cakes.

(ii) **Vitamin E** is naturally occurring food preservative found in vegetable oil.

(iii) The jams and squashes-pickles are preserved by adding sodium metabisulphite ($Na_2S_2O_5$) or potassium metabisulphite, $K_2S_2O_5$. The sulphurous acid present in it inhibit the growth of microbes.

$$Na_2S_2O_5 \longrightarrow Na_2SO_3 + SO_2$$
$$SO_2 + H_2O \longrightarrow H_2SO_3$$

(iv) In cheese, baked food, pickles and meat, sorbic acid and its salts are used as preservative.

(v) Epoxides and ethyl formates are used for the preservation of species, nuts and dried fruits.

(vi) Table salt, sugar and vegetable oils are also used as preservatives.

Sample Problem 14 *Hippuric acid is a metabolic products of*

(a) *sodium propionate* (b) *vitamin E*
(c) *sodium benzoate* (d) *sodium salt of sorbic acid*

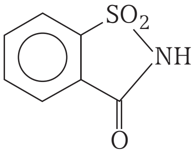
Interpret (c) Sodium benzoate is metabolised to hippuric acid in body, which is excreted with urine.

Artificial Sweetening Agents

The chemicals which are not sugars (carbohydrates) but give sweetening effect to the food and ehnance its odour and flavour are called **artificial sweetening agents**. Usual sweeteners such as sucrose and fructose add calorific intake in addition to sweetness while artificial sweeteners give sweetening effect without producing any calories. This is because these chemicals do not undergo the biochemical reactions in the body *i.e.,* they pass through the human body unmetabolised. Therefore, these chemicals are also called low calorie sweeteners or calorie-free sweeteners.

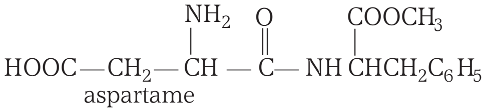
Important artificial sweeteners are

(a) **Saccharin** It is the first discovered artificial sweetener. It is very popular sweetening agent. It is about 300 times sweeter than cane sugar. It is non-biodegradable compound but has no calorific value. In market, it is available in the form of its sodium or calcium salt as these are water soluble. Saccharin has proved to be a life saver for countless diabetics and is of great value to people who need to control intake of calories.



saccharin

(b) **Aspartame** It is an another artificial sweetener. It is methyl ester of the dipeptide obtained from phenylalanine and aspartic acid. Its structure is

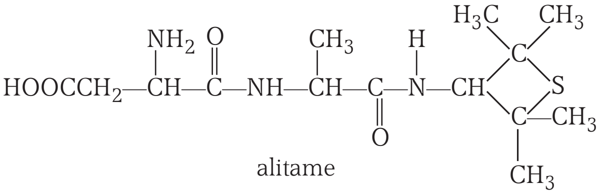


$$HOOC—CH_2—\overset{\overset{NH_2}{|}}{CH}—\overset{\overset{O}{||}}{C}—NH\,\overset{\overset{COOCH_3}{|}}{CH}CH_2C_6H_5$$

aspartame

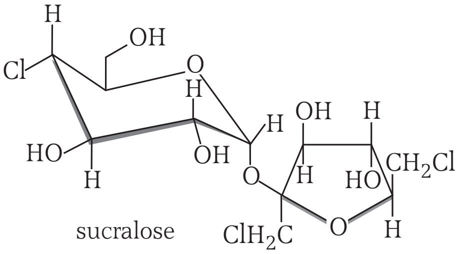
It is also known as "Nutra sweet". It is about 180 times sweeter than cane sugar. The only limitation for it is that at baking or higher temperatures, it gets decomposed, so its use is limited only in cold foods and soft drinks.

(c) **Alitame** It is more stable than aspartame at high temperature. It is about 2000 times sweeeter than sucrose.



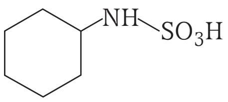
alitame

(d) **Sucralose** It is a trichloro derivative of sucrose. It is about 650 times sweeter than cane sugar. It is a zero calorie sugar.



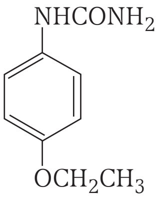
sucralose

(e) **Cyclamate** It is also an artificial sweetener. Chemically, it is N-cyclohexylsulphamate. It is only twenty times sweeter than cane sugar.



cyclamate

(f) **Dulcin** (a urea sweetener) It is only twenty five times sweeter than cane sugar. It has the following structure

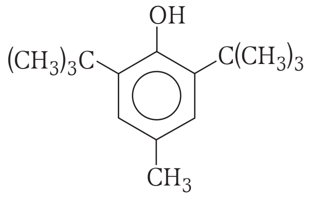


dulcin

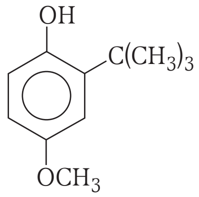
Other examples of this category are nitro anilines, dihydrochalcones (DHC) etc.

Antioxidants

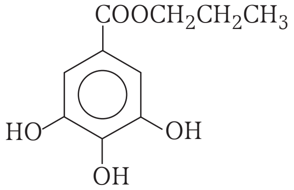
Unsaturated oils and fats containing food materials, when stored, undergo deterioration because of the oxidation by atmospheric oxygen. To avoid their oxidation and to prevent their spoilage, certain chemicals which are able to prevent their oxidation are added. These chemicals are known as **antioxidants**. Therefore, the chemicals which retard the action of oxygen on the food material and thereby help in its preservation, are called **antioxidants**. BHA (butylated *p*-hydroxyanisole), BHT (butylated *p*-hydroxy toluene), esters of gallic acid and lecithin are some examples of antioxidants.



BHT
(butylated hydroxy toluene)



BHA
(butylated hydroxy anisole)



propyl gallate
(an ester of gallic acid)

Some antioxidants are already present in food materials. *e.g.*,

Table 15.2 **Sources of Some Antioxidant**

Antioxidants	Food materials containing antioxidants
Vitamin C (ascorbic acid)	Fruits and vegetables
Vitamin E (tocopherols)	Vegetable oils
Carotenoids	Fruits and vegetables
Polyphenolic antioxidants	Tea, coffee, soyabean, red wine, chocolate etc.

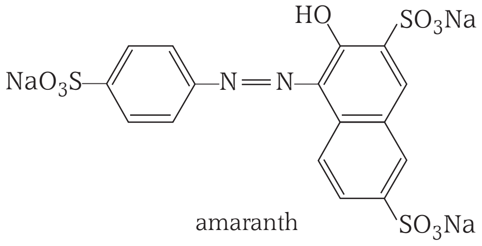
Sulphur dioxide and sulphite are useful antioxidants for wine and beers, sugar syrups, peeled fruits.

Edible Colours

The chemicals which are used for imparting colour to the food and to increase the eye appeal are called **edible colours**. These are essentially dyes which may be either of natural or synthetic origin. Azo dyes are used as synthetic edible colours. However, these are harmful for young children and asthma patients. The most important synthetic dye is tetrazine but its use is banned now.

The common natural colour are chlorophyll (green colouring matter extracted from leaves), saffron (prepared from flowers), caramel (obtained by heating sugar), turmeric (obtained from dried and ground root of ginger) etc.

The other synthetic colours used in food products are amaranth (a red brown powder with saline taste), indigo carmine (blue), ponceau (fast green), erythrosin etc.



amaranth

Check Point 2

1. Sugar is the main source of energy as it produces energy on metabolic decomposition. But these days low calorie drinks are more popular, why?
2. Name two α-amino acids which form a dipeptide which is 100 times more sweet than cane sugar?
3. $Na_2S_2O_5$ is used as a preservative for jams and squashes-pickles. Explain, why?
4. 'Nutra sweet' is about 180 times sweeter than cane sugar but its use is limited only to soft drinks. Explain why?
5. Pickles have a long shelf life and do not get spoiled for mouths. Why?

15.3 Cleansing Agents

These are also known as surfactants or surface active agents. In fact, those chemicals which concentrate at the surface of the solution or interfaces or surface films, reduce surface tension of the solution and help in removing dirt and dust by emulsifying grease are known as **surfactants**. Soaps and detergents belong to this class.

Soaps

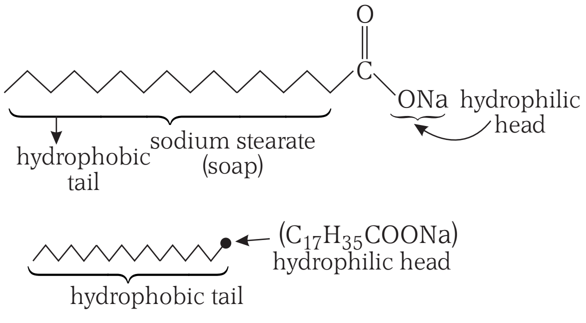
The mineral salts of higher fatty acids such as oleic acid ($C_{17}H_{33}COOH$), stearic acid ($C_{17}H_{35}COOH$) and palmitic acid ($C_{15}H_{31}COOH$) etc., are called **soaps**. Out of these, only sodium and potassium salts of fatty acids being water soluble, are widely used for cleaning purposes and are commonly known as **common soaps**. Other soaps, being water insoluble are less useful. Sodium soaps are hard whereas potassium soaps are soft to skin. Therefore, sodium soaps are used for washing purposes and potassium soaps are as liquid soaps, shaving creams and toilet soaps.

Composition of Soaps

Chemically, soaps contain two parts

(i) **Non-polar hydrocarbon part** which is fat soluble and also called hydrophobic or lipohilic (*lipo* = fat; *philic* = loving) part.

(ii) **Polar carboxylate part** which is water soluble and also called hydrophilic or lipophobic (*lipo* = fat; *phobic* = hating) part.



A soap molecule

Cleansing Action of Soap

On applying soap to a dirty wet cloth, the hydrocarbon part (non-polar part) of soap dissolves in grease or dust while the polar carboxylate part is directed towards water. Thus, an emulsion is formed between grease particles and water molecules, which appears in the form of foam. On washing the cloth with excessive water, these dirt or dust or grease particles are washed away from the surface of cloth along with soap and the cloth becomes clean.

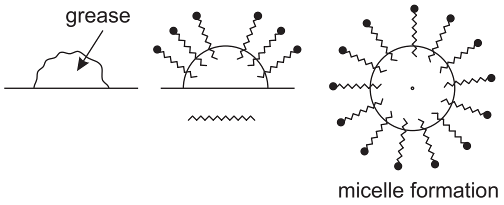


Fig. 15.1 Cleansing action of soap

Advantages and limitations of soaps Soaps are 100% biodegradable, *i.e.,* these are completely degraded by the microorganisms. Therefore, these do not cause water pollution.

Soaps cannot be used in hard water because calcium and magnesium ions present in hard water form curdy white precipitate with soap. Soaps also cannot be used in acidic solution. This is because insoluble fatty acids are precipitated by acids which adhere to the fabrics and prevent dyeing process.

$$2\,\underset{\text{soap}}{RCOONa} + \underbrace{Ca^{2+} \text{ or } Mg^{2+}}_{\text{from hard water}} \longrightarrow \underset{\text{white curdy ppt}}{(RCOO)_2Ca \text{ or } Mg}$$

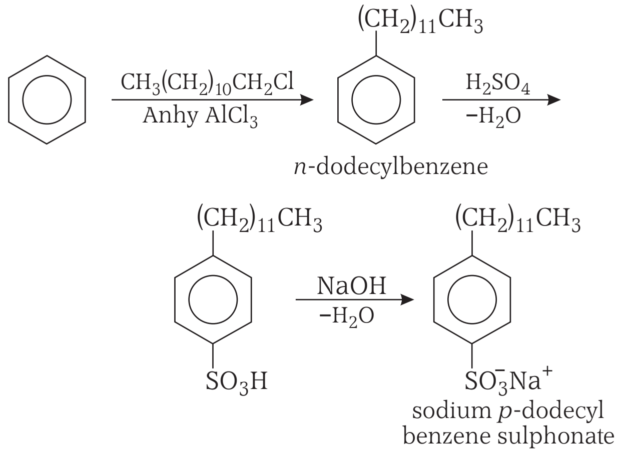
Detergents

The structure of detergents is similar to that of soaps. These are also used for cleansing purpose, although these do not contain usual soaps like sodium salts of fatty acids. Hence, these are also known as "**soapless soap**". These are better cleansing agents than soaps. This is because these do not form insoluble precipitates with calcium and magnesium salts of hard water. There are also effective in acidic solution to form alkyl hydrogen sulphate which is soluble.

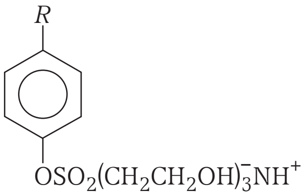
Chemically, detergents are sodium or potassium salts of long chain alkyl or aryl sulphonates or sulphates. Thus, detergents are of two types :

(a) Sodium Alkyl Benzene Sulphonates

These are obtained from derivatives of benzene sulphonic acid. The common example of such detergents is sodium *p*-dodecyl benzene sulphonate which is prepared from benzene by treating it with dodecyl chloride in the presence of anhydrous $AlCl_3$, followed by sulphonation and base catalysed hydrolysis.



Sulphonates with triethanol ammonium ion in place of sodium serve as highly soluble material for liquid detergents.



Unbranched or less branched alkyl group containing sulphonates are soft and highly branched alkyl group containing sulphonates are hard detergents.

(b) Sodium Alkyl Sulphate

Oils and fats on hydrogenolysis give alcohols with 10-15 carbon atoms. These alcohols on esterification with sodium salts of sulphuric acid give sodium alkyl sulphates. Examples of such detergents are sodium dodecyl sulphate, sodium lauryl sulphate, sodium cetyl sulphate.

$$\underset{\text{alkyl alcohol}}{RCH_2OH} + HOSO_3H \xrightarrow[-H_2O]{\text{Sulphonation}} \underset{\text{alkyl hydrogen sulphate}}{RCH_2OSO_3H}$$

$$\xrightarrow[-H_2O]{NaOH} \underset{\text{sodium alkyl sulphate}}{RCH_2OSO_3^-Na^+}$$

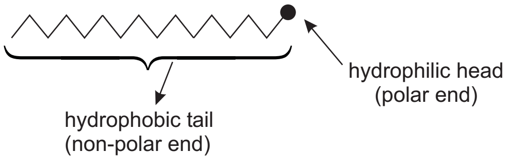
where, $R = CH_3(CH_2)_{10}^-$ or $C_{15}H_{31}^-$

Composition of Detergents

Detergents have structure similar to soaps. These contain

(i) a long non-polar hydrocarbon chain with 12 or more carbon atoms which is hydrophobic or lipophilic in nature.

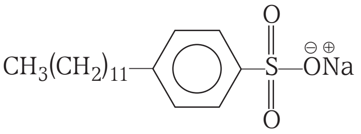
(ii) a polar ionic part which is hydrophilic or lipophobic in nature.



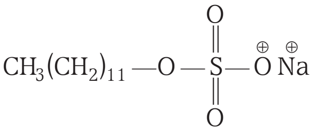
Structure of detergents

The hydrophilic surface active group may be anionic, cationic or netural. On the basis of nature of surface active group, detergents may be classified into three categories.

(i) **Anionic detergents** contain anionic hydrophilic group such as alkyl hydrogen sulphates and alkyl benzene sulphonates.



sodium *p*-*n*-dodecyl benzenesulphonate (SDS)

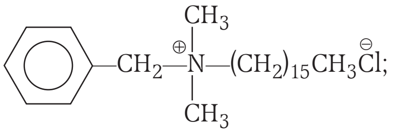


$$CH_3(CH_2)_{11}—O—\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}—\overset{\oplus}{O}\overset{\oplus}{Na}$$

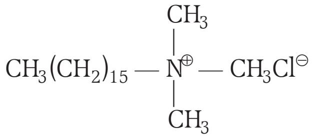
sodium lauryl sulphate

In anionic detergents, the anionic part of the molecule is involved in the cleansing action. These are used for household work and used in toothpastes also.

(ii) **Cationic detergents** are also called **invert detergents**. In these, the polar head of the detergent is positively charged. These are infact, quaternary ammonium salts (chlorides, bromides, acetates) containing one or more long chain alkyl groups, *e.g.,*



benzylcetyldimethyl ammonium chloride

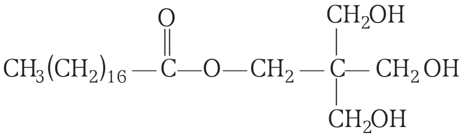


$$CH_3(CH_2)_{15}-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N^{\oplus}}}-CH_3Cl^{\ominus}$$

cetyl trimethyl ammonium chloride

These detergents are widely used as fabric softeners and germicides. Cetyl trimethyl ammnonium bromide is a popular cationic detergent and is used in hair conditioners.

(iii) **Neutral detergents** contain non-ionic but polar groups capable of forming H-bonding with water. These are monoesters of polyhydric alcohols or polyethers derived from ethylene oxides *e.g.,*



$$CH_3(CH_2)_{16}-\overset{\displaystyle O}{\overset{\|}{C}}-O-CH_2-\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}-CH_2OH$$

non-ionic detergent

These detergents are also called non-ionic detergents and used as liquid dish washing detergent.

Applications and Limitations of Detergents

Detergents do not produce hydroxyl ions on hydrolysis, so these can be used safely for woollen garments.

Straight chain alkyl groups containing detergents are biodegradable whereas branched chain alkyl groups containing detergents are non-biodegradable. Hydrocarbon side chains stops the bacteria from attacking and breaking the chains. This results in the slow degradation of detergent molecule These detergents persist in water even after sewage treatment and cause foaming in river water.

Sample **Problem 17** *Dish washing soaps are synthetic detergents. Chemically these are* **[NCERT Exemplar]**

(a) *cationic detergent* (b) *anionic detergent*
(c) *neutral detergent* (d) *Any of these*

Interpret (c) Dish washing soaps are non-ionic detergents. These remove oil and grease by micelle formation.

Check Point 3

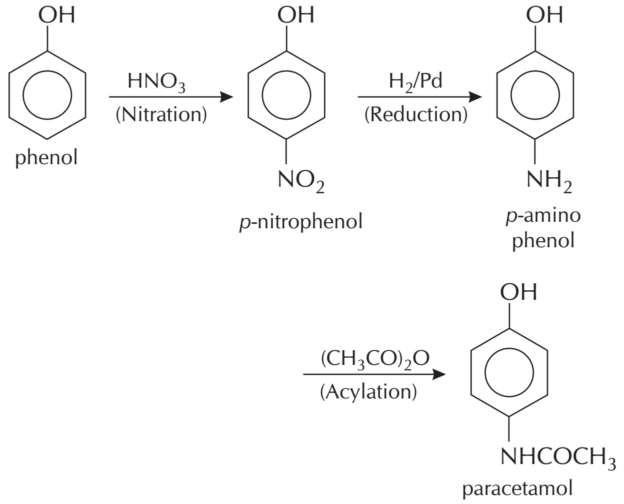
1. Why, sometimes foaming is seen in river water near the place where sewage water is poured after treatment? **[NCERT Exemplar]**
2. Why is the term surfactant used for cleansing agents?
3. Acidic water is not suitable for washing clothes with soap. Explain why?
4. Washing of woolen garments with detergent is safe but with soap is not. Explain.
5. How does the branching of hydrocarbon chain of synthetic detergents after their biodegradability? **[NCERT Exemplar]**

WORKED OUT Examples

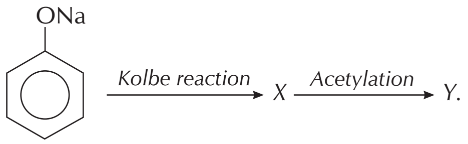
Example 1 *Which of the following sets of reactants is used for the preparation of paracetamol from phenol?*

(*a*) HNO_3, H_2/Pd, $(CH_3CO)_2O$
(*b*) H_2SO_4, H_2/Pd, $(CH_3CO)_2O$
(*c*) $C_6H_5N_2Cl$, $SnCl_2/HCl$, $(CH_3CO)_2O$
(*d*) Br_2/H_2O, Zn/HCl, $(CH_3CO)_2O$

Solution (*a*)

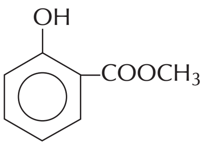


Example 2

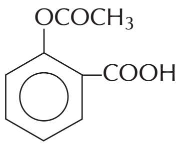


Product 'Y' is

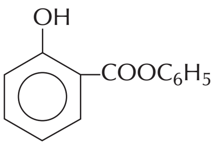
(a)



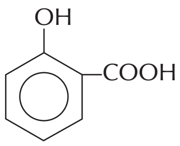
(*b*)



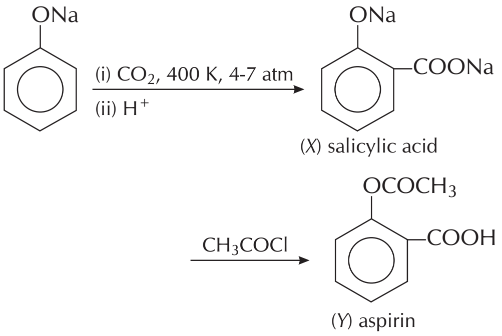
(*c*)



(*d*)



Solution (*b*)



Product '*Y*' is aspirin.

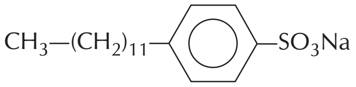
Example 3 *Which type of drugs come under anti-microbial drugs?*

(*a*) *Antiseptics, antibiotics, disinfectants*
(*b*) *Tranquilizers, analgesics, antiseptics*
(*c*) *Tranquilizers, antiseptics, antifertility*
(*d*) *Antiseptics, antacids, antihistamines*

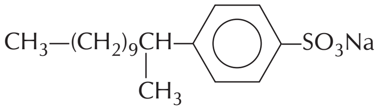
Solution (*a*) Bacteria, virus, fungi and other pathogens are microorganisms. These may cause diseases in human beings and animals. An antimicrobial drug prevents the development or inhibit the pathogenic action of microorganisms such as bacteria (antibacterial drug), virus (antiviral drugs) fungi (antifungal drugs) or other parasite (antiparasite drugs selectively). Antibiotics, antiseptics and disinfectants are antimicrobial drugs.

Example 4 *Which of the following is a example of non-biodegradable detergent?*

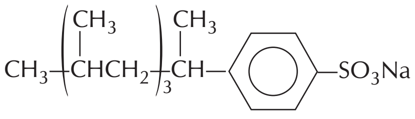
(*a*)



(*b*)



(*c*)



(*d*) $CH_3(CH_2)_{10}CH_2OSO_3Na$

Solution (*c*) Biodegradable detergents have less branching in their structure whereas non-biodegradable detergents have more branching in their structure. Bacteria cannot degrade this highly branched hydrocarbon chain easily. Hence, detergents given in option (c) is an example of non-biodegradable detergent.

Example 5 *Which of the following is known as invert detergent?*

(*a*) *Pentaerythritol monostearate*
(*b*) *Sodium stearyl sulphate*
(*c*) *Trimethyl cetyl ammonium bromide*
(*d*) *Ethoxylated non phenol*

Solution (*c*) Cationic detergents are also known as invert detergents. Cetyl trimethyl ammonium bromide is an example of invert detergent.

Example 6 *Detergents are prepared by the action of* H_2SO_4 *followed by neutralisation by starting with*

(*a*) *cholesterol* (*b*) *cyclohexanol*
(*c*) *lauryl alcohol* (*d*) *p-nitrophenol*

Solution (*c*)

$$\underset{\text{lauryl alcohol}}{CH_3(CH_2)_{10}CH_2OH} \xrightarrow{H_2SO_4} \underset{\text{lauryl hydrogen sulphate}}{CH_3(CH_2)_{10}CH_2OSO_3H}$$

$$\xrightarrow{NaOH\,(aq)} \underset{\substack{\text{sodium lauryl sulphate}\\ \text{(anionic detergent)}}}{CH_3(CH_2)_{10}CH_2OSO_3Na}$$

Example 7 *Low level of noradrenaline is the cause of depression. What type of drugs are needed to cure this problem?* **[NCERT]**

(*a*) *Sedatives*
(*b*) *Antidepressants*
(*c*) *Hypnotics*
(*d*) *Psychedic*

Solution (*b*) Antidepressants such as iproniazid and phenylzine are needed because noradrenaline is a neuro transmitter and it plays an important role in mood changes. Its low level causes depression.

Example 8 *Which forces are involved in holding the drugs to the active site of enzymes?*

(I) Ionic bonding (II) Hydrogen bonding (III) van der Waals' interaction (IV) dipole-dipole interaction. **[NCERT]**

(*a*) *I and II*
(*b*) *I and III*
(*c*) *II and IV*
(*d*) *I, II, III and IV*

Solution (*d*) Ionic bonding, H-bonding, van der Waals' interactions, dipole-dipole interaction etc., are involved in holding the drugs to the active site of enzyme.

Start Practice for JEE Main

Round I (Topically Divided Problems)

Chemicals in Medicines

1. Which of the following statements is not correct? **[NCERT Exemplar]**
- (a) Some antiseptics can be added to soaps
- (b) Dilute solutions of some disinfectants can be used as antiseptic
- (c) Disinfectants are antimicrobial drugs
- (d) Antiseptic medicines can be ingested

2. Which is the correct statement about birth control pills? **[NCERT Exemplar]**
- (a) Contain estrogen only
- (b) Contain progesterone only
- (c) Contain a mixture of estrogen and progesterone derivatives
- (d) Progesterone enhances ovulation

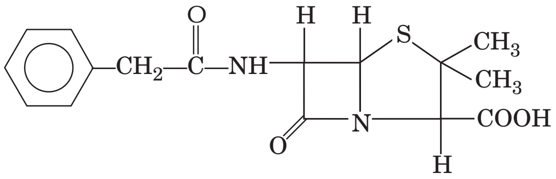
3. Which statement about aspirin is not true? **[NCERT Exemplar]**
- (a) Aspirin belongs to narcotic analgesics
- (b) It is effective in relieving pain
- (c) It has antiblood clotting action
- (d) It is a neurologically active drug

4. The most useful classification of drugs for medicinal chemists is **[NCERT Exemplar]**
- (a) on the basis of chemical structure
- (b) on the basis of drug action
- (c) on the basis of molecular targets
- (d) on the basis of pharmacological effect

5. Which of the following statements is not true?
- (a) Some disinfectants can be used as antiseptics at low concentration
- (b) Sulphadiazine is a synthetic antibacterial
- (c) Ampicillin is natural antibiotic
- (d) Aspirin is analgesic and antipyretic both

6. Equanil is
(a) artificial sweetener (b) tranquillizer
(c) antihistamine (d) antifertility drug

7. The structure given below is known as



(a) penicillin-F (b) penicillin-G
(c) penicillin-K (d) ampicillin

8. Which of the following statement is not true about the drug barbital?
(a) It causes addiction (b) It is a non-hypnotic drug
(c) It is a tranquillizer (d) It is used in sleeping pills

9. Select the incorrect statement.
- (a) Equanil is used to control depression and hypertension
- (b) Mifepristone is a synthetic steroid used as "morning after pill"
- (c) 0.2 per cent solution of phenol is an antiseptic while its 1.0 per cent solution is a disinfectant
- (d) A drug which kills the organism in the body is called bacteriostatic

10. Which set has different class of compounds?
- (a) Tranquillizers : equanil, heroin, valium
- (b) Antiseptics : bithional, dettol, boric acid
- (c) Analgesics : naproxen, morphine, aspirin
- (d) Bactericidal : Penicillin, aminoglycosides, ofloxacin

11. Salol can be used as
(a) antiseptic (b) antipyretic
(c) analgesic (d) disinfectant

12. Which of these is a hypnotic?
(a) Metaldehyde (b) Acetaldehyde
(c) Paraldehyde (d) None of these

13. Which of the following is used as an antiseptic?
(a) Phenol (b) Benzaldehyde
(c) Benzalamine (d) Malic anhydride

14. One of the most known antiseptic, dettol is a mixture of terpineol and

(a) bithional
(b) chloroxylenol
(c) *o*-cresol
(d) serotonin

15. Sulpha drugs are the derivatives of

(a) benzenesulphonic acid
(b) sulphanilic acid
(c) sulphanilamide
(d) *p*-aminobenzoic acid

16. Heroin is acetyl derivative of

(a) caffeine
(b) cocaine
(c) nicotine
(d) morphine

17. Acetoxybenzoic acid is

(a) antiseptic
(b) aspirin
(c) antibiotic
(d) mordant dye

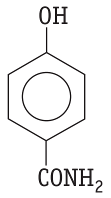
18. Medicine which is an antibiotic is

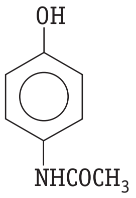
(a) ampicillin
(b) aspirin
(c) compose
(d) All of these

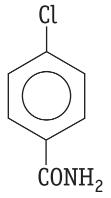
19. A drug that is antipyretic as well as analgesic is

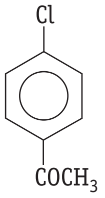
(a) chloropromazine hydrochloride
(b) *para*-acetamidophenol
(c) chloroquin
(d) penicillin

20. The correct structure of the drug paracetamol is

(a)


(b)


(c)


(d)


21. Which of the following can possibly be used as analgesics without causing addiction and any modification?

(a) Morphine
(b) N-acetylparaaminophenol
(c) Diazepam
(d) Tetrahydrocatecol

22. A substance which can act both as an antiseptic and disinfectant is

(a) aspirin
(b) chloroxylenol
(c) bithional
(d) phenol

23. The drug, which is not a tranquillizer, is

(a) ibuprofen
(b) veronal
(c) luminal
(d) seconal

24. Anti-allergy drugs are

(a) antimicrobials
(b) antihistamines
(c) antivirals
(d) antifungals

25. Oral contraceptive drugs contain

(a) mestranol
(b) Norethindrone
(c) Both (a) and (b)
(d) None of these

26. The drug used for the prevention of heart attacks is

(a) aspirin
(b) valium
(c) chloramphenicol
(d) cephalsoprin

27. Which of the following is not an analgesic?

(a) Ibuprofen
(b) Dichlofenac sodium
(c) Naproxen
(d) Ofloxacin

28. An antibiotic effective in treatment of pneumonia, bronchitis etc., is

(a) penicillin
(b) patalin
(c) chloromycetin
(d) tetracycline

29. Which of the following is used as a local anaesthetic agent?

(a) Diazepam
(b) Procaine
(c) Mescaline
(d) Seconal

30. An ester used as medicine is

(a) ethyl acetate
(b) methyl acetate
(c) methyl salicylate
(d) ethyl benzoate

31. Drug which helps to reduce anxiety and brings about calmness is

(a) tranquillizer
(b) diuretic
(c) analgesic
(d) antihistamine

32. Which of the following is not used as an antacid?

(a) Magnesium hydroxide
(b) Sodium carbonate
(c) Sodium bicarbonate
(d) Aluminium phosphate

33. Which of the following drugs is an analgesic ?

(a) Sulphaguanidine
(b) Paludrin
(c) Analgin
(d) Iodex

34. Luminal, a barbiturate drug, is used as a/an

(a) antihistamine
(b) sedative
(c) antiseptic
(d) antimalarial

Chemicals in Food

35. The preservative which is used to preserve breads and cakes is

(a) sodium benzoate
(b) sodium metabisulphite
(c) sodiumpropionate
(d) sodium sorbate

36. Which of the following is not a artificial sweetener?
(a) Sucralose (b) Alitame (c) Saccharin (d) Sucrose

37. Trade name of aspartame is
(a) alitame (b) saccharin
(c) sucralose (d) nutra sweet

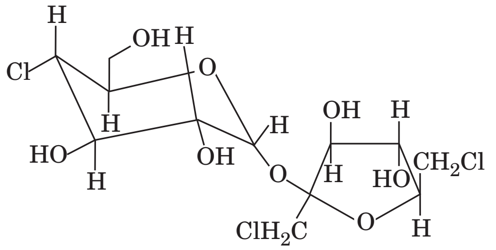
38. Hippuric acid has the formula
(a) $CH_3CONHCH_2COOH$ (b) $C_6H_5CONHCH_2COOH$
(c) $C_6H_5NHCOOH$ (d) $NH_2CONHCOOH$

39. Choose the correct statement.
(a) Saccharin is 650 times sweeter than sugar
(b) Aspartame is 550 times sweeter than sugar
(c) Sucralose is 160 times sweeter than sugar
(d) Alitame is 2000 times sweeter than sugar

40. Which of the following is an aritificial edible colour?
(a) Saffron (b) Carotene (c) Tetrazine (d) Melamine

41. Which of the following is used as an antioxidant in food?
(a) BTX (b) BHT
(c) BHC (d) All the three

42. The following structure represents



(a) sucrose (b) sucralose
(c) aspartame (d) alitame

43. Which of the following is used as food preservative?
(a) Sodium benzoate (b) Potassium chloride
(c) Sodium bicarbonate (d) Both (b) and (c)

Cleansing Agents

44. Which of the following is a *germicide* also?
(a) Cationic detergent (b) Anionic detergent
(c) Non-ionic detergent (d) None of these

45. Structurally biodegradable detergents should contain
(a) highly branched alkyl chain
(b) normal alkyl chain or less branched alkyl chain
(c) cyclopentyl side chain
(d) benzyl side chain

46. Soaps are classified as
(a) esters
(b) ethers
(c) carbohydrates
(d) sodium salts of fatty acids

47. The group commonly present in synthetic detergents is
(a) HCOONa (b) RONa
(c) RCOONa (d) $RC_6H_4SO_3Na$

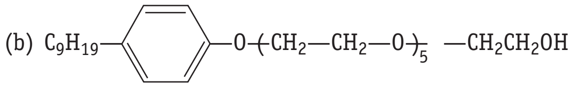
48. The detergent which is used as a *germicide* is
(a) sodium lauryl sulphate
(b) cetyltrimethyl ammonium chloride
(c) lauryl alcohol ethoxylate
(d) sodium-2-dodecylbenzenesulphonate

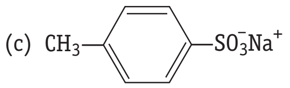
49. Which of the following is an anionic detergent?
(a) $CH_3(CH_2)_{16}CH_2OSO_3Na$
(b) $CH_3(CH_2)_{16}\overset{+}{N}(CH_3)_3Cl^-$
(c) $CH_3(CH_2)_{16}COO(CH_2CH_2O)_nCH_2CH_2OH$
(d) $C_6H_5SO_3Na$

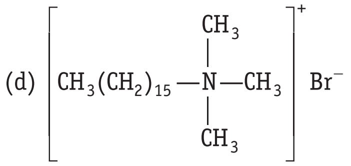
50. Compound which is added to soap to impart antiseptic properties is **[NCERT** Exemplar**]**
(a) sodium lauryl sulphate
(b) sodium dodecyl benzene sulphonate
(c) resin
(d) bithional

51. Polyethyleneglycols are used in the preparation of which type of detergents? **[NCERT** Exemplar**]**
(a) Cationic detergents (b) Anionic detergents
(c) Non-ionic detergents (d) Soaps

52. Which of the following is an example of liquid dishwashing detergent?
(a) $CH_3(CH_2)_{10}—CH_2OSO_3^-Na^+$

(b) 

(c) 

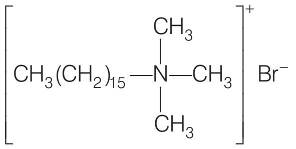
(d) 

$$\left[\begin{array}{c} CH_3 \\ | \\ CH_3(CH_2)_{15}—N—CH_3 \\ | \\ CH_3 \end{array}\right]^+ Br^-$$

53. Which category of the synthetic detergents is used in toothpaste? **[NCERT** Exemplar**]**
(a) Anionic detergents (b) Cationic detergents
(c) Non-ionic detergents (d) All of these

54. Hair shampoos belong to which class of synthetic detergents? **[NCERT** Exemplar**]**
(a) Anionic detergents
(b) Cationic detergents
(c) Non-ionic detergents
(d) All of the above

55. Match structures given in Column I with the type of detergents given in Column II.

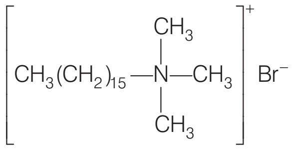
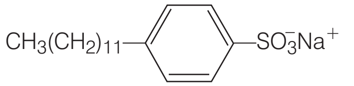
	Column I		Column II
A.	$CH_3(CH_2)_{16}COO(CH_2CH_2O)_nCH_2CH_2OH$	1.	Cationic detergent
B.	$C_{17}H_{35}COO^-Na^+$	2.	Anionic detergent
C.	$CH_3—(CH_2)_{10}CH_2SO_3^-Na^+$	3.	Non-ionic detergent
D.	 $\left[CH_3(CH_2)_{15}—\overset{CH_3}{\underset{CH_3}{N}}—CH_3\right]^+ Br^-$	4.	Soap

[NCERT Exemplar]

Codes

	A	B	C	D
(a)	2,	1,	3,	4
(b)	3,	4,	2,	1
(c)	4,	3,	1,	2
(d)	2,	3,	4,	1

56. Match the detergents given in Column I with their uses given in Column II. [NCERT Exemplar]

	Column I		Column II
A.	 $\left[CH_3(CH_2)_{15}—\overset{CH_3}{\underset{CH_3}{N}}—CH_3\right]^+ Br^-$	1.	Dish washing powder
B.		2.	Laundry soap
C.	$C_{17}H_{35}CO\overset{-}{O}\overset{+}{Na} + Na_2CO_3 + \text{Rosin}$	3.	Hair conditioners
D.	$CH_3(CH_2)_{16}COO(CH_2CH_2O)_nCH_2CH_2OH$	4.	Toothpaste

Codes

	A	B	C	D		A	B	C	D
(a)	3,	2,	1,	4	(b)	4,	1,	2,	3
(c)	3,	4,	2,	1	(d)	2,	4,	4,	1

Round II (Mixed Bag)

Single Correct Option

1. Which of the following statements is correct? [NCERT Exemplar]

(a) Some tranquillizers function by inhibiting the enzymes which catalyse the degradation of noradrenaline

(b) Tranquillizers are non-narcotic drugs

(c) Transquillizers are chemical compounds that do not affect the message transfer from nerve to receptor

(d) Tranquillizers are chemical compounds that can relieve pain and fever

2. Salvarsan is arsenic containing drug which was first used for the treatment of [NCERT Exemplar]

(a) syphilis (b) typhoid

(c) meningitis (d) dysentry

3. A narrow spectrum antibiotic is active against [NCERT Exemplar]

(a) gram positive or gram negative bacteria

(b) gram negative bacteria only

(c) single organism or one disease

(d) both gram positive and gram negative bacteria

4. The compound that causes general antidepressant action on the central nervous system belongs to the class of [NCERT Exemplar]

(a) analgesics (b) tranquillizers

(c) narcotic analgesics (d) antihistamines

5. Glycerol is added to soap. It functions …… . [NCERT Exemplar]

(a) as a filler

(b) to increase leathering

(c) to prevent rapid drying

(d) to make soap granules

6. An antibiotic contains nitro group attached to aromatic nucleus in its structure. It is

(a) pencillin (b) streptomycin

(c) tetracyclin (d) chloramphenicol

7. Which of the following is not a surfactant?

(a) $CH_3—(CH_2)_{15}—N^+(CH_3)_3Br^-$

(b) $CH_3—(CH_2)_{14}—CH_2NH_2$

(c) $CH_3—(CH_2)_{16}—CH_2OSO_2^-Na^+$

(d) $OHC—(CH_2)_{14}—CH_2—COO^-Na^+$

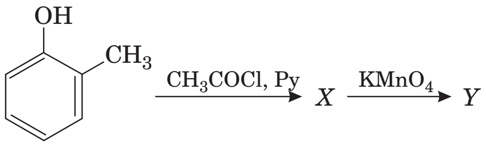
8. In the following sets of compounds, the one which contains only medicinal compounds is

(a) alizarin, phenacetin, morphine

(b) aspirin, gention violet, phenolphthalein

(c) boric acid, chloramphenicol, aspirin

(d) 9-oxodecanoic acid, boric acid, morphine

9. 

The final product '*Y*' is medicine. Which of the following is incorrect regarding '*Y*'?

(a) It has analgesic as well as antipyretic properties
(b) It helps to prevent heart attack
(c) It has anti-blood clotting action
(d) It suppresses the gastric anomalies

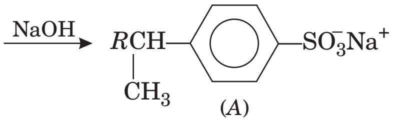
10. Aspartame is one of the good artificial sweeteners whose use is limited to cold foods and soft drinks because

(a) it has very low boiling point
(b) it gets dissociated at cooking temperature
(c) it is sweetener at low temperature only
(d) it is insoluble at higher temperatures

11. For the preparation of a detergent '*A*' (given below) from benzene, the following steps are involved

I. $\xrightarrow[\text{HF, Friedel-Crafts}]{RCH=CH_2}$

II. $\xrightarrow{H_2SO_4/SO_3}$

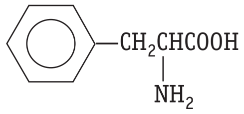
III. 

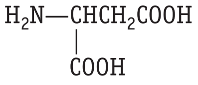
(*A*)

These steps should be in sequence

(a) I, II, III (b) II, I, III (c) II, III, I (d) I, III, II

12. Aspartame is a non-nutritive sweetener. Assuming that both, amide and ester bonds are hydrolysed in the stomach, the amino acids obtained is

(a) 

(b) 

$H_2N—\underset{\underset{\displaystyle COOH}{|}}{C}HCH_2COOH$

(c) Both (a) and (b) (d) None of these

13. Which detergent can cause maximum pollution?

(a) $CH_3CH(C_4H_9) — CH_2CH_2CH(C_4H_9)(CH_2)_3CH(C_4H_9)CH_2CH_2SO_3Na$
(b) $CH_3(CH_2)_{10}CH_2OSO_3Na$
(c) $CH_3CH(C_3H_7)—(CH_2)_6CH(C_4H_9)CH_2SO_3Na$
(d) $[CH_3(CH_2)_{15}N(CH_3)_3]^+Br^-$

14. Which of the following chemicals can be added for sweetening of food items at cooking temperature and does not provide calories? **[NCERT** Exemplar**]**

(a) Sucrose (b) Glucose (c) Aspartame (d) Sucralose

15. Which of the following will not enhance nutritional value of food? **[NCERT** Exemplar**]**

(a) Minerals (b) Artificial sweeteners
(c) Vitamins (d) Aminoacids

More than One Correct Option

16. Which of the following statements are incorrect about receptor proteins? **[NCERT** Exemplar**]**

(a) Majority of receptor proteins are embedded in the cell membranes
(b) The active site of receptor proteins opens on the inside region of the cell
(c) Chemical messengers are received at the binding sites of receptor proteins
(d) Shape of receptor doesn't change during attachment of messenger

17. Which of the following are not used as food preservatives? **[NCERT** Exemplar**]**

(a) Table salt
(b) Sodium hydrogencarbonate
(c) Cane sugar
(d) Benzoic acid

18. Compounds with antiseptic properties are **[NCERT** Exemplar**]**

(a) $CHCl_3$
(b) CHI_3
(c) Boric acid
(d) 0.3 ppm aqueous solution of Cl_2

19. Which of the following statements are incorrect about penicillin? **[NCERT** Exemplar**]**

(a) An antibacterial drug
(b) Ampicillin is its synthetic modification
(c) It has bacteriostatic effect
(d) It is a broad spectrum antibiotic

20. Amongst the following antihistamines, which are antacids? **[NCERT** Exemplar**]**

(a) Ranitidine
(b) Brompheniramine
(c) Terfenadine
(d) Cimetidine

Assertion and Reason

Directions (Q. Nos. 21 to 25) *Each of these questions contains two statements : Statement* I (*Assertion*) *and Statement* II (*Reason*). *Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes* (*a*), (*b*), (*c*), (*d*) *given below :*

(a) Statement I is true; Statement II is true; Statement II is a correct explanation for Statement I.
(b) Statement I is true; Statement II is true; Statement II is not a correct explanation for Statement I.
(c) Statement I is true; Statement II is false.
(d) Statement I is false; Statement II is true.

21. **Statement I** Non-competitive inhibitor inhibits the catalyic activity of enzyme by binding with its active site.

Statement II Non-competitive inhibitor changes the shape of the active site in such a way that substrate can't recognise it. [**NCERT** Exemplar]

22. **Statement I** Penicillin (G) is an antibiotic.

Statement II Penicillin (G) is effective against gram positive as well as gram negative bacteria.

[**NCERT** Exemplar]

23. **Statement I** Receptors are crucial to body's communication process.

Statement II Receptors are proteins.

[**NCERT** Exemplar]

24. **Statement I** Chemical messenger gives message to the cell without entering the cell.

Statement II Chemical messenger is received at the binding site of receptor proteins. [**NCERT** Exemplar]

25. **Statement I** All chemicals added to food items are called food additives.

Statement II All these chemicals increase the nutritive value of the food. [**NCERT** Exemplar]

Comprehension Based Questions

Directions (Q. Nos. 26 and 27) Body possesses an efficient natural defence mechanism, which works against pathogenic microorganisms (disease causing microorganisms). Many body secretions inhibit the growth of microorganisms. For example, Lysozyme in tears, nasal secretion and saliva lactic acid in sebacious secretions and HCl in stomach. When a break in defence mechanism takes place, pathogens reach the tissues and causes infections. Pathogens multiply in the host, produce toxins, which affects the cell metabolism. Microbial diseases can be controlled by the following three ways :

A. By increasing immunity and resistance to infection of the body.
B. By using a drug which inhibits the growth of the microorganisms (bacteriostatic)
C. By using a drug which kills the microorganisms in the body (bactericidal)

Antibiotics, antiseptics and disinfectants are antimicrobial drugs.

26. Which one is an antibiotic?
(a) Chloramphenicol (b) Aspirin
(c) Veronal (d) Seldane

27. Which one of the following is not bacteriostatic antibiotic?
(a) Erythromycin
(b) Tetracycline
(c) Chloramphenicol
(d) Ofloxacin

Directions (Q. Nos. 28 to 30) Soaps and synthetic detergents are used as cleansing agents. These days, detergents are much in vogue and get preference over soaps because they work even in hard water. Detergents molecules with highly branched hydrocarbon tail is a source of pollution because hydrocarbon side chain stops the bacteria from attacking and breaking the chains resulting in slow degradation of detergent molecule and leads its accumulation in water bodies. Hence, detergents with straight chain of hydrocarbons are preferred over side chain (branched chain) because latter are non-biodegradable and cause pollution.

28. A synthetic detergent is a
(a) cleansing agent (b) catalyst
(c) drug (d) soap

29. Select the incorrect statement regarding detergents.
(a) These have a non-polar organic part and a polar group
(b) These are surface active reagent
(c) These are sodium salt of fatty acids
(d) These are not easily biodegradable

30. Detergents obtained from LAB are biodegradable. LAB stands for
(a) laboratory tested raw material
(b) low anionic balance
(c) linear alkyl benzene
(d) None of the above

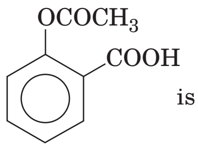
Previous Years' Questions

31. Aspirin is known as [AIEEE 2012]

(a) acetyl salicylic acid (b) phenyl salicylate
(c) acetyl salicylate (d) methyl salicylic acid

32. The drug used to bring down fever are known as [AIEEE 2005]

(a) analgesic (b) antibiotic
(c) antipyretic (d) tranquillizer

33. The compound  is used as [AIEEE 2002]

(a) antiseptic
(b) antibiotic
(c) analgesic
(d) pesticide

Answers

Round I

1. (d)	**2.** (c)	**3.** (a)	**4.** (c)	**5.** (c)	**6.** (b)	**7.** (b)	**8.** (b)	**9.** (d)	**10.** (a)
11. (a)	**12.** (c)	**13.** (a)	**14.** (b)	**15.** (c)	**16.** (d)	**17.** (b)	**18.** (a)	**19.** (b)	**20.** (b)
21. (b)	**22.** (d)	**23.** (a)	**24.** (b)	**25.** (c)	**26.** (a)	**27.** (d)	**28.** (c)	**29.** (b)	**30.** (c)
31. (a)	**32.** (b)	**33.** (c)	**34.** (b)	**35.** (c)	**36.** (d)	**37.** (d)	**38.** (b)	**39.** (d)	**40.** (c)
41. (b)	**42.** (b)	**43.** (a)	**44.** (a)	**45.** (b)	**46.** (d)	**47.** (d)	**48.** (b)	**49.** (a)	**50.** (d)
51. (c)	**52.** (b)	**53.** (a)	**54.** (b)	**55.** (b)	**56.** (c)				

Round II

1. (a)	**2.** (a)	**3.** (a)	**4.** (b)	**5.** (c)	**6.** (d)	**7.** (b)	**8.** (c)	**9.** (d)	**10.** (b)
11. (a)	**12.** (c)	**13.** (a)	**14.** (d)	**15.** (b)	**16.** (b,d)	**17.** (b,d)	**18.** (b,c)	**19.** (c,d)	**20.** (a,d)
21. (d)	**22.** (c)	**23.** (a)	**24.** (a)	**25.** (c)	**26.** (a)	**27.** (d)	**28.** (a)	**29.** (c)	**30.** (c)
31. (a)	**32.** (c)	**33.** (c)							

the Guidance

Round I

1. Antiseptics are applied to the living tissues such as wounds, cuts, diseased skin surfaces. These are not ingested like antibiotics.

4. Carbohydrates, lipids, proteins and nucleic acids are target molecules or drug targets. Drugs possessing some common structural features have same action on targets. That's why the classification based on molecular targets is the most useful classification for medicinal chemists.

8. Barbital or varonal is a sleep producing drug, *i.e.*, hypnotic tranquillizer. It is used in sleeping pills and causes addiction.

9. Bacteriostatic drugs inhibit the growth of microorganism while bactericidal drugs kill the microorganisms.

10. Heroin is not a tranquillizer, it is a narcotic analgesic.

13. 0.2% solution of phenol is used as an antiseptic.

15. Sulpha drugs are the derivatives of sulphanilamide.

22. 0.2% solution of phenol is an antiseptic while its one per cent solution is disinfectant.

25. Oral contraceptive drugs contain mestranol (an estrogen) and norethindrone (a progesterone derivative).

26. Due to anti-blood clotting action of aspirin, it is used to prevent heart attack.

27. Ofloxacin is used as antibiotic.

36. Sucrose is a natural sweetener whereas sucralose, alitame and saccharin are artificial sweeteners.

39. Saccharin is 110 times sweeter than sugar, aspartame is 180 times sweeter than sugar. Sucralose is 650 times sweeter than sugar.

42. Sucrolose is trichloro derivative of sucrose. Its appearance and taste are like sugar.

44. Cationic detergents are quaternary ammonium salts, containing long chain alkyl groups and possesing *germicidal* properties.

50. Bithional is added to soap to impart antiseptic properties.

51. Polyethylene glycol are used to prepare non-ionic detergents. These do not contain any ion in their constitution.

52. Non-ionic detergents are used as liquid dishwashing detergents.

53. Toothpaste—anionic detergents

54. Hair shampoos — cationic detergents

Round II

1. Various types of tranquillizers function by different mechanism. For example, noradrenaline is one of the neurotransmitters. If the level of noradernaline is low, then the signal-sending activity becomes low and the person suffers from depression. In such situation, person requires antidepressant drugs. These drugs inhibit the enzymes which catalyse the degradation of noradrenaline. Due to this the level of neurotransmitter becomes normal, it can activate its receptor for longer periods of time, thus counteracting the effect of depression.

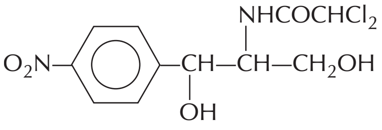
2. Salvarsan contains —As═As— linkage. It is used for the treatment of syphilis. Although it is toxic to human beings, but its effect on the bacteria, spirochete, which causes syphilis is much greater than on human beings.

3. Narrow spectrum antibiotics are effective mainly against gram-positive or gram-negative bacteria. If antibiotics are effective against a single organisms or disease, they are known as **limited spectrum antibiotics.**

4. Tranquillizers causes general antidepressant action on the cental nervous system. They affect the message transfer mechanism from nerve to receptor.

5. Glycerol is added to soap (toilet soap and shaving creams) to prevent rapid drying.

6. Among the given antibiotics, only chloramphenicol contains a nitro group attached to aromatic ring.

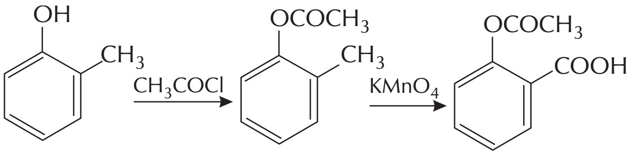


chloramphenicol

7. Every surfactant contains two parts *viz* a hydrophobic part and a hydrophilic part. The compound $CH_3(CH_2)_{14}CH_2NH_2$ contains only hydrophobic part but no hydrophilic part, hence it is not a surfactant.

8. Boric acid is a mild antiseptic, chloramphenicol is an broad spectrum antibiotic and aspirin is an analgesic as well as antipyretic.

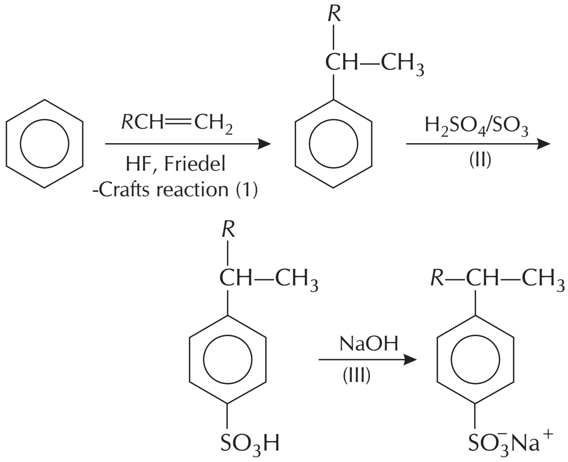
9.



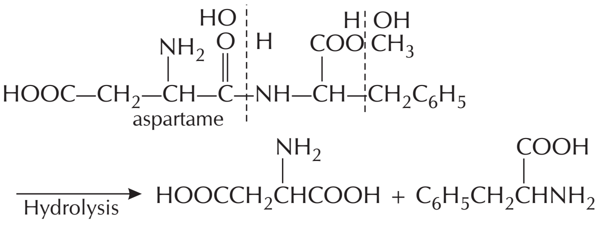
o-acetyl salicylic acid (aspirin)

10. Aspartame gets dissociated at cooking temperature.

11.



12.



$$\mathrm{HOOC{-}CH_2{-}\overset{NH_2}{CH}{-}\overset{\overset{HO}{O}}{\overset{\|}{C}}{-}\overset{H}{NH}{-}\overset{\overset{H}{COO}}{CH}{-}\overset{\overset{OH}{CH_3}}{CH_2C_6H_5}}$$

aspartame

$$\xrightarrow[\text{Hydrolysis}]{} \mathrm{HOOCCH_2\overset{NH_2}{CH}COOH + C_6H_5CH_2\overset{COOH}{CH}NH_2}$$

13. Greater the branching, greater is the non-biodegradability of a detergent. A non-biodegradable detergent cause maximum pollution.

14. Sucrose and glucose provide energy. Aspartame is used in cold foods and soft drinks because it is unstable at cooking temperature. Sucralose is stable at cooking temperature and it does not provide calories.

15. Minerals, vitamins and amino acids have nutritive value but artificial sweeteners are only sweetening agent.

16. (*b*) The active site of receptor proteins opens on the outside region of the cell membrane.

(*d*) To accommodate a messenger, shape of the receptor site changes.

17. (*b*) Sodium hydrogen carbonate is not used as a preservative.

(*d*) Sodium benzoate is used as preservative (not benzoic acid).

18. CHI_3, iodoform is used as an antiseptic for wounds. Boric acid in dilute aqueous solution is weak antiseptic for eyes. 0.3 ppm aqueous solution of Cl_2 is disinfectant.

19. Penicillin is bactericidal (has killing effect) and it is a narrow spectrum antibiotic.

20. Ranitidine and cimetidine are used as antacids.

21. Non-competitive inhibitor inhibits the catalytic activity of enzyme by binding with its allosteric site, this results in changing the shape of the active site in such a way that substrate can't recognize it.

22. Penicillin-G is an antibiotic. It has bactericidal effect and it is narrow spectrum antibiotic (effective against gram-positive or Gram-negative bacteria.

23. Receptors are proteins that are crucial to body's communication process.

24. Statement II is the correct explanation of statement I.

25. All chemicals added to food items are called food additives. Only nutritional supplements such as vitamins, minerals and amino acids increase the nutritive value of the food whereas others are added either to increase the shelf life of stored food or for cosmetic purposes.

26. Chloramphenicol — antibiotic, aspirin — analgesics as well as antipyretics, veronal — tranquillizer and seldane — antihistamines.

27. Erythromycin, tetracycline and chloramphenicol are bacteriostatic type antibiotic whereas ofloxacin is bactericidal type antibiotic.

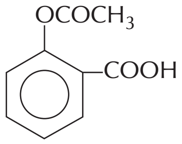
28. A synthetic detergent is a cleansing agent which has all the properties of soap but do not contain any soap.

29. Sodium salt of fatty acids are known as soaps.

30. LAB stands for linear alkyl benzene.

31. Acetyl salicylic acid is the chemical name of aspirin.

32. Antipyretics are used to bring down the body temperature in fever.

33.  is aspirin. It is an acetylated product of salicylic acid as an analgesics.

16 Principles Related to Practical Chemistry

JEE Main MILESTONE

- Qualitative Analysis of Organic Compounds
- Preparation of Some Inorganic and Organic Compounds
- Salt Analysis or Qualitative Inorganic Analysis
- Chemical Principles Involved in Some Experiments

16.1 Qualitative Analysis of Organic Compounds

Two major steps involved in the characterisation of an organic compound are (1) Element detection (For it see chapter 12 purification and characterisation of organic compounds) (2) Detection of functional group.

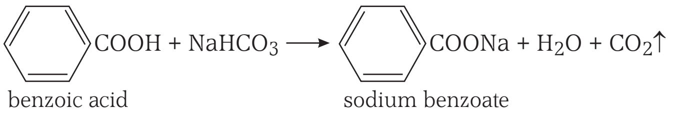
Detection of Functional Groups in Organic Compounds

Element detection shows the presence or absence of different elements. On the basis of element present, the test of corresponding functional group is performed. Tests for different functional groups are given below.

Tests for Carboxylic (—COOH) Group

(i) **Litmus paper test** Dip blue litmus paper in the aqueous solution or suspension of the compound. It turns red.

(ii) **Sodium bicarbonate test** In a test tube, take a little quantity of the compound and then, add a saturated solution of sodium bicarbonate. Formation of brisk effervescence shows the presence of —COOH group.



Experimental (practical) Chemistry involves the study of concerned material under specific experimental conditions. It can be divided into two branches : synthetic chemistry and analytical chemistry.

(iii) **Ester formation** Heat a small quantity of organic compound with ethyl alcohol and a little conc H_2SO_4 · Cool the solution and pour in a tube containing water. A fruity smell, due to formation of an ester, indicates the presence of carbxylic group.

$$R\text{—COOH} + C_2H_5OH \xrightarrow{\text{Conc } H_2SO_4} \underset{\substack{\text{ester} \\ \text{(fruity smell)}}}{RCOOC_2H_5} + H_2O$$

Sample Problem 1 *A compound liberated* CO_2 *with* $NaHCO_3$ · *Thus, it contains*

(*a*) —CHO *group*
(*b*) —OH *phenolic group*
(*c*) —NH_2 *group*
(*d*) —COOH *group*

Interpret (*d*) *Carboxylic acid decomposes* $NaHCO_3$ *giving* CO_2.

$$R\text{—COOH} + NaHCO_3 \longrightarrow RCOONa + CO_2 + H_2O$$

Tests for Alcoholic (—OH) Group

(i) **Sodium test** In a test tube, take some organic compound and add a thin slice of sodium metal to it. A brisk effervescence due to the formation of hydrogen gas takes place.

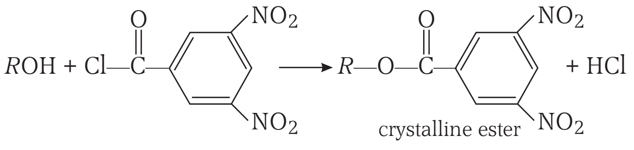
$$2ROH + 2Na \longrightarrow 2RONa + H_2 \uparrow$$

(ii) **Ester test**

(a) Heat the given compound with acetic acid in the presence of sulphuric acid. A fragrant fruity smell indicates the formation of ester.

$$ROH + CH_3COOH \xrightarrow{\text{conc. } H_2SO_4} CH_3COOR + H_2O$$

(b) Alcohols give crystalline esters with 3,5-dinitrobenzoyl chloride. These esters have sharp melting points and can be used for testing a given alcohol.



(iii) **Ceric ammonium nitrate test** To small amount of organic compound or its aqueous solution, add a few drops of ceric ammonium nitrate. A red colour indicates the presence of alcoholic hydroxy group.

$$2ROH + (NH_4)_2Ce(NO_3)_6 \longrightarrow \underset{\text{red colour}}{Ce(NO_3)_4 \cdot (ROH)_2} + 2NH_4NO_3$$

This test is useful when the compound contains less than 10 C-atoms.

(iv) **Lucas test** This test is used to distinguish between primary, secondary and tertiary alcohols. In this test, treat 2 mL of organic compound with about 8 mL of Lucas reagent (for preparing Lucas reagent dissolve 32 g of anhy $ZnCl_2$ in 20 mL of conc HCl) and shake.

(a) Immediate formation of turbidity indicates the presence of **tertiary alcohol.**

(b) Formation of turbidity after 4-5 min shows the presence of **secondary alcohols.**

(c) If solution remains clear, then **primary alcohol** is present.

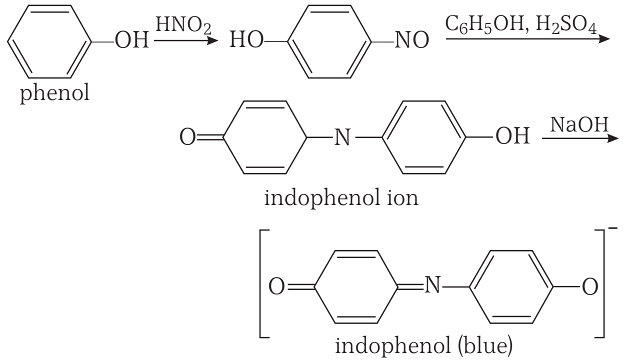
Tests for Phenolic (Ph—OH) Group

(i) **Ferric chloride test** To aqueous or alcoholic solution of compound, add few drops of ferric chloride ($FeCl_3$). Formation of green, blue or violet colour shows the presence of phenol.

$$6C_6H_5OH + FeCl_3 \longrightarrow 3H^+ + \underset{\text{violet}}{[Fe(OC_6H_5)_6]^{3-}} + 3HCl$$

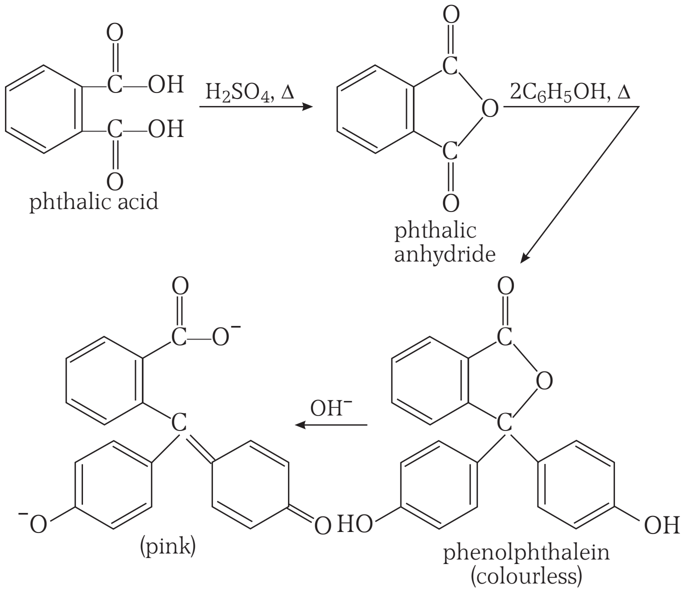
This test is also given by enols.

(ii) **Liebermann's nitroso reaction** Fuse a little amount of compound with a crystal of $NaNO_2$ in a test tube. Cool the mixture and add 1 mL conc H_2SO_4. A deep green to blue solution is formed which turns red when poured in a large excess of water. The red aqueous solution becomes again deep green or blue if made alkaline with NaOH. It shows the presence of phenol.



Caution Point *Nitrophenol do not respond to* $FeCl_3$ *test as well as Liebermann's nitroso reaction.*

(iii) **Phthalein test** Phenol on heating with phthalic acid in the presence of conc. H_2SO_4 gives colourless compound called phenolpthalein, which changes to pink coloured compound in alkaline medium.



Phenolphthalein is used as an indicator in acid-base titrations. It is colourless in acidic medium and pink in basic medium.

Tests for Aldehyde (—CHO) Group

(i) **Tollen's reagent test** Take a little quantity of the compound in a test tube and add 2 mL of freshly prepared reagent. Shake, warm and allow the contents to stand for 2-3 minutes. Formation of silver mirror or a grey ppt indicates the presence of an aldehydic group.

$$2Ag(NH_3)_2OH + R\cdot CHO \longrightarrow \underset{\text{silver mirror or grey ppt}}{2Ag\downarrow} + RCOONH_4 + 3NH_3 + H_2O$$

(ii) **Fehling's solution test** Take a mixture of equal amounts of Fehling's solution *A* and *B*, and a few drops of organic compound and boil the contents. Formation of a red ppt shows the presence of an aldehyde.

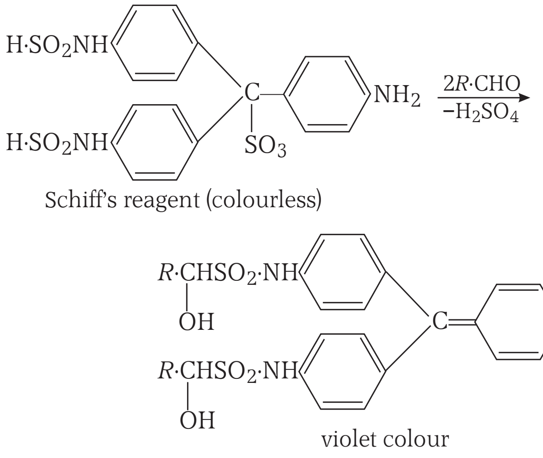
$$2CuO + R\cdot CHO \longrightarrow \underset{\text{red ppt.}}{Cu_2O\downarrow} + RCOOH$$

Caution Points

(*i*) *Both the above tests are also given by reducing sugars.*

(*ii*) *Benzaldehyde does not reduce Fehling's solution (a distinction from other aldehydes). Benzaldehyde is confirmed by malachite green test.*

(iii) **Schiff's reagent test** Add 5-6 drops of organic compound to 2 mL of the reagent. Shake vigorously. After some time formation of a deep red or violet colour indicates the presence of an aldehydic group.



Schiff's reagent (colourless)

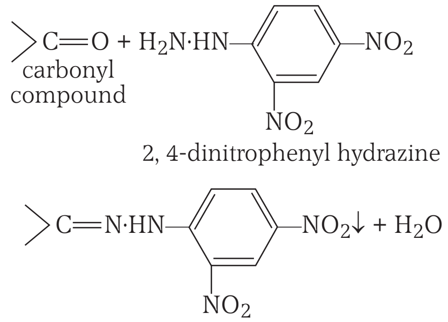
violet colour

(iv) **Benedict's solution test** Boil the compound with 2-3 mL of Benedict's solution for few minutes. Appearance of a red-yellow ppt confirms the presence of aliphatic aldehydes.

Caution Point *This test is usually given by only aliphatic aldehydes, thus used to differentiate between aliphatic and aromatic aldehydes.*

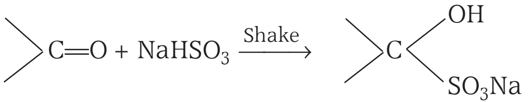
Tests for Ketone $\left(\begin{matrix}R\\R\end{matrix}\!\!>C{=}O\right)$ Group

(i) **2,4-dinitro phenyl hydrazine test** In a dry test tube add few drops of the organic compound (if liquid) or its alcoholic solution (if solid) to about 2 mL of the reagent and one drop of conc H_2SO_4. Shake vigorously, heat (if necessary) and allow to stand for about 5 minutes. A yellow or orange ppt separates out in case of a compound containing carbonyl group due to the formation of respective hydrazones.



yellow or orange red coloured crystalline derivative of 2 : 4 dinitrophenyl hydrazine of carbonyl compound

(ii) **Sodium bisulphite test** Add a very small quantity of organic compound to 1 mL of saturated solution of sodium bisulphite and shake vigorously. Formation of white ppt shows the presence of carbonyl group.



$$>C{=}O + NaHSO_3 \xrightarrow{\text{Shake}} >C\begin{matrix}OH\\SO_3Na\end{matrix}$$

Sodium bisulphite derivative of carbonyl compound (white crystalline ppt)

(iii) **Sodium nitroprusside test** Add 0.1 g of solid or 0.2 cc of liquid compound to 2 cc of sodium nitroprusside, $Na_2[Fe(CN)_5NO]$ solution and then, make it alkaline with 2-3 drops of sodium hydroxide. A red or purple colour indicates the presence of ketone (benzophenone does not give this test).

Caution Point *The first two tests are given by aldehydes also. Therefore, to differentiate between aldehydes and ketones it should be known that ketone do not give any test with Tollen's reagent, Schiff's solution, Fehling's solution and Benedict's solution.*

Sample **Problem 2** *Which of the following tests can be used to distinguish between acetone and α-hydroxy acetone?*

(a) *Tollen's test*

(b) *Iodoform test*

(c) *Both (a) and (b)*

(d) *None of the above*

Interpret (*a*) Acetone does not give Tollen's test but α-hydroxy acetone forms silver mirror with Tollen's reagent.

$$CH_3COCH_2OH + \underset{\text{Tollen's reagent}}{Ag_2O} \xrightarrow{\Delta} CH_3COCHO + \underset{\text{silver mirror}}{2Ag\downarrow} + H_2O$$

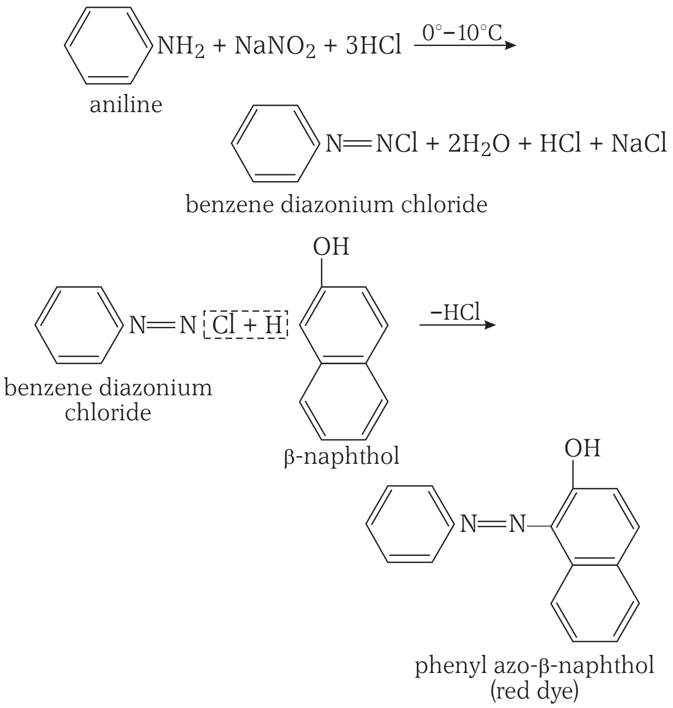
Iodoform test is given by both hence can't used for distinction.

Tests for Primary Amine (—NH_2) Group

(i) **Carbylamine test** Boil a little quantity of the compound with 2 drops of chloroform and 2 mL of alcoholic caustic potash. An intolerable offensive odour of carbylamine indicates the presence of primary amine.

$$\underset{\text{primary amine}}{R—NH_2} + CHCl_3 + 3KOH \longrightarrow \underset{\text{carbylamine}}{R\cdot NC\uparrow} + 3KCl + 3H_2O$$

(ii) **Dye test** Dissolve about 0.2 g of the compound in dil HCl and cool. Now, add 10% aq $NaNO_2$ solution. Pour all this content into a beaker containing alkaline β-naphthol solution. Formation of a red or orange dye indicates the presence of aromatic primary amino group.



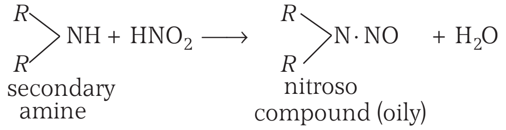
Tests to Distinguish between Primary, Secondary and Tertiary Amines

(i) **Nitrous acid test** Prepare a solution of nitrous acid by adding ice cold dil HCl to a solution of 1% aq $NaNO_2$. Add gradually this solution to 0.2 g of the organic compound in 10 mL dil HCl.

(a) Formation of brisk effervescence shows the presence of **aliphatic primary amine.**

$$R—NH_2 + HNO_2 \longrightarrow ROH + H_2O + N_2\uparrow$$

(b) Formation of an oily dark coloured liquid indicates the presence of **secondary amine.**



(c) No reaction indicates the presence of **aliphatic tertiary amine** while production of green or brown colour indicates the presence of **aromatic tertiary amines.**

(ii) **Hinsberg's test** To about 0.2 g of the compound, add 1 mL of 5% NaOH and 3 mL pyridine. Shake well and add few drops of benzene sulphonyl chloride (Hinsberg's reagent) with continuous shaking.

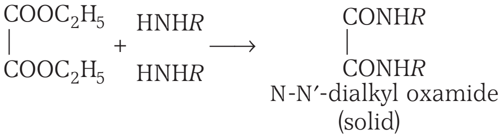
(a) Formation of yellow colour indicates the presence of **primary amine.**

(b) Formation of orange colour shows the presence of **secondary amine.**

(c) Formation of a red or purple colour shows the presence of **tertiary amines.**

(iii) **Hofmann's method** Take same organic compound in a test tube and add diethyl oxalate solution to it, shake well.

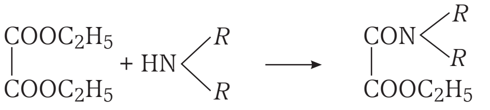
(a) Formation of solid product (N, N′-dialkyl oxamide) indicates the presence of 1° amine.



$$\begin{array}{l}COOC_2H_5\\ |\\ COOC_2H_5\end{array} + \begin{array}{l}HNHR\\ \\ HNHR\end{array} \longrightarrow \begin{array}{l}CONHR\\ |\\ CONHR\end{array}$$

N-N′-dialkyl oxamide (solid)

(b) Formation of liquid product (oxamic ester) indicates the presence of 2° amine.



$$\begin{array}{l}COOC_2H_5\\ |\\ COOC_2H_5\end{array} + HN\begin{array}{l}R\\ R\end{array} \longrightarrow \begin{array}{l}CON\begin{array}{l}R\\ R\end{array}\\ |\\ COOC_2H_5\end{array}$$

oxamic ester (liquid)

(c) 3° amine does not react with diethyl oxalate.

Check Point 1

1. Give simple chemical tests to distinguish between
   (a) Phenol and benzoic acid **[NCERT]**
   (b) Propanal and propanone
2. Describe a method for the identification of primary, secondary and tertiary amines. **[NCERT]**
3. Phenol on heating with phthalic acid in the presence of conc. H_2SO_4 forms a colourless compound '*A*', which turns to pink on making it alkaline. What is the name of this test and what is the name of the compound *A*?
4. Why is the reactivity of all the three classes of alcohols with conc. HCl and $ZnCl_2$ (Lucas reagent) different?

16.2 Preparation of Some Inorganic and Organic Compounds

Preparation of Inorganic Compounds

(i) **Mohr's salt or Ferrous ammonium sulphate,** $[FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O]$

It is a double salt. When solutions of ferrous sulphate and ammonium sulphate are mixed together, evaporated and cooled, light green crystals of Mohr's salt are obtained.

$$(NH_4)_2SO_4 + FeSO_4 + 6H_2O \longrightarrow \underset{\text{Mohr's salt}}{FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O}$$

During the preparation of ferrous sulphate solution in boiling water, dilute H_2SO_4 in small amount is also added to boiling water to prevent the hydrolysis of ferrous sulphate *i.e.*, to prevent conversion of ferrous sulphate into ferrous hydroxide.

(ii) **Potash Alum,** $KAl(SO_4)_2 \cdot 12H_2O$ It is also a double salt.

Potash alum is prepared by dissolving K_2SO_4 and $Al_2(SO_4)_3$ in equimolar ratio in small amount of water containing some drops of conc. H_2SO_4. On cooling potash alum separates as colourless crystals.

$$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \longrightarrow K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$$

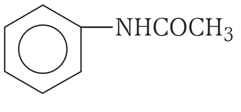
Sample Problem 3 *Alum is found to contain hydrated monovalent cation* $[M(H_2O)]^+$, *trivalent cation* $[M'(H_2O)_6]^{3+}$ *and* SO_4^{2-} *in the ratio of*

(a) 1:1:1
(b) 1:2:3
(c) 1:3:2
(d) 1:1:2

Interpret (*d*) General formula for potash alum is $KAl(SO_4)_2 \cdot 12H_2O$ (1 : 1 : 2)

$$K^+ = \text{monovalent cation}$$
$$Al^{3+} = \text{trivalent cation}$$

Preparation of Organic Compounds

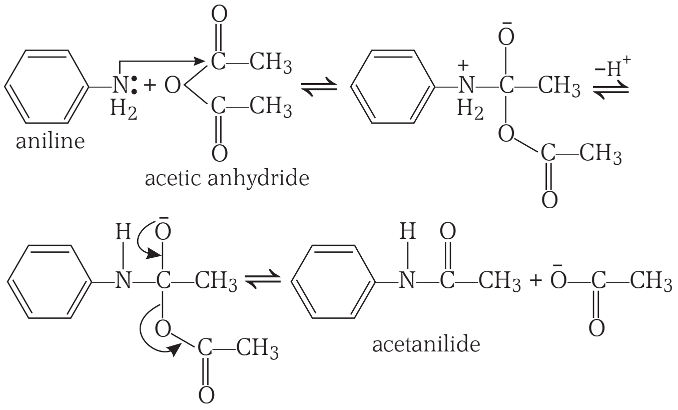
Acetanilide, 

It is prepared by direct acetylation of aniline by using the mixture of equal volumes of acetic anhydride and acetic acid.

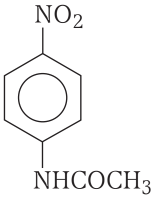
Amines containing —NH_2 or $>NH$ groups respectively can be directly acetylated. Their reactive hydrogen atoms get replaced by acetyl group (—$COCH_3$) to give acetyl derivatives of the type $RNH \cdot COCH_3$ and $R_2N \cdot COCH_3$ respectively which may be regarded as mono and di-alkyl substituted acetamide.

$$R—NH_2 + (CH_3CO)_2O \longrightarrow RNH \cdot COCH_3 + CH_3COOH$$

The mechanism of this reaction is as follows

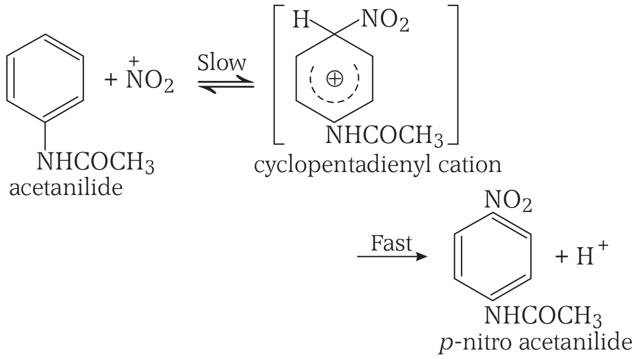


Small amount of zinc is added to the reaction mixture to prevent the oxidation of aniline and to reduce the coloured impurities present in aniline during the reaction.

p-Nitro acetanilide, 

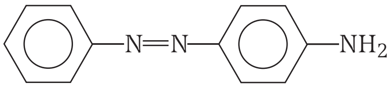
It is prepared by the nitration of acetanilide. Acetanilide is dissolved in glacial acetic acid. Concentrated H_2SO_4 is added to it with vigorous stirring. Temperature of reaction mixture should be maintained below 10°C. Now add fuming HNO_3 drop by drop with regular stirring. It gives *p*-nitro acetanilide along with a little amount of *o*-isomer. In this process fuming HNO_3 in the presence of conc H_2SO_4, gives nitronium ion (NO_2^+) which attack on acetanilide to form *p*-nitro acetanilide through the cyclopentadienyl cation (intermediate) formation.

$$HNO_3 + H_2SO_4 \longrightarrow \underset{\text{nitronium ion}}{NO_2^+} + H_2O + HSO_4^-$$



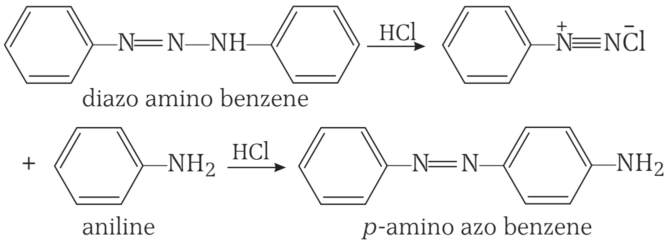
$$H^+ + HSO_4^- \longrightarrow H_2SO_4$$

Aniline yellow or *p*-amino azobenzene,

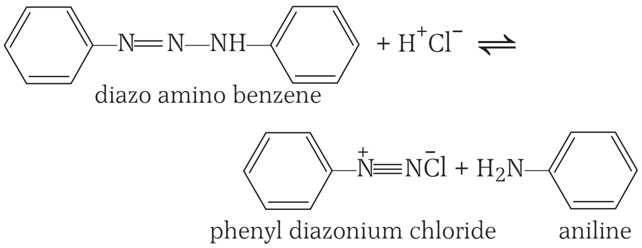


It is prepared from diazo amino benzene.

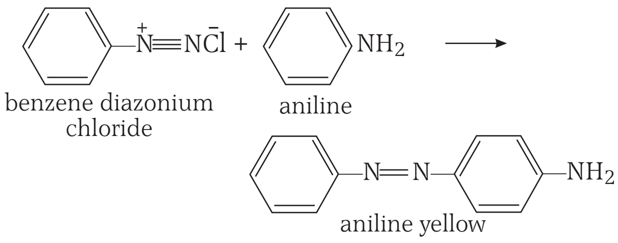
When diazo amino benzene is heated with aniline and a little amount of aniline hydrochloride at about 40°C, for a short time, it gives *p*-amino azo benzene or aniline yellow in good yield.



The mechanism of the reaction is based on the equilibrium involving the diazo amino compound, phenyl diazonium chloride and aniline.



The reaction takes place between the two latter compounds under weakly acidic conditions.

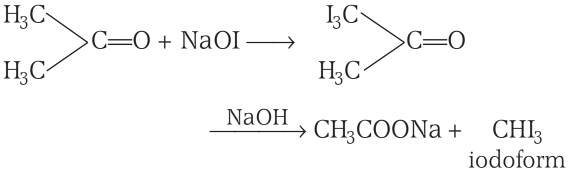


Iodoform, CHI_3

It is prepared from acetone.

Acetone when treated with potassium iodide and sodium hypochlorite (NaOCl), gives iodoform.

$$NaOCl + KI \longrightarrow NaOI + KCl$$



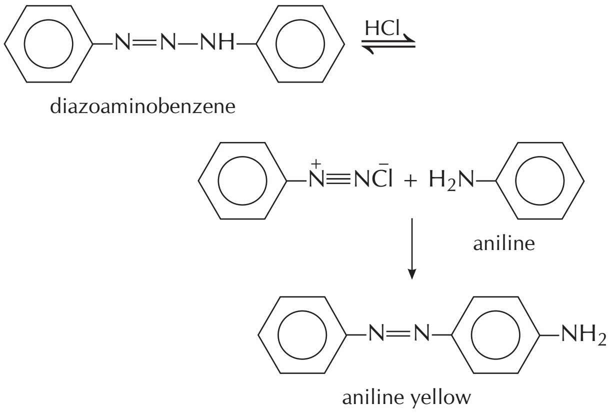
$$(H_3C)_2C{=}O + NaOI \longrightarrow (I_3C)(H_3C)C{=}O \xrightarrow{NaOH} CH_3COONa + \underset{\text{iodoform}}{CHI_3}$$

Caution Point *The compounds containing* $CH_3-\overset{O}{\overset{\|}{C}}-$ *and* $CH_3-\underset{OH}{\underset{|}{CH}}-$ *groups give iodoform test.*

Sample Problem 4 *When aniline hydrochloride reacts with diazoamino benzene at 40°C, it gives*

(*a*) *aniline yellow*
(*b*) *hydrazo compound*
(*c*) *azobenzene*
(*d*) *no reaction takes place*

Interpret (a)



Check Point 2

1. Why is dilute H_2SO_4 added in boiling water during the preparation of ferrous sulphate solution?
2. In the preparation of acetanilide, zinc is added to reaction mixture. Explain.
3. Identify the functional groups present in *p*-nitroacetanilide.
4. Mention the name of the reactants for the synthesis of *p*-amino azobenzene. Write chemical reaction involved in its synthesis also.

Hot Spot

TITRIMETRIC Exercises

Titrimetric exercises is one of the important topic of this chapter. Generally questions are seen from this topic. The level of question vary from moderate to difficult.

Titration

A titration is an experiment where the volume of reactant solution (titrant) needed to react exactly with some amount of another reactant is measured. This volume is called equivalence point. A titration is performed by slowly adding a standard solution from a burette to a solution under examination until the reaction between the two is observed to be complete. The volume or mass of the reagent needed to complete the titration is determined from the difference between the initial and final readings.

It is sometimes necessary to add an excess of the standard titrant and then determine the excess amount by **back titration** with a second titrant. (The solution taken in the burette during titration is known as titrant and the other solution being titrated is called the titrate).

Standard Solutions

A volumetric method employs one or more standard solutions which are reagents of exactly known concentrations. A standard solution used for acid-base titration is usually a solution of strong acids or bases *e.g.*, HCl, H_2SO_4, NaOH, KOH and $Ba(OH)_2$. Bases, however, are not as good as acid for permanent standards because they absorb CO_2 whenever they come in contact with air. Therefore, the accuracy of a volumetric method is limited by the accuracy with which the concentration of the standard solution is known.

The ideal standard solution (of known concentration) must have the following characteristics

(i) It should be sufficiently stable so that it is necessary to determine its concentration only once.

(ii) It must react rapidly with the analyte.

If concentration of a substance can be known simply by dissolving its known amount in a given volume of solution, then the substance is called **primary standard and the solution formed as primary standard solutions.** *e.g.,* Oxalic acid, potassium dichromate. In most cases, concentration can be determined by standardisation against primary standard solution. Such solutions are called **secondary standard solutions.** *e.g.*, Ferrous sulphate, mineral acids (H_2SO_4, HNO_3), Their solutions are prepared by dissolving a known amount or volume but they have to be standardised using primary standard. Thus, all these are secondary standards.

Equivalence Point and End Point

The equivalence point in a titration is a theoretical point reached when the amount of added titrant is chemically equivalent to the amount of analyte (titrate) in the sample. It cannot be determined experimentally. We can only estimate its position by observing some physical change associated with the condition so equivalence. This is called end point of titration. For example, equivalent point is reached when 1 mole of HCl is neutralized by 1 mole of NaOH. But we cannot detect this equivalent point. If one drop of suitable indicator such as phenolphthalein is added in HCl (analyte), then additional drop of NaOH (from burette) will give light pink colour. This is the **end point.** Therefore, end point is the point of completion of the reaction indicated by suitable indicator. It has additional drop of titrating reagent but, we use

$$N_1V_1 = N_2V_2$$

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

$$1 \text{ equivalent of NaOH} \equiv 1 \text{ equivalent of HCl}$$

$$\equiv 1 \text{ mol of HCl}$$

$$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$$

$$1 \text{ equivalent of NaOH} \equiv 1 \text{ equivalent of } H_2SO_4$$

$$\equiv 0.5 \text{ mol of } H_2SO_4$$

Caution Point *The volume of titrant at the end point is larger than that at the equivalence point.*

Acid-Base Indicators

Acid-base indicators are special types of substances which possess one colour in acid solution and different colour in alkaline medium. For acid-base titration, a weak acid or weak base is used as an indicator. Since, the concentration of acid or base is controlled by pH, the colour of an indicator solution is pH dependent. The Henderson-Hasselbalch equation shows that when pH $= pK_a$, the acid and base concentrations are equald. Thus, the colour will be a mixture of both the acid and base forms. Since, there is at least 20 times higher acid concentration than base, the acidic form and colour predominate at pH $< pK_a - 1.0$ Likewise, the basic form and colour predominate at pH $> pK_a + 1.0$.

Table 16.1 **pH Transition Ranges and Colours of Some Common Indicators**

	Indicator	pH range	Colour in acid solution	Colour in alkaline solution
1.	Thymol blue	1.2 – 2.8	Red	Yellow
2.	Bromophenol blue	3.1 – 4.6	Yellow	Purple
3.	Methyl orange	3.1 – 4.5	Red	Yellow
4.	Methyl red	4.2 – 6.3	Red	Yellow
5.	Bromothymol blue	6.0 – 7.5	Orange	Blue
6.	Phenol red	6.4 – 8.2	Yellow	Red
7.	Thymol blue (base)	8.1 – 9.6	Yellow	Blue
8.	Phenolphthalein	8.0 – 9.8	Colourless	Pink
9.	Thymophthalein	9.3 –10.5	Colourless	Blue
10.	Alizarin yellow R	10.1 – 12.1	Yellow	Lilac

Acid-base Titration

(Neutralization Method of Analysis)

The neutralization method of analysis commonly called "acid-base titration" is a very common method of determining amount of acids, bases or salts of weak acids or bases in an unknown sample. An acid-base titration involves a neutralisation reaction in which an acid is reacted with an equivalent amount of a base. The reaction is characterised by a rapid change in pH near the equivalence point, which is detected by the colour change of indicator that occur at the end point. The analysis that can be done by neutralisation method may be grouped in two general classes.

(i) Determination of acid or base or their anhydride in a sample by titrating with a standard solution of base or acid.

(ii) Determination of salts of weak acids or bases by titrating with a standard solution of a strong base or acid.

The titration of a very weak base with strong acid and a titration of a very weak acid with strong base can not be performed because a sharp end point cannot be observed for them. Usually when acid is too weak to be titrated with a standard base, a salt of acid can be titrated with standard acid solution. For example, carbonic acid cannot be titrated by sodium hydroxide quantitatively, but sodium carbonate can be titrated by hydrochloric acid or sulphuric acid.

$$CO_3^{2-} + 2H^+ \longrightarrow H_2O + CO_2$$

Table 16.2 **Indicators in Acid-base Titrations**

S.N.	Acid-base titrations	Indicators
1.	Strong acid *vs* strong base	Bromothymol blue, phenolphthalein methyl orange, thymophthalein
2.	Strong acid *vs* weak base	Methyl orange, methyl red, bromocresol green
3.	Weak acid *vs* strong base	Phenolphthalein, thymophthalein
4.	Weak acid *vs* weak base	Phenol red

Titration Curve

By constructing a titration curve, we can easily explain how the end point of a titration can be detected. A titration curve is constructed by plotting the pH of the solution as a function of the volume of titrant added. The titrant is always a strong acid or a strong base.

Redox Titrations Reducing agents such as Fe, Fe^{2+}, H_2O_2, $CaOCl_2$, MnO_2 can be determined by suitable oxidising agents such as as $KMnO_4$, $K_2Cr_2O_7$ in acidic or basic or neutral medium. These are called redox titrations. *e.g.*, Fe^{2+} is oxidised to Fe^{3+} by MnO_4^- which in turn is reduced to Mn^{2+} in acidic medium.

$$5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

In all cases, $N_1V_1 = N_2V_2$

but $M_1V_1 \neq M_2V_2$

$$\text{Equivalent weight} = \frac{\text{molecular weight}}{\text{total change in ON}}$$

$$= \frac{\text{molecular weight}}{\text{number of electrons gained or lost}}$$

Some Important Examples of Titrations

(i) Na_2CO_3 *vs* HCl Titration

The titration of Na_2CO_3 *vs* HCl is a neutralisation titration (acidimetry and alkalimetry) which involve the neutralisation of an acid with a base. *e.g.,* sodium carbonate is attacked by dil HCl in the following way

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2\uparrow$$

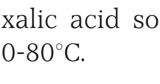
Methyl orange is used as an indicator for end pont detection. In this titration, sodium carbonate is estimated by titrating it with a standard solution of HCl.

(ii) Oxalic Acid *vs* $KMnO_4$ Titration

This is an example of redox titration in which a reducing agent (as oxalic acid) is estimated by titrating it with a standard solution of oxidising agent (as $KMnO_4$). Such reactions are accompanied by the change in valency of ions. In these titrations oxidation and reduction takes place simultaneously *i.e.*, while one substance is being oxidised, the other one is being reduced.

$$\underset{\substack{\text{oxidising}\\\text{agent}}}{2KMnO_4} + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O];$$

$$\left(E_{KMnO_4} = \frac{M}{5}\right)$$



$$\underset{\text{reducing agent}}{5\begin{array}{c}COOH\\|\\COOH\end{array}} + 5[O] \longrightarrow 5H_2O + 10CO_2\uparrow; \quad \left(E_{H_2C_2O_4} = \frac{M}{2}\right)$$

$KMnO_4$ acts as self indicator for end point detection.

This titration is carried out in the presence of HCl or H_2SO_4 but not in the presence of conc. HNO_3 because it is a strong oxidising agent and hence interfere with oxidising action of $KMnO_4$. In $KMnO_4$ *vs* oxalic acid titration, the oxalic acid solution is heated with dilute H_2SO_4 up to 70-80°C.

Mohr's Salt, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ *vs* $KMnO_4$ Titration

This titration is also an example of redox titration and work on the same principle as oxalic acid *vs* $KMnO_4$ titration. In this titration, the active constituent of ferrous ammonium sulphate (Mohr's salt) is ferrous sulphate, which is oxidised to ferric sulphate by acidified potassium permanganate as follows.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]; \quad \left(E_{KMnO_4} = \frac{M}{5}\right)$$

$$\frac{[2FeSO_4 + H_2SO_4 + [O] \longrightarrow Fe_2(SO_4)_3 + H_2O] \times 5}{2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O} \quad \left(E_{FeSO_4} = \frac{M}{1}\right)$$

$KMnO_4$ acts as self indicator for end point detection.

This titration is carried out at room temperature because Mohr's salt is oxidised by air on heating.

Sulphuric acid should be present in excess otherwise a brown precipitate due to the formation of MnO_2 will be formed.

Table 16.3 **Redox Titrations** (Excluding Iodometric/Iodimetric Titrations)

Estimation of	By Titrating with	Reactions	Relation between O.A and R.A
Fe^{2+}	MnO_4^-	$Fe^{2+} \longrightarrow Fe^{3+} + e^-$ $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	$5Fe^{2+} \equiv MnO_4^-$ eq.wt. $Fe^{2+} = \frac{M}{1}$; eq.wt $MnO_4^- = \frac{M}{5}$
Fe^{2+}	$Cr_2O_7^{2-}$	$Fe^{2} \longrightarrow Fe^{3+} + e^-$ $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	$6Fe^{2+} \equiv Cr_2O_7^{2-}$ eq.wt. $Cr_2O_7^{2-} = M/6$
$C_2O_4^{2-}$	MnO_4^-	$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$ $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	$5C_2O_4^{2-} \equiv 2MnO_4^-$ eq.wt. $C_2O_4^{2-} = M/2$; eq.wt. $MnO_4^- = \frac{M}{5}$
H_2O_2	MnO_4^-	$H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$	$5H_2O_2 = 2MnO_4^-$ eq.wt $H_2O_2 = M/2$; eq.w.t $MnO_4^- = \frac{M}{5}$
As_2O_3	MnO_4^-	$As_2O_3 + 5H_2O \longrightarrow 2AsO_4^{3-} + 10H^+ + 4e^-$	eq.wt of $As_2O_3 = M/4$
AsO_3^{3-}	BrO_3^-	$AsO_3^{3-} + H_2O \longrightarrow AsO_4^{3-} + 2H^+ + 2e^-$ $BrO_3^- + 6H^+ + 6e^- \longrightarrow Br^- + 3H_2O$	eq.wt. $AsO_3^{3-} = M/2$ eq.wt. of $BrO_3^- = M/6$

Sample **Problem 5** Oxalic acid ($H_2C_2O_4$) is present in many plants and vegetables. If 24.0 *mL of* 0.01 *M* $KMnO_4$ *solution is needed to titrate* 1.00 *g of* $H_2C_2O_4$ *to the equivalence-point, what is the per cent by mass of* $H_2C_2O_4$ *in the sample?*

(*a*) 0.54%
(*b*) 5.4%
(*c*) 54%
(*d*) 0.054%

Interpret (*b*) 24 mL of 0.01 M $KMnO_4 = 0.24 \times 10^{-3}$ mol $KMnO_4$

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

$$\therefore \quad C_2O_4^{2-} \text{ (pure) reacted } = \frac{5}{2} \times 0.24 \times 10^{-3} \text{ mol}$$
$$= 0.60 \times 10^{-3} \text{ mol}$$

Thus, oxalic acid (pure) $= 0.60 \times 10^{-3} \times 90$ g $= 0.054$ g in 1.0 g impure oxalic acid

% purity = 5.4%

Sample **Problem 6** *A mixture of* HCl *and* H_3PO_4 *is titrated with* 0.1 *M* NaOH. *The first end point (methyl red) occurs at* 35.00 *mL and the second end-point (bromothymol blue) occurs at a total of* 50.00 *mL* (15.00 *mL after the first end point). Calculate the millimoles of* HCl *and* H_3PO_4 *present in the solution respectively.*

(*a*) 2.0 *and* 1.5
(*b*) 1.5 *and* 2.0
(*c*) 20 *and* 15
(*d*) 15 *and* 20

Interpret (*a*) $HCl \rightleftharpoons H^+ + Cl^-$ end point indicated by methyl red.

$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$ end pont indicated by methyl red.

$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$ end point indicated by bromothymol blue.

Let HCl $= x$ milimol

$H_3PO_4 = y$ millimol

then $x + y = 35 \times 0.1 = 3.5$ millimol (first step ionization)

$y = 15 \times 0.1 = 1.5$ millimol (second step ionization)

$\therefore$ HCl $= 3.5 - 1.5 = 2.00$ millimol

and $H_3PO_4 = 1.5$ millimol

Check Point 3

1. What is the difference between equivalence point and end point?
2. Urea sample is 60% pure. Calculate volume of 1 NHCl required to absorb NH_3 from 1.0 g of urea sample on decomposition with NaOH.
3. What is the molarity of a MnO_4^- solution, if 32.00 mL of the solution is required to titrate 40.00 mL of 0.400 N Fe^{2+}?

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

4. Why does colour of $KMnO_4$ disappear when oxalic acid is added to its solution in acidic medium? **[NCERT** Exemplar**]**

16.3 Salt Analysis or Qualitative Inorganic Analysis

Qualitative analysis of given inorganic mixture is done in the following steps

1. **Dry tests** Dry tests involve following tests
   - (a) Physical observation
   - (b) Effect of heating
   - (c) Smell of compound
   - (d) Solubility of salts
   - (e) Flame tests
   - (f) Charcoal cavity test
   - (g) Cobalt nitrate test
   - (h) Borax bead test
   - (i) Microcosmic salt bead test
   - (j) Sodium carbonate bead test
2. **Wet tests** Dry tests tells us about the presence of possible radicals in the mixture but these are confirmed by wet tests.

Dry Test

These are preformed in the following manner

(a) **Physical Observation of Salt or Mixture**

In physical examination, colour, smell and density of a given mixture are observed.

S.N.	Observation	Inference
A.	**Colour of the substance**	
(i)	Blue, its aqueous solution is also blue.	Cupric salt
(ii)	Green, its aqueous solution is also green.	Salts of nickel
(iii)	Dark green, its aq. solution is also dark green but becomes light on dilution.	Salts of chromium
(iv)	Violet-pink, its aq. solution is pink.	Salts of cobalt
(v)	Light pink, its aqueous solution is colourless.	Salts of manganese
(vi)	Reddish brown	Fe_2O_3
(vii)	Red	$HgO, HgI_2, Pb_3O_4, Cu_2O$
(viii)	Orange red	Sb_2S_3
(ix)	Black	CuO, NiO, SnO, FeS, CuS, HgS, PbS, CoS, FeO, $Co_3O_4, Ni_2O_3, Cu_2S, CuBr_2$, NiS etc.
(x)	Yellow	As_2S_3, CdS, Bi_2O_3, As_2S_5, PbI_2, AgI, chromates etc.
(xi)	Yellow-green, aqueous solution is light green or almost colourless.	Salts of Fe^{2+}
(xii)	Yellow-brown, aqueous solution is yellow	Salts of Fe^{3+}
(xiii)	Colourless	Transition metals absent except some salts of Mn^{2+}
(xiv)	Purple	Some Cr^{3+} salts and permanganates.

S.N.	Observation	Inference
B.	**Odour of the substance**	
(i)	Vinegar like smell	Acetates
(ii)	Rotten egg like smell	Sulphides
(iii)	Ammoniacal smell	Ammonia salts mainly $(NH_4)_2CO_3$ Some ammonium salts and sulphides do not give smell.
C.	**Density**	
	Mixture or salt is light	Salts of Zn, Bi, Al, Ba, Sr, Ca and Mg.
	Mixture of salts is heavy	Salts of Hg and Pb.

(b) Effect of Heating

Take the given substance in a clear, dry test tube and heat it first gently and then strongly. Observe the changes takes place upon heating.

S.N.	Observation	Inference
(i)	Substance melts	Salts of alkali metals, chlorides of Hg, Ag and Pb and salts having water of crystallisation.
(ii)	Substance cracks	$Pb(NO_3)_2$, $Ba(NO_3)_2$, NaCl and KI
(iii)	Substance swells	Alums, salts of phosphate and borate.
(iv)	Substance sublimes on heating and the colour of sublimate is	
	White	$HgCl_2$, As_2O_3, Hg_2Cl_2, $AlCl_3$, Sb_2O_3, halides of NH_3
	Yellow	As_2S_3 and HgI_2
	Black	Sulphides of Hg, Sb, As
	Blue, yellow or violet vapours	Iodides
	Grey (having garlic odour)	As
(v)	Colour of residue obtained after heating (Residue mainly contains metallic oxides	
	White and non-fusible	Oxides of Ca, Ba, Sr, Mg, Zn and Al.
	Red-brown	Fe_2O_3
	Yellow-brown when hot, on cooling it is brown	SnO_2
	Black and infusible	NiO, MnO_2 and CuO
	Dark orange red in heating state and sublimes	HgO
	White, infusible, becomes yellow on heating	ZnO
	Initially it is blue or green but becomes white on heating	$CuSO_4 \cdot 5H_2O$
(vi)	Observations of gases evolved	
A.	Colourless, odourless gas	
	O_2, which supports combustion.	Nitrates of Na and K
	CO_2, which turns lime water milky.	Carbonates and oxalates.
B.	Colourless, odorous gas	
	H_2S, smell of rotten eggs	Sulphides.
	HCl, Pungent smell and forms white fumes with NH_3	Hydrated chloride salts
	NH_3, turns red litmus to blue	Ammonium salts
	SO_2, smell of burning sulphur	Sulphite and thiosulphate.
C.	Coloured, odorous gas	
	Cl_2, yellow-green pungent smelling gas.	Chloride
	I_2, violet gas	Iodides
	Br_2, red-brown gas	Bromides
	NO_2, brown gas	Nitrates or nitrites of heavy metals

(c) Smell of Compound

Smell of compound also gives an idea about the radical present in the salt.

Smell	Inference
Ammoniacal smell	Ammonium salts
Vinegar like smell	Acetates
Chlorine like smell	Hypochlorites

(d) Solubility of Salts

Type of the salts	Observation
Nitrates and nitrites	All metal salts are soluble in water
Acetates	All metal acetates are soluble in water
Chlorides	All common chlorides are soluble in water except AgCl, Hg_2Cl_2 and $PbCl_2$.
Bromides	All common bromides are soluble in water except AgBr, Hg_2Br_2, $PbBr_2$ and $HgBr_2$.
Iodides	All common iodides are soluble in water except AgI, Hg_2I_2, HgI_2, PbI_2.
Sulphides	All common sulphides are insoluble in water except sulphides of group I and group II metals and ammonium ion.
Carbonates	All common carbonates are insoluble in water except carbonates of group I and $(NH_4)_2CO_3$.
Sulphates	All common sulphates are soluble in water except $PbSO_4$, Hg_2SO_4, $BaSO_4$, $CaSO_4$ and Ag_2SO_4 which are sparingly soluble.
Phosphates	All common phosphates are insoluble in water except phosphates of group I and $(NH_4)_3PO_4$.
Hydroxides	All common metal hydroxides are insoluble in water except group I hydroxides and $Ba(OH)_2$, $Sr(OH)_2$ and $Ca(OH)_2$.

(e) Flame Test

This test is bases upon the fact that in a state of high ionisation of chloride some of the cations impart characteristic colour to the flame, as the cation absorbs energy from the flame and transmit the same as light of characteristic colour.

Paste of the salt and conc. HCl is taken into the lower oxidising zone and colour imparted to the flame by salts is observed. Salts particularly of group V (Ba^{2+}, Ca^{2+}, Sr^{2+}) are identified by colours of the flame.

Colour	Cation
Golden yellow	Na^+
Violet	K^+
Carmine red	Li^+
Brick red	Ca^{2+}
Apple-green	Ba^{2+}, Mo^{2+}
Green	Cu^{2+}, BO_3^{3-}, Tl^{3+}
Crimson red	Sr^{2+}
Blue	Cu^{2+}, As^{3+}, Sb^{3+}, Bi^{3+}

(f) Charcoal Cavity Test

When a salt is fused with anhydrous Na_2CO_3 or oxidising mixture in a cavity on charcoal block in reducing flame, first metallic carbonates and finally metallic oxides are formed.

$$Pb(NO_3)_2 + Na_2CO_3 \xrightarrow{\Delta} PbCO_3 + 2NaNO_3$$

$$PbCO_3 \xrightarrow{\Delta} PbO + CO_2\uparrow$$

or

$$CuSO_4 + Na_2CO_3 \xrightarrow{\Delta} CuCO_3 + Na_2SO_4$$

$$CuCO_3 \xrightarrow{\Delta} CuO + CO_2\uparrow$$

These metallic oxides reduce to metals by the action of carbon present in reducing flame. On cooling these metals form beads.

$$PbO + C \longrightarrow Pb + CO\uparrow$$
$$CuO + C \longrightarrow Cu + CO\uparrow$$

Conclusions can be made by the following table.

Table 16.4 **Colour in Charcoal Cavity Test**

S.N.	Bead	Crust	Inference
(i)	Greyish white soft bead which marks paper.	Brown which turns yellow on cooling	Pb^{2+}
(ii)	Lustrous white bead	—	Ag^+
(iii)	White-browm bead	Orange which turns yellow on cooling	Bi^{3+}
(iv)	Garlic like smelly fumes without bead	—	As^{3+}
(v)	—	Red-brown precipitate, easily turns into vapour	Cd^{2+}
(vi)	Smell of ammonia	Red	NH_4^+
(vii)	—	Black precipitate	$Fe^{3+}, Co^{2+}, Mn^{2+}$

(g) Cobalt Nitrate Test

This test is performed only when infusible mass is obtained in charcoal-cavity test. Infusible mass contains metallic oxides like CaO, Al_2O_3, MgO and ZnO.

In this test, 1-2 drops cobalt nitrate is added to infusible mass obtained in charcoal cavity and heat the mixture in oxidising flame.

Conclusions can be made by the following table.

Table 16.5 **Colour Shown in Cobalt Nitrate Test**

S.N.	Colour of the residue	Inference
1.	Green	Zn^{2+}
2.	Pink-dirty residue	Mg^{2+}
3.	Bluish green	Sn^{2+}
4.	Blue	$Al^{3+}, PO_4^{3-}, BO_3^{3-}$

Cobalt nitrate should not be used in excess otherwise black coloured cobalt oxide (Co_3O_4), may be formed and it is different to identify other colours in the presence of black colour.

(h) **Borax Bead Test**

If borax, $Na_2B_4O_7 \cdot 10\,H_2O$ is heated on the platinum loop, a transparent colourless glass like bead of sodium metaborate ($NaBO_2$) and boric anhydride (B_2O_3) is formed.

$$Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3.$$

Characteristics coloured beads are produced with salts of Cu, Fe, Cr, Mn, Co and Ni. The colour of the bead depends upon the flame in which it has been heated.

$$CuO + B_2O_3 \longrightarrow \underset{\substack{\text{copper (II) metaborate} \\ \text{(green when hot} \\ \text{blue when cold)}}}{Cu(BO_2)_2} \qquad \text{(oxidising flame)}$$

$$2Cu(BO_2)_2 + C \longrightarrow 2CuBO_2 + B_2O_3 + CO\uparrow \qquad \text{(reducing flame)}$$

$$2CuBO_2 + C \xrightarrow{\text{Colourless}} \underset{\text{red}}{2Cu\downarrow} + B_2O_3 + CO\uparrow$$

Conclusions can be made by the following table

Table 16.6 **Colour in Borax Bead Test**

	Oxidising flame		Reducing flame		Metal
S.N.	Hot	Cold	Hot	Cold	
1.	Green	Blue	Colourless	Opaque red-brown	Cu
2.	Yellowish- brown	Yellow	Green	Green	Fe
3.	Yellow	Green	Green	Green	Cr
4.	Violet	Amethyst	Colourless	Colourless	Mn
5.	Blue	Blue	Blue	Blue	Co
6.	Violet	Reddish-brown	Grey	Grey	Ni
7.	Yellow	Colourless	Brown	Brown	Mo
8.	Rose-violet	Rose-violet	Red	Violet	Au
9.	Yellow	Colourless	Yellow	Yellowish to brown	W
10.	Yellow	Pale yellow	Green	Bottle Green	U
11.	Yellow	Greenish yellow	Brownish	Emerald green	V
12.	Yellow	Colourless	Grey	Pale violet	Ti
13.	Orange-red	Colourless	Colourless	Colourless	Ce

(i) **Microcosmic Salt Bead Test**

A test similar to borax bead test is used for identification of coloured cations, if microcosmic salt $Na(NH_4)HPO_4 \cdot 4H_2O$ is used.

$$Na(NH_4)HPO_4 \xrightarrow{\Delta} \underset{\text{transparent bead}}{NaPO_3} + H_2O\uparrow + NH_3\uparrow$$

$$NaPO_3 + CoO \longrightarrow \underset{\text{blue bead}}{NaCoPO_4}$$

Conclusions can be made by the following table

Table 16.7 **Colour Obtained in Microcosmic Salt Bead Test**

S.N.	Oxidising flame	Reducing flame	Metal
1.	Green when hot, blue when cold	Colourless when hot, red when cold	Cu
2.	Yellow or red-brown when hot, yellow when cold	Yellow when hot, colourless to green when cold	Fe
3.	Green, hot and cold	Green, hot and cold	Cr
4.	Violet, hot and cold	Colourless, hot and cold	Mn
5.	Blue, hot and cold	Blue, hot and cold	Co
6.	Brown, hot and cold	Grey when cold	Ni
7.	Yellow, hot and cold	Green when cold	V
8.	Yellow when hot, yellow green when cold	Green hot and cold	U
9.	Pale yellow when hot, colourless when cold	Green when hot, blue when cold	W
10.	Colourless, hot and cold.	Yellow when hot, violet when cold	Ti

(j) **Sodium Carbonate Bead Test**

The sodium carbonate bead is prepared by fusing small quantity of sodium carbonate on a platinum wire loop in the Bunsen flame, a white opaque bead is formed. If this is moistened, dipped into a little KNO_3 and then into a small quantity of the given salt and the whole is heated in the oxidising flame, a coloured bead is formed. For example.

$$MnO + Na_2CO_3 + O_2 \xrightarrow{\Delta} \underset{\substack{\text{sodium manganate}\\ \text{(green bead)}}}{Na_2MnO_4} + CO_2$$

$$2Cr_2O_3 + 4Na_2CO_3 + 3O_2 \xrightarrow{\Delta} \underset{\substack{\text{sodium chromate}\\ \text{(yellow bead)}}}{4Na_2CrO_4} + 4CO_2$$

Wet Tests

In wet analysis, the substance is first dissolved in water to bring it in solution form and is analysed for acid and basic radicals. In the analysis of inorganic salt mixture, first acid radicals are analysed and then basic radicals.

Analysis of Acid Radicals

Analysis of acid radicals (anions) is done in the following sequence.

Analysis of First Group Anions $(CO_3^{2-}, S^{2-}, NO_2^-)$

Acidic radicals or anions of first group, when treated with dil H_2SO_4, (Group reagent) evolve gases with characteristic colour and smell. On the basis of action of these gases, anions are identified.

Table 16.8 **Test for CO_3^{2-}**

S.N.	Experiment	Observation	Inference
1.	Take mixture in a dry test tube and add dill HCl or H_2SO_4. Warm gently	Brisk effervescence with the evolution of colourless and odourless gas (CO_2)	CO_3^{2-} may be
2.	Pass the evolved gas into limewater [$Ca(OH)_2$]	Lime water turns milky	CO_3^{2-} confirmed
3.	If, in lime water the gas is passed in excess	Milkiness disappears	CO_3^{2-} confirmed

Reactions Involved in the Test of Carbonate (CO_3^{2-})

(i) $Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + \underset{\substack{\text{colourless,}\\ \text{odourless}\\ \text{gas}}}{CO_2 \uparrow}$

(ii) $Ca(OH)_2 + CO_2 \longrightarrow \underset{\substack{\text{calcium carbonate}\\ \text{(milky)}}}{CaCO_3} \downarrow + H_2O$

(iii) $CaCO_3 + H_2O + CO_2(\text{excess}) \longrightarrow \underset{\substack{\text{calcium bicarbonate}\\ \text{(colourless)}}}{Ca(HCO_3)_2}$

Table 16.9 **Tests for S^{2-}**

S.N.	Experiment	Observation	Inference
1.	Take mixture in a dry test tube and add dil HCl or H_2SO_4 and warm gently	A colourless gas (H_2S) with smell of rotten eggs evolved	S^{2-} may be
2.	Take filter paper dipped in lead acetate on the mouth of test tube	Filter paper turns black due to formation of PbS	S^{2-} confirmed

Reactions Involved in the Test of Sulphide (S^{2-})

(i) $Na_2S + H_2SO_4 \longrightarrow H_2S + Na_2SO_4$ (ii) $(CH_3COO)_2Pb + H_2S \longrightarrow \underset{\text{black}}{PbS\downarrow} + 2CH_3COOH$

Table 16.10 **Tests for Nitrate**

S.N.	Experiment	Observation	Inference
1.	Take mixture in a dry test tube and add dil HCl. Warm gently	Brown fumes (NO_2) with pungent odour are evolved	NO_2^- may be
2.	Take filter paper dipped in (strach + KI) solution, on the mouth of test tube	The evolved gas turns filter paper blue	NO_2^- confirmed
3.	Add 2-3 drops of KI and starch solution in the test tube	Deep blue or violet colour appears	NO_2^- confirmed

Reactions Involved in the Test of Nitrite (NO_2^-)

(i)

$$2NaNO_2 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HNO_2$$

$$3HNO_2 \longrightarrow HNO_3 + 2NO\uparrow + H_2O$$

$$2NO + O_2 \longrightarrow \underset{\text{(brown)}}{2NO_2\uparrow}$$

(ii)

$$2KI + 2NO_2 \longrightarrow 2KNO_2 + I_2$$

$$I_2 + \text{starch} \longrightarrow \text{Blue colour}$$

Analysis of Second Group Anions (Cl^-, Br^-, I^-, NO_3^-)

Acidic radicals or anions of second group give no response with dil. acids but with conc. acids (Conc. H_2SO_4 group reagent), they evolve gases with characteristic colour and smell, thus can be identified by using conc. acids.

Table 16.11 **Tests for Chloride**

S.N.	Experiment	Observation	Inference
1.	Heat the mixture with 1-2 mL conc H_2SO_4 in a dry test tube	A colourless, pungent gas (HCl) is evolved	Cl^- may be
2.	Bringe a glass rod dipped in NH_4OH near the mouth of test tube	White dense fumes of NH_4Cl is evolved	Cl^- confirmed
3.	Heat the mixture with conc H_2SO_4 and MnO_2 in a dry test tube	Greenish-yellow (Cl_2) pungent gas is evolved	Cl^- confirmed
4.	**Chromyl chloride test** Heat the mixture with solid $K_2Cr_2O_7$ and conc H_2SO_4. Now collect these vapours in a test tube containing NaOH. Acidified it with acetic acid and add lead acetate solution	Orange yellow vapours of chromyl-chloride (CrO_2Cl_2) are evolved A yellow ppt or solution of lead chromate is formed	Cl^- confirmed

Reactions Involved in the Test of Chloride (Cl^-)

(i) $NaCl + H_2SO_4 \longrightarrow NaHSO_4 + \underset{\text{pungent smelling gas}}{HCl\uparrow}$

(ii) $HCl + NH_4OH \longrightarrow \underset{\text{white fumes}}{NH_4Cl\uparrow} + H_2O$

(iii) $2NaCl + MnO_2 + 3H_2SO_4 \longrightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + \underset{\text{yellowish-green}}{Cl_2\uparrow}$

(iv) **Chromyl chloride test**

$$4NaCl + K_2Cr_2O_7 + 3H_2SO_4 \longrightarrow \underset{\substack{\text{chromyl chloride} \\ \text{(orange yellow gas)}}}{2CrO_2Cl_2} + 2Na_2SO_4 + K_2SO_4 + 3H_2O$$

$$CrO_2Cl_2 + 4NaOH \longrightarrow \underset{\text{yellow}}{Na_2CrO_4} + 2NaCl + 2H_2O$$

$$(CH_3COO)_2Pb + Na_2CrO_4 \longrightarrow \underset{\text{yellow}}{PbCrO_4\downarrow} + 2CH_3COONa$$

Caution Point *If a mixture contains chlorates, chromyl chloride test for chloride anion is not performed because chlorates on reaction with* H_2SO_4 *form chlorine dioxide gas which dissolves in* H_2SO_4 *and form highly explosive orange yellow solution.*

$3KClO_3 + 3H_2SO_4 \longrightarrow 2ClO_2\uparrow + ClO_4^- + 3SO_4^{2-} + 4H^+ + 3K^+ + H_2O$

Table 16.12 **Test for Bromide**

S.N.	Experiment	Observation	Inference
1.	Heat the mixture with 1-2 mL conc H_2SO_4 in a dry test tube	A colourless, pungent gas (HBr) or sometimes brown fumes are evolved	Br^- may be
2.	Heat the mixture with MnO_2 and conc H_2SO_4	Red brown vapour of Br_2 evolved	Br^- confirmed
3.	To the solution of mixture in dil HNO_3, add $AgNO_3$ solution	A pale yellow ppt of AgBr is formed (hardly soluble in NH_4OH)	Br^- confirmed

Reactions Involved in The Test of Bromide (Br^-)

(i) $NaBr + \underset{\text{conc}}{H_2SO_4} \longrightarrow NaHSO_4 + HBr\uparrow$

$2HBr + H_2SO_4(\text{conc}) \longrightarrow 2H_2O + SO_2\uparrow + \underset{\text{reddish brown}}{Br_2\uparrow}$

(ii) $2NaBr + MnO_2 + 3H_2SO_4 \longrightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + \underset{\text{reddish brown}}{Br_2\uparrow}$

(iii) $NaBr + AgNO_3 \longrightarrow \underset{\text{pale yellow}}{AgBr\downarrow} + NaNO_3$

$AgBr + 2NH_4OH \longrightarrow \underset{\substack{\text{diammine silver (I)}\\\text{bromide}}}{[Ag(NH_3)_2]Br} + 2H_2O$

Table 16.13 **Test for Iodide**

S.N.	Experiment	Observation	Inference
1.	Heat the mixture with 1-3 mL conc H_2SO_4 in a dry test tube	Dark violet fumes (I_2) are evolved	I^- may be
2.	Heat the mixture with MnO_2 and conc H_2SO_4	Violet vapours in excess are evolved	I^- may be
3.	Take a paper dipped in starch solution on the mouth of test tube	Paper turns blue	I^- confirmed
4.	To the solution of mixture in dil HNO_3, add $AgNO_3$ solution	A yellow ppt of AgI is formed (insoluble in NH_4OH)	I^- confirmed

Reactions Involved in the Test of Iodide (I^-)

(i) $NaI + \underset{\text{conc}}{H_2SO_4} \longrightarrow HI + NaHSO_4$

$H_2SO_4 + 2HI \longrightarrow \underset{\substack{\text{violet}\\\text{vapours}}}{I_2\uparrow} + SO_2 + 2H_2O$

(ii) $2NaI + MnO_2 + 3H_2SO_4 \longrightarrow I_2\uparrow + 2NaHSO_4 + MnSO_4 + 2H_2O$

(iii) $I_2 + \text{starch} \longrightarrow \text{Blue colour}$

(iv) $NaI + AgNO_3 \longrightarrow \underset{\text{yellow}}{AgI\downarrow} + NaNO_3$

Sample Problem 7 *Which one of the following is more soluble in ammonia?*

(*a*) AgCl (*b*) AgBr (*c*) AgI (*d*) *None of these*

Interpret (*a*) The order of solubility in ammonia is AgCl > AgBr > AgI.

Table 16.14 **Tests for Nitrate**

S.N.	Experiment	Observation	Inference
1.	Heat the mixture with 1-2 mL conc H_2SO_4 in a dry test tube	Pungent light brown gas (NO_2) is evolved	NO_3^- may be
2.	Heat the mixture with copper turnings and conc H_2SO_4	Deep brown fumes (NO_2) in excess are evolved	NO_3^- may be
3.	**Ring test** To the solution of mixture in dil HCl, add freshly prepared solution of $FeSO_4$. Shake well gradually and add conc H_2SO_4 by the sides of test tube	A brown ring of $FeSO_4 \cdot NO$ is formed at the junction of two liquids	NO_3^- confirmed

Reactions Involved in the Test of Nitrate (NO_3^-)

(i) $NaNO_3 + \underset{\text{(conc)}}{H_2SO_4} \longrightarrow NaHSO_4 + HNO_3$

$4HNO_3 \longrightarrow \underset{\text{brown}}{4NO_2\uparrow} + O_2\uparrow + 2H_2O$

(ii) $3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO\uparrow + 4H_2O$

$2NO + O_2 \longrightarrow 2NO_2\uparrow$

(iii) **Ring test**

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2NO\uparrow$$

$$FeSO_4 + NO \longrightarrow \underset{\substack{\text{ferrous nitroso} \\ \text{sulphate} \\ \text{(Brown ring)}}}{FeSO_4 \cdot NO}$$

Sample Problem 8 *The brown ring in the test of* NO_3^- *is formed due to the formation of ferrous nitroso sulphate. This test depends upon*

(a) *the reduction of nitrate to nitric oxide*
(b) *oxidation of nitric oxide to nitrogen dioxide*
(c) *reduction of ferrous sulphate to iron*
(d) *oxidising action of sulphuric acid*

Interpret (a) Reduction of nitrate ions by Fe^{2+} ions

$$NO_3^- + 3Fe^{2+} + 4H^+ \longrightarrow NO + 3Fe^{3+} + 2H_2O$$

$$Fe^{2+} + NO + 5H_2O \longrightarrow [Fe(H_2O)_5NO]^{2+}$$

Analysis of Third Group Anion (SO_4^{2-})

Third group radical is identified on the basis of precipitate obtained.

Table 16.15 **Tests for Sulphate**

Radical or anion	S.N.	Experiment	Observation	Inference
Sulphate (SO_4^{2-})	1.	In the solution of mixture in dil HNO_3 add $BaCl_2$ solution	A curdy white ppt ($BaSO_4$) is formed (insoluble in all conc acids)	SO_4^{2-} may be
	2.	In the solution of mixture, add lead acetate solution	White ppt of $PbSO_4$ is formed	SO_4^{2-} confirmed

Reactions Involved in the Test of Sulphate (SO_4^{2-})

(i) $Na_2SO_4 + BaCl_2 \longrightarrow \underset{\text{white}}{BaSO_4}\downarrow + 2NaCl$

(ii) $(CH_3COO)_2Pb + Na_2SO_4 \longrightarrow \underset{\text{white}}{PbSO_4}\downarrow + 2CH_3COONa$

Analysis of Basic Radical (Cations)

Based on the values of solubility products (K_{sp}), basic radicals are classified into following groups.

Table 16.16 **Classification of Basic Radicals into Groups Based on K_{sp} Values**

Group	Basic radicals	Group reagent	Precipitate as	Explanation
(I)	Ag^+, Hg_2^{2+}, Pb^{2+}	Dil. HCl	Chlorides ($AgCl$, Hg_2Cl_2, $PbCl_2$)	K_{sp} values of chlorides are low, hence precipitated. Other have higher K_{sp} values, hence not precipitated.
(II)	Cu^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+} Bi^{3+}, Sb^{3+}, Sn^{2+}, As^{3+}	H_2S gas in presence of dil. HCl	Sulphides (CuS, As_2S_3 etc.)	K_{sp} values of IInd group sulphides are low, hence precipitated by low $[S^{2-}]$ ion. HCl (due to H^+ common ion) decreases the ionisation of weak acid H_2S which gives low $[S^{2-}]$ ions. Hence, group II sulphides are precipitated while others with high K_{sp} values are not precipitated.
(III)	Al^{3+}, Cr^{3+}, Fe^{3+}	NH_4OH in presence of NH_4Cl	Hydroxides $[Al(OH)_3$ etc.]	K_{sp} values of IIIrd group hydroxides are low. NH_4Cl decreases ionisation of weak NH_4OH due to common ion effect. Low $[OH^-]$ is only sufficient to precipitate group III cations as their hydroxides.
(IV)	Zn^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+}	H_2S in ammoniacal medium	Sulphides (ZnS, NiS etc.)	K_{sp} values of sulphides of group IV are high. Ionisation of H_2S increases in basic medium. Hence, group IV cations are precipitated as sulphides due to increasing $[S^{2-}]$.
(V)	Ca^{2+}, Ba^{2+}, Sr^{2+}	$(NH_4)_2CO_3$ + NH_4Cl	Carbonates ($CaCO_3$, $BaCO_3$, $SrCO_3$)	K_{sp} values of carbonates are less than that of group VI (Mg^{2+}) hence, precipitated before Mg^{2+}.
(VI)	Mg^{2+} (Na^+, K^+) also included	NH_4OH + Na_2HPO_4 (only for Mg^{2+})	White precipitate ($MgHPO_4$)	
Zero	NH_4^+	Dilute NaOH	NH_3 gas is evolved	

Sample **Problem 9** *The principle involved in the classification of basic radicals is*

(*a*) *common ion effect* (*b*) *solubility product* (*c*) *valency of radicals* (*d*) *strength of salt*

Interpret (*b*) Basic radicals have been classified into six groups on the basis of the solubility products of their salts with group reagent. The radicals have been grouped in the order of increasing solubility product. That's why $NiCl_2$ does not precipitate with 1st group chlorides or $Zn(OH)_2$ doesn't precipitate with $Al(OH)_3$ in third group.

Preparation of Original Solution

To prepare transparent solution of salt, following solvents are used strictly in the order given below :

(i) cold water (ii) hot water (iii) dilute HCl (iv) conc. HCl

Caution Point HNO_3 *or* H_2SO_4 *cannot be used to prepare original solution because both are oxidising agents.*

Analysis of Group I Cations (Basic Radicals)

In cold original solution, dilute HCl is added drop by drop. Formation of white precipitate indicates the presence of group I. Cations of group I are precipitated as chlorides such as AgCl, $PbCl_2$ and Hg_2Cl_2. Among these chlorides, only $PbCl_2$ is soluble in hot water. Hence, hot filtrate contain Pb^{2+} ions.

Table 16.17 **Test for Lead**

S.N.	Experiment	Observation	Inference
1.	Hot filtrate is taken in the test tube and add K_2CrO_4	Yellow ppt. of $PbCrO_4$ is obtained which is soluble in NaOH but insoluble in CH_3COOH	Indicates the presence of Pb^{2+}.
2.	Hot filtrate is taken in the test tube and add KI.	Yellow ppt. of PbI_2 is formed	Pb^{2+} confirmed
3.	Dilute H_2SO_4 is added to hot filtrate and mixture is cooled.	White precipitate of $PbSO_4$ is obtained which is soluble in CH_3COONH_4 solution	Pb^{2+} confirmed

Reactions Involved in the Tests of Cation Pb^{2+}

$$\underset{\text{in cold O.S.}}{Pb^{2+}} + \underset{\text{from HCl}}{2Cl^-} \longrightarrow \underset{\text{white ppt.}}{PbCl_2\downarrow}$$

$PbCl_2$ is soluble in hot water, hence filtrate contains $PbCl_2$.

1.

$$\underset{\text{(hot and soluble)}}{PbCl_2} + K_2CrO_4 \longrightarrow \underset{\text{yellow ppt}}{PbCrO_4\downarrow} + 2KCl$$

$$PbCrO_4 + 4NaOH \longrightarrow \underset{\substack{\text{sodium plumbite}\\\text{(soluble)}}}{Na_2PbO_2} + Na_2CrO_4$$

2.

$$PbCl_2 + 2KI \longrightarrow \underset{\text{yellow}}{PbI_2} + 2KCl$$

3.

$$PbCl_2 + H_2SO_4 \longrightarrow \underset{\text{white ppt.}}{PbSO_4\downarrow} + 2HCl$$

$$PbSO_4 + 2CH_3COONH_4 \longrightarrow \underset{\text{soluble}}{(CH_3COO)_2Pb} + (NH_4)_2SO_4$$

Analysis of Group IInd Cations

Add dilute HCl in filtrate of group I and pass H_2S gas in warm solution. Formation of coloured ppt. indicates the presence of group II cations. Sulphides of group II B cations (As_2S_3, SnS, Sb_2S_3) are soluble in yellow ammonium sulphide while sulphides of group II A (PbS, CdS, CuS, Bi_2S_3) cations are soluble in HNO_3 (HgS is soluble in aquaregia).

Table 16.18 **Tests for Copper**

S.N.	Experiment	Observation	Inference
1.	Black ppt of CuS is taken in the test tube and add HNO_3(1 :)	Blue coloured solution is obtained	It indicates the presence of Cu^{2+}.
2.	Blue solution obtained above is divided into three parts.		
(i)	Add CH_3COOH and $K_4[Fe(CN)_6]$ to first part.	Chocolate brown ppt. is formed	Cu^{2+} confirmed
(ii)	Add aqueous NH_3 (excess) in second part of blue solution.	deep blue solution is obtained	Cu^{2+} confirmed
(iii)	Add KSCN is the third part of blue solution	Black ppt is obtained	Cu^{2+} confirmed

Reactions Involved in the Test of Cation Cu^{2+}

1.

$$\underset{\substack{\text{black}\\\text{ppt}}}{3CuS} + 8HNO_3 \longrightarrow \underset{\text{soluble blue}}{3Cu(NO_3)_2} + 2NO + 3S + 4H_2O$$

2.

$$Cu(NO_3)_2 + 2CH_3COOH \longrightarrow (CH_3COO)_2Cu + 2HNO_3$$

$$2(CH_3COO)_2Cu + K_4[Fe(CN)_6] \longrightarrow \underset{\text{chocolate brown ppt}}{Cu_2[Fe(CN)_6]} + 4CH_3COOK$$

3.

$$Cu^{2+} + 4NH_3(\text{excess}) \longrightarrow \underset{\text{deep blue}}{[Cu(NH_3)_4]^{2+}}$$

4.

$$Cu(NO_3)_2 + 2KSCN \longrightarrow \underset{\text{black ppt}}{Cu(SCN)_2} + 2KNO_3$$

Analysis of Group III Cations

Add few drops of conc. HNO_3 in the filtrate of group II to remove H_2S. Add NH_4Cl and NH_4OH. group III cations (if present) are precipitated as their hydroxides. ($Fe(OH)_3$-raddish brown ppt, $Cr(OH)_3$-dirty green ppt. $Al(OH)_3$-white gelatinous ppt).

Table 16.19 **Tests for Aluminium**

S.N.	Experiment	Observation	Inference
1.	Add NaOH solution in excess to white ppt.	white ppt dissolves due to the formation of sodium meta aluminate.	It indicates the presence of Al^{3+}
2.	In soluble meta-aluminate add NH_4Cl and boil	White ppt of $Al(OH)_3$ reappears	Al^{3+} confirmed

Reactions Involved in the Test of Cation Al^{3+}

1. $$\underset{\text{white ppt}}{Al(OH)_3} + NaOH \longrightarrow \underset{\substack{\text{sodium meta-aluminate}\\ \text{(soluble)}}}{NaAlO_2} + 2H_2O$$

2. $$NaAlO_2 + NH_4Cl + H_2O \xrightarrow{\Delta} NaCl + \underset{\text{white ppt.}}{Al(OH)_3} + NH_3$$

Table 16.20 **Tests for Iron**

S.N.	Experiment	Observation	Inference
1.	Add dilute HCl in reddish brown ppt. and divide it into two parts.	Precipitate dissolves	Fe^{3+} confirmed
(i)	Add $K_4[Fe(CN)_6]$ in the first part of the above solution.	Dark blue colour is obtained	Fe^{3+} confirmed
(ii)	Add KCNS in the second part of the solution.	Dark (Blood) red colour is obtained	Fe^{3+} confirmed

Reactions Involved in the Test of Cation Fe^{3+}

1. $$Fe(OH)_3 + \underset{\text{reddish brown ppt}}{3HCl} \longrightarrow \underset{\text{soluble}}{FeCl_3} + 3H_2O$$

2. $$4FeCl_3 + 3K_4[Fe(CN)_6] \longrightarrow \underset{\text{dark blue colour}}{Fe_4[Fe(CN)_6]_3} + 12KCl$$

3. $$FeCl_3 + \underset{\substack{\text{potassium}\\ \text{sulphocyanide}}}{KCNS} \longrightarrow \underset{\text{blood red colour}}{[Fe(CNS)]Cl_2} + KCl$$

Analysis of Group IV Cations

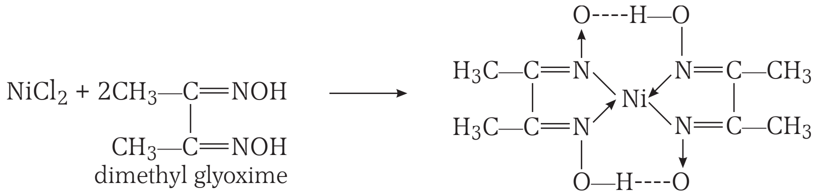
Add NH_4OH to the filtrate of group III and pass H_2S. In alkaline medium, H_2S is highly ionised so, concentration of S^{2-} is high. Due to this, group IV cations are precipitated as sulphides (ZnS, MnS, CoS and NiS).

Table 16.21 **Tests for Nickel**

S.N.	Experiment	Observation	Inference
1.	Dissolve black ppt of NiS in aquaregia (3 part conc. HCl + 1 part conc. HNO_3) and divide it into two parts.	Soluble chloride is formed	It indicates the presence of Ni^{2+}
(i)	Add NH_4OH and dimethyl glyoxime to the solution	Cherry red ppt.	Ni^{2+} confirms
(ii)	Add sodium bicarbonate and heat and add $NaOH/Br_2$ water and again heat.	Black ppt is obtained	Ni^{2+} confirms

Reactions Involved in the Test of Cation Ni^{2+}

1. $3NiS + \underbrace{6HCl + 2HNO_3}_{\text{aquaregia}} \longrightarrow 3NiCl_2 + 2NO + 3S + 4H_2O$

2. 

cherry red ppt.
(dimethyl glyoximate)

3. $NiCl_2 + 2NaHCO_3 \xrightarrow{\Delta} NiCO_3 + 2NaCl + H_2O + CO_2$

$$2NiCO_3 + 4NaOH + O(Br_2\ \text{water}) \xrightarrow{\Delta} \underset{\text{black ppt.}}{Ni_2O_3\downarrow} + 2Na_2CO_3 + 2H_2O$$

Table 16.22 **Tests for Zinc**

S.N.	Experiment	Observation	Inference
1.	Dissolve white ppt. of ZnS in dil. HCl and divide it into two parts.	Soluble chloride is formed.	It indicates the presence of Zn^{2+}.
(i)	Add NaOH in the solution. White ppt is obtained which is soluble in excess of NaOH.	White ppt. of ZnS reappears on passing H_2S into soluble sodium zincate solution	Zn^{2+} confirmed
(ii)	Solution is acidified with acetic acid and add $K_4[Fe(CN)_6]$	Bluish white ppt. is obtained	Zn^{2+} confirmed

Reactions Involved in the Test of Cation Zn^{2+}

1. $ZnS + 2HCl \longrightarrow ZnCl_2 + H_2S$
2. $ZnCl_2 + 2NaOH \longrightarrow \underset{\text{white ppt}}{Zn(OH)_2\downarrow} + 2NaCl$

$$Zn(OH)_2 + 2NaOH \longrightarrow \underset{\substack{\text{sodium zincate}\\ \text{(soluble)}}}{Na_2ZnO_2} + 2H_2O$$

$$Na_2ZnO_2 + H_2S \longrightarrow 2NaOH + \underset{\text{white ppt.}}{ZnS\downarrow}$$

3. $2ZnCl_2 + K_4[Fe(CN)_6] \longrightarrow \underset{\text{bluish white ppt.}}{Zn_2[Fe(CN)_6]\downarrow} + 4KCl$

Analysis of Group V Cations

Boil off H_2S from the filtrate of group IV and add NH_4OH and $(NH_4)_2CO_3$. Formation of white ppt. indicates the presence of group V cations. Group V cations are precipitated as their carbonates. ($CaCO_3$, $BaCO_3$ and $SrCO_3$).

Table 16.23 **Tests for Barium**

Experiment	Observation	Inference
Dissolve the ppt in acetic acid, and heat gently and add potassium chromate solution and again heat	Yellow ppt appears	Ba^{2+} confirmed

Reactions Involved in the Test of Cation Ba^{2+}

$$\underset{\text{white ppt.}}{BaCO_3} + 2CH_3COOH \xrightarrow{\Delta} (CH_3COO)_2Ba + H_2O + CO_2$$

$$(CH_3COO)_2Ba + K_2CrO_4 \longrightarrow \underset{\text{yellow ppt.}}{BaCrO_4 \downarrow} + 2CH_3COOK$$

Table 16.24 **Tests for Calcium**

S.N.	Experiment	Observation	Inference
1.	Dissolve the ppt. in acetic acid ,add ammonium oxalate solution (excess) and heat.	White ppt. appears	Ca^{2+} confirmed
2.	Acidified white ppt. obtained above by adding dilute CH_3COOH and add $KMnO_4$ solution drop wise and HCl	Pink colour of $KMnO_4$ disappears	Ca^{2+} confirmed

Reactions Involved in The Test of Cation Ca^{2+}

1.

$$\underset{\text{white ppt}}{CaCO_3} + 2CH_3COOH \xrightarrow{\Delta} (CH_3COO)_2Ca + H_2O + CO_2$$

$$(CH_3COO)_2Ca + (NH_4)_2C_2O_4 \longrightarrow \underset{\text{white ppt}}{CaC_2O_4 \downarrow} + 2CH_3COONH_4$$

$$5CaC_2O_4 + \underset{\text{pink}}{2KMnO_4} + 16HCl \longrightarrow 5CaCl_2 + \underset{\text{colourless}}{2MnCl_2} + 10CO_2 + 8H_2O + 2KCl$$

Analysis of Group VI Cation

Table 16.25 **Tests for Ammonium**

Experiment	Observation	Inference
Filtrate of group V is heated with NH_4OH and Na_2HPO_4	A fine crystalline ppt on scratching the side of the test tube.	Mg^{2+} confirmed

Reactions Involve in the Test of Cation Mg^{2+}

$$MgCl_2 + \underset{\substack{\text{disodium}\\\text{hydrogen}\\\text{phosphate}}}{Na_2HPO_4} + NH_4OH \longrightarrow \underset{\substack{\text{magnesium ammonium}\\\text{phosphate (white ppt)}}}{Mg(NH_4)PO_4} + 2NaCl + H_2O$$

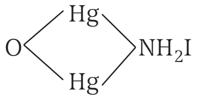
Analysis of Zero Group Cation, NH_4^+

Ammonium salts are decomposed by alkali and NH_3 is liberated which can be identified by a number of methods.

Table 16.26 **Tests for Ammonium**

S.N.	Experiment	Observation	Inference
1.	Small amount of mixture is taken in the test tube and heat it with NaOH solution.	Smell of ammonia	NH_4^+ confirmed
2.	On bringing the moisted glass rod with conc. HCl near the mouth of the test tube.	White fumes are formed	NH_4^+ confirmed
3.	Take small amount of salt in the test tube and add NaOH and heat. Add Nessler's reagent to the solution.	Brown ppt is obtained	NH_4^+ confirmed

Reactions Involved in the Tests of Cation NH_4^+

1. $\underset{\text{from mixture}}{NH_4Cl} + NaOH \xrightarrow{\Delta} NH_3(g) + NaCl + H_2O$
2. $NH_3(g) + HCl \longrightarrow \underset{\text{white fumes}}{NH_4Cl}$
3. $NH_3 + 3\,NaOH + \underset{\text{Nessler's reagent}}{2K_2HgI_4} \longrightarrow$ 

iodide of Millon's base (brown ppt)

$+ 4KI + 3NaI + 2H_2O$

Check Point 4

1. Chromyl chloride test for chlorides is not performed if mixture contains chlorates, why?
2. Both NO_2 and Br_2 are brown gas. How can they be identified if placed separately in two containers?
3. Why a salt containing lead turns black in colour, when placed for a long time in laboratory?
4. Why original solution is not prepared in conc HNO_3?
5. Hydrochloric acid contains Cl^- ions but it does not give positive chromyl chloride test, why?

   Hint Because in the presence of water, chromic acid is formed in place of chromyl chloride.

   $$K_2Cr_2O_7 + 2HCl + H_2O \longrightarrow 2H_2CrO_4 + 2KCl$$

16.4 Chemical Principles Involved in Some Experiments

Enthalpy of Solution of Copper Sulphate

Enthalpy of solution of a substance is defined as the change in heat enthalpy when 1 mole of a substance is dissolved in excess of water, so that further dilution does not involve any heat change. Enthalpy of solution of copper sulphate is determined by dissolving a known amount of salt in a measured volume of water in a calorimeter. The rise or fall in temperature is recorded as Δt. ΔH is calculated by using the following formula.

$$\Delta H = \frac{(W - w) \times \Delta t \times M}{m}$$

where, W = water equivalent of calorimeter
w = mass of water taken
M = molar mass of solute
m = mass of solute

$$\Delta t = t_{\text{final}} - t_{\text{initial}}$$

The dissolution of solute in a solvent is exothermic or endothermic depending upon the nature of solute. If heat is absorbed, enthalpy changes comes with **positive sign** and if heat is evolved, enthalpy changes comes with negative sign

$$\Delta H_{\text{solution}} = \Delta H_{\text{ionisation}} + \Delta H_{\text{hydration}}$$

Enthalpy of Neutralisation of Strong Acid and Strong Base

(See chapter 5 XI chemical Thermodynamics)

Preparation of Lyophilic and Lyophobic Sol

(See chapter 5 XII Surface chemistry)

Kinetic Study of Reaction of Iodide ion with Hydrogen Peroxide at Room Temperature

In acidic medium, iodide ions are oxidised to I_2 by H_2O_2. The reaction is studied by adding a known amount of sodium thiosulphate solution and a little of strach solution to the reaction mixture. The addition of thiosulphate ions $(S_2O_3^{2-})$ allows an accurate measurement of the rate at which the peroxide iodide reaction is taking place. Iodine which is liberated after the oxidation of iodide ions reacts immediately with thiosulphate ions.

(i) $H_2O_2 + 2I^- + 2H^+ \longrightarrow 2H_2O + I_2$

(ii) $I_2 + \underset{\substack{\text{thiosulphate}\\\text{colourless}}}{2S_2O_3^{2-}} \longrightarrow 2I^- + \underset{\substack{\text{dithionate}\\\text{colourless}}}{S_4O_6^{2-}}$

As long as the excess thiosulphate ions are present in the solution, no free iodine can accumulate because it is immediately turned into iodide ions which are colourless. Here thiosulphate ions are limiting reagent. So once all the thiosulphate ions are consumed, iodine starts to form in the solution, it reacts with starch to give blue colour.

Rate of reaction is compared by taking various concentration of iodide ions and time taken from the blue colour to appear.

Check Point 5

1. Lyophilic sols are more stable than lyophobic colloids why?
2. Why heat of solutions of electrolytes are sometimes positive and sometime negative?
3. Heat of neutralization of HF is much higher than that of strong acid and strong base. Explain.

WORKED **OUT** *Examples*

Example 1 *For the given aqueous reaction which of the statement(s) is false?*

$$KI + K_3[Fe(CN)_6] \xrightarrow{\text{dil. } H_2SO_4} \textit{brownish yellow solution.}$$

$$\downarrow ZnSO_4$$

$$\text{Colourless solution} \longleftarrow \textit{(White ppt. + brownish yellow filtrate)}$$

$$\downarrow$$

(a) *The first reaction is redox reaction*
(b) *White ppt. is* $Zn_3[Fe(CN)_6]_2$
(c) *Addition of filtrate to starch solution gives blue colour*
(d) *White ppt. is soluble in* NaOH *solution*

Solution (*b*)

$$K_3[\overset{+3}{Fe}(CN)_6] + \overset{-1}{KI}\text{(excess)} \longrightarrow K_4[\overset{+2}{Fe}(CN_6] + \underset{\substack{\text{brownish yellow}\\ \text{solution}}}{\overset{-1,0}{KI_3}}$$

(redox)

$$K_4[Fe(CN)_6] + ZnSO_4 \longrightarrow \underset{\text{white ppt}}{K_2Zn[Fe(CN)_6]}$$

$$\underset{\substack{\text{brownish}\\ \text{yellow}\\ \text{filtrate}}}{I_3^-} + 2Na_2S_2O_3 \longrightarrow \underset{\text{clear solution}}{Na_2S_4O_6} + 2NaI + \underset{\substack{\text{turns starch}\\ \text{solution blue}}}{I_2}$$

$K_2Zn[Fe(CN)_6]$ reacts with NaOH as

$$K_2Zn[Fe(CN)_6] + 4NaOH \longrightarrow [Zn(OH)_4]^{2-} + [Fe(CN)_6]^{4-}$$

Example 2 *An organic compound 'A' burns with a sooty flame. It is negative towards Tollen's reagent test and positive for Brady's reagent test. The compound 'A' is*

(a) *acetophenone*
(b) *acetone*
(c) *salicylic acid*
(d) *benzaldehyde*

Solution (*a*) Since, given compound '*A*' burns with flame therefore it must be aromatic compound. Again when it reacts with Brady's reagent (acidic 2, 4-dinitrophenyl hydrazine solution), it yields orange precipitate. Therefore, it must be aldehyde or ketone. But ketone does not perform Tollen's reagent test therefore, it must be a ketone. Hence, '*A*' is acetophenone.

Example 3 *A white crystalline salt 'A' reacts with dilute* HCl *to liberate a suffocating gas 'B' and also forms a yellow precipitate. The gas 'B' turns potassium dichromate acidified with dilute* H_2SO_4 *to a green coloured solution 'C'. A, B and C are respectively*

(a) Na_2SO_3, SO_2, $Cr_2(SO_4)_3$ (b) Na_2S, SO_2, $Cr_2(SO_4)_3$
(c) $Na_2S_2O_3$, SO_2, $Cr_2(SO_4)_3$ (d) Na_2SO_4, SO_2, $Cr_2(SO_4)_3$

Solution (*c*) Gas '*B*' turns the colour of acidified $K_2Cr_2O_7$ green thus it is SO_2 and SO_2 is obtained along with yellow precipitate of S when thiosulphate is treated with dilute acids. Thus, *A* is $Na_2S_2O_3$, *B* is SO_2 and *C* is $Cr_2(SO_4)_3$.

Example 4 $CuSO_4$ *decolourises on addition of* KCN, *the product is*

(a) $[Cu(CN)_4]^{2-}$ (*b*) $[Cu(CN)_4]^{3-}$
(c) $Cu(CN)_2$ (*d*) CuCN

Solution (*b*) $CuSO_4$ decolourises on addition of KCN. The product is CuCN along with $(CN)_2$ but in excess of KCN, colourless potassium tetracyanocuperate (I). is obtained.

$$CuSO_4 + 2KCN \longrightarrow Cu(CN)_2 + [K_2SO_4] \times 2$$

$$\underset{\text{unstable}}{2Cu(CN)_2} \rightleftharpoons 2CuCN + \underset{\text{cyanogen}}{(CN)_2}$$

$$CuCN + 3KCN \rightleftharpoons \underset{\text{colourless}}{K_3[Cu(CN)_4]}$$

Example 5 *The mass of potassium dichromate crystals required to oxidise 750* cm^3 *of 0.6 M Mohr's salt solution is (Given, molar mass; potassium dichromate = 294, Mohr's salt = 392)*

(a) 0.49 g (*b*) 0.45 g (*c*) 22.05 g (*d*) 2.2 g

Solution (*c*)

$$\underset{\text{from Mohr's salt}}{Fe^{2+}} \longrightarrow Fe^{3+} + e^-] \times 6$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

$$\text{Millimoles of } Fe^{2+} = 750 \times 0.6 = 450$$

$$\text{Moles of } Fe^{2+} = \frac{450}{1000} = 0.450 = 0.450 \text{ mol}$$

$$6 \text{ mol } Fe^{2+} \equiv 1 \text{ mol } Cr_2O_7^{2-}$$

$$\therefore \quad 0.450 \text{ mol } Fe^{2+} = \frac{0.450}{6} = 0.075 \text{ mol } Cr_2O_7^{2-}$$

$$= 0.075 \times 294 \text{ g} = 22.05 \text{ g}$$

Start **Practice** *for* JEE Main

Round I (Topically Divided Problems)

Qualitative Organic Analysis

1. In organic analysis, the reagent 2, 4-dinitrophenyl hydrazine is used for the detection of which of the following functional groups?

(a) Alcohol (b) Acid

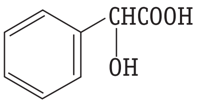
(c) Aldehyde (d) Amines

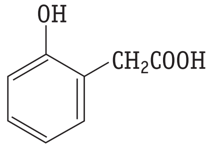
2. An organic compound gave positive iodoform and Tollen's tests. The organic compound is

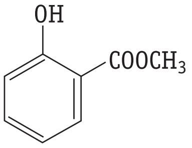
(a) CH_3CH_2OH (b) $CH_3CH_2CH_2CHO$

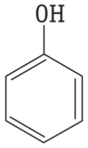
(c) CH_3CHO (d) CH_3COCH_3

3. A compound liberates CO_2 with $NaHCO_3$ and also gives colour with neutral $FeCl_3$ solution. The compound can be

(a) 

(b) 

(c) 

(d) 

Chemistry Involved in the Preparation of Compounds

4. During the preparation of acetanilide from aniline a small amount of zinc is added to the reaction mixture because

(a) zinc induces the precipitation

(b) zinc prevents the reduction of aniline during the reaction

(c) zinc reduces the coloured impurities in the aniline and also prevents its oxidation during the reaction

(d) zinc forms a white crystalline complex with aniline

5. In the preparation of *p*-nitro acetanilide from aniline, nitration is not done by nitrating mixture (a mixture of conc H_2SO_4 and conc HNO_3) because

(a)on nitration it gives *o*-nitroacetanilide

(b) it gives a mixture of *o*-and *p*-nitroaniline

(c) —NH_2 group gets oxidised

(d) it forms a mixture of *o*-and *p*-nitro acetanilide

6. Which of the following compounds cannot used in preparation of iodoform?

(a) CH_3CHO (b) CH_3COCH_3

(c) HCHO (d) 2-propanol

7. Which of the following statement is wrong about aniline yellow?

(a) It is carcinogenic

(b) It is also called *p*-aminoazobenzene

(c) It is an acid dye

(d) It is also called 4-phenylazoaniline

8. Which of the following substances is not used in the preparation of Mohr's salt?

(a) Ferrous sulphate (b) Ammonium sulphate

(c) Dil. sulphuric acid (d) All are used

Chemistry Involved in the Titrimetric Exercises

9. Phenolphthalein is an indicator for acid-base titration, it exists as

(a) benzenoid form in acid and quinonoid form in basic solution

(b) quinonoid form in acid and benzenoid form in basic solution

(c) quinonoid form in both

(d) benzenoid form in both

10. In the titration of oxalic acid *vs* potassium permanganate, potassium permanganate acts as

(a) external indicator (b) self indicator

(c) reductant (d) Both (b) and (c)

11. In the reaction of $KMnO_4$ with an oxalate in acidic medium, MnO_4^- is reduced to Mn^{2+} and $C_2O_4^{2-}$ is oxidised to CO_2 · Hence, 50 mL of 0.04 M $KMnO_4$ is equivalent to

(a) 100 mL of 0.1 M $H_2C_2O_4$
(b) 50 mL of 0.2 M $H_2C_2O_4$
(c) 50 mL of 0.1 M $H_2C_2O_4$
(d) 25 mL of 0.1 $H_2C_2O_4$

12. For preparing 250 mL of N/20 solution of Mohr's salt, the amount of Mohr's salt needed is

(a) 9.8 g (b) 4.9 g (c) 19.6 g (d) 3.2 g

13. 0.5 g mixture of $K_2Cr_2O_7$ and $KMnO_4$ was treated with excess of KI in acidic medium. I_2 liberated required 100 cm^3 of 0.15 N $Na_2S_2O_3$ solution for titration. The percentage amount of $K_2Cr_2O_7$ in the mixture is

(a) 85.36% (b) 14.64%
(c) 58.63% (d) 26.14%

14. Which of the following will oxidise 126 g of oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) in acidic medium?

(a) 1/3 mole of $K_2Cr_2O_7$ (b) 2 mole of $K_2Cr_2O_7$
(c) 1/3 mole of $KMnO_4$ (d) 5/2 mole of $KMnO_4$

15. The titration of Mohr's salt *vs* $KMnO_4$ is an example of redox titration. In this titration, $KMnO_4$ oxidises only ferrous salt to the ferric salt (no effect on other ions) but we can not use ferrous sulphate in place of Mohr's salt because

(a) it is less stable than Mohr's salt
(b) in air it is oxidised to ferric sulphate
(c) in air it loses water of crystallisation
(d) All of the above

16. 3.92 g of ferrous ammonium sulphate (Mohr's salt) react completely with 50 mL $\frac{N}{10}$ $KMnO_4$ solution. The percentage purity of the sample is

(a) 50 (b) 78.4 (c) 80 (d) 39.2

17. Which of the following statements is not true?

(a) An acidified solution of $K_2Cr_2O_7$ liberates iodine from iodides
(b) In acidic solution, dichromate ions are converted to chromate ions
(c) $(NH_4)_2Cr_2O_7$ on heating undergo exothermic decomposition to give Cr_2O_3
(d) Potassium dichromate is used as a titrant for estimation of Fe^{2+} ions

18. An aqueous solution of 6.3 g oxalic acid dihydrate is made up to 250 mL. The volume of 0.1 N NaOH required to completely neutralize 10 mL of this solution is

(a) 40 mL (b) 20 mL (c) 10 mL (d) 4 mL

Chemical Principles Involved in the Qualitative Salt Analysis

19. Which statement is correct?

(a) Fe^{2+} gives brown colour with ammonium thiocyanate
(b) Fe^{2+} gives blue precipitate with potassium ferricyanide
(c) Fe^{3+} gives brown colour with potassium ferricyanide
(d) Fe^{3+} gives red colour with potassium ferrocyanide

20. An aqueous solution of colourless metal sulphate *M* gives a white precipitate with NH_4OH. This was soluble in excess of NH_4OH. On passing H_2S through this solution a white ppt is formed. The metal *M* in the salt is

(a) Ca (b) Ba (c) Al (d) Zn

21. A white sodium salt dissolves readily in water to give a solution which is neutral to litmus. When silver nitrate solution is added to the solution, a white precipitate is obtained which does not dissolve in dill HNO_3. The anion could be

(a) CO_3^{2-} (b) Cl^- (c) SO_4^{2-} (d) S^{2-}

22. A laboratory reagent imparts green colour to the flame. On heating with solid $K_2Cr_2O_7$ and conc H_2SO_4, it evolves a orange red gas. Identify the reagent.

(a) $CaCl_2$ (b) $BaCl_2$
(c) $CuCl_2$ (d) None of these

23. Which reagent can be used to identify nickel ion?

(a) Resorcinol (b) Dimethyl glyoxime
(c) Diphenyl benzidine (d) Potassium ferrocyanide

24. Which of the following reagents can be used to distinguish between sodium carbonate and sodium sulphite?

(a) Lime water
(b) Baryta water
(c) Acidified $K_2Cr_2O_7$ solution
(d) H_2SO_4 solution

25. The gas liberated on treating a mixture of two salts with dil H_2SO_4 turns lime water milky and turbidity disappears with the passage of excess of gas. The aqueous solution of mixture gives white crystalline ppt with NaCl solution. The filtrate gives a black precipitate, when H_2S is passed into it. The aqueous solution of mixture on heating gives reddish brown gas and when treated with ammonium hydroxide and excess of disodium hydrogen phosphate gives a white crystalline precipitate. The mixture contains

(a) CO_3^{2-}, Pb^{2+}, NO_3^{2-}, Mg^{2+} (b) CO_3^{2-}, Pb^{2+}, NO_3^{2-}, Ca^{2+}
(c) CO_3^{2-}, Pb^{2+}, Cl^-, Mg^{2+} (d) CO_3^{2-}, Pb^{2+}, Cl^-, Ca^{2+}

Chemical Principles Involved in Some Experiments

26. Four samples of acids and bases are taken for an experiment

(1) 100 mL of 1 M NaOH and 100 mL of 1 M HCl

(2) 100 mL of 2 M KOH and 100 mL of 1 M H_2SO_4

(3) 100 mL of 1 M CH_3COOH and 100 mL of 1 M NaOH

(4) 100 mL of 0.5 M KOH and 100 mL of 0.5 M HNO_3

Now for each sample enthalpy of neutralisation is calculated. Now the result shows that

(a) enthalpy of neutralisation calculated in each case is found same

(b) in case (1) and (4), the value of enthalpy of neutralisation is same

(c) in case (1) and (2) and (4) the value of enthalpy calculated is same

(d) the value of enthalpy calculated is different for each sample

27. During the preparation of egg albumin sol (lyophilic sol), water taken should be cold because

(a) in cold water precipitation of egg albumin takes place which helps in preparation of sol

(b) in cold water precipitation of egg albumin does not take place

(c) in cold water egg albumin mix well whereas yolk get separated

(d) cold water is purest form of water

28. In the kinetic study of reaction of iodide ion with hydrogen peroxide, a known volume of sodium thiosulphate solution is added to

(a) oxidise iodide ion to iodine

(b) reduce iodine to iodide ion

(c) form a soluble blue complex

(d) induce the reaction rate

29. Which of the following pairs has heat of neutralisation equal to 13.7 kcals?

(a) HCl, NH_4OH (b) HNO_3, KOH

(c) NaOH, CH_3COOH (d) H_2SO_4, NH_4OH

30. One desires to prepare a positively charged sol of silver iodide. This can be achieved by

(a) adding a little $AgNO_3$ solution to KI solution in slight excess

(b) adding a little KI solution to $AgNO_3$ solution in slight excess

(c) mixing equal volumes of equimolar solutions of $AgNO_3$ and KI

(d) None of the above

31. Leveling bulb is used during experiment to study kinetics of the dissociation of hydrogen peroxide to ensure

(a) uniform pressure difference between the room and the gases in the system

(b) pressure within the reaction vessel is same as that in the room

(c) same temperature as that of room

(d) None of the above

32. The enthalpy of neutralisation of weak acid in 1 M solution with a strong base is -56.1 kJ mol^{-1}. If the enthalpy of ionisation of acid is 1.5 kJ mol^{-1} and enthalpy of neutralisation of the strong acid with a strong base is -57.3 kJ eq^{-1}, what is the percentage ionisation of the weak acid in molar solution (assume the acid is monobasic)?

(a) 25 (b) 20 (c) 15 (d) 10

33. In case of weak acid and strong base, the heat of neutralisation is less than 13.7 kcal because some part of heat is utilized in

(a) dissociation of base

(b) association of base

(c) dissociation of acid

(d) association of acid

34. The methods used for the preparation of lyophilic and lyophobic sols are respectively

(a) oxidation and reduction

(b) dissolution in water and peptisation

(c) peptisation and oxidation

(d) All of the above

Round II (Mixed Bag)

Only One Correct Option

1. How H_2S is liberated in laboratory?

(a) $FeSO_4 + H_2SO_4$

(b) FeS + dil H_2SO_4

(c) FeS + conc. H_2SO_4

(d) Elementary H_2 + elementary S

2. On addition of conc. H_2SO_4 to a chloride salt, colourless fumes are evolved but in case of iodide salt, violet fumes come out. This is because **[NCERT Exemplar]**

(a) H_2SO_4 reduces HI to I_2

(b) HI is of violet colour

(c) HI gets oxidised to I_2

(d) HI changes to HIO_3

3. A brown ring is formed in the ring tests for NO_3^- ion. It is due to the formation of **[NCERT Exemplar]**

(a) $[Fe(H_2O)_5(NO)]^{2+}$ (b) $FeSO_4 \cdot NO_2$

(c) $[Fe(H_2O)_4(NO_2)]^{2+}$ (d) $FeSO_4 \cdot HNO_3$

4. In qualitative analysis when H_2S is passed through an aqueous solution of salt acidified with dilute HCl, a black ppt. is obtained. On boiling the precipitate with dil. HNO_3, it forms a solution of blue colour. Addition of excess of aq. solution of NH_3 to this solution gives **[NCERT Exemplar]**

(a) deep blue ppt. of $Cu(OH)_2$

(b) deep blue solution of $[Cu(NH_3)_4]^{2+}$

(c) deep blue solution of $Cu(NO_3)_2$

(d) deep blue solution of $Cu(OH)_2 \cdot Cu(NO_3)_2$

5. When $KMnO_4$ solution is added to oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after sometime because **[NCERT Exemplar]**

(a) CO_2 is formed as the products

(b) reaction is exothermic

(c) MnO_4^- catalyses the reaction

(d) Mn^{2+} acts as auto catalyst

6. Why is HCl not used to make the medium acidic in oxidation reaction of $KMnO_4$ in acidic medium? **[NCERT Exemplar]**

(a) Both HCl and $KMnO_4$ act as oxidising agent

(b) $KMnO_4$ oxidises HCl into Cl_2 which is also an oxidising agent

(c) $KMnO_4$ is a weaker oxidising agent than HCl

(d) $KMnO_4$ acts as a reducing agent in the presence of HCl

7. The reagent which does not react with both, acetone and benzaldehyde is **[NCERT Exemplar]**

(a) sodium hydrogen sulphite

(b) phenyl hydrazine

(c) Fehling's solution

(d) Grignard reagent

8. Which of the following will give blood red colour with $FeCl_3$ in sodium extract?

(a) NH_2CONH_2 (b) NH_2CSNH_2

(c) $C_2H_5NHNH_2$ (d) $CH_3C \equiv N$

9. Sodium nitroprusside, $Na_2[Fe(CN)_5NO]$ is used as a reagent for detection of —and the compound formed is

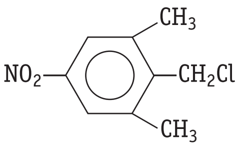
(a) sulphur, $Na_4[Fe(CN)_5NOS]$

(b) nitrogen, $Na_4[Fe(CN)_6]$

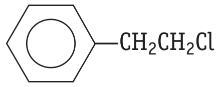
(c) sulphur, $Na_2[Fe(CN_4)NOS]$

(d) sulphur, $Na_2[Fe(CN)NOS]$

10. Detection of chlorine is possible without preparing sodium extract in

(a) 

(b) $CHCl_3$

(c) 

(d) $CH_2{=}CH{-}CH_2Cl$

11. In Nessler's reagent for the detection of ammonia the active species is

(a) Hg_2Cl_2 (b) Mg^{2+} (c) Hg_2I_2 (d) HgI_4^{2-}

12. Nessler's reagent is used to detect

(a) CrO_4^{2-} (b) PO_4^{3-} (c) MnO_4^- (d) NH_4^+

13. 100 mL of HCl + 35 mL of NaOH, colour of methyl orange in the solution will be

(a) red

(b) yellow

(c) can't be predicted

(d) methyl orange is not suitable indicator.

14. Titration of 0.1467 g of primary standard $Na_2C_2O_4$ required 28.85 mL of $KMnO_4$ solution. Calculate the molar concentration of $KMnO_4$ solution.

(a) 0.01518 M (b) 0.001518 M

(c) 0.15180 M (d) 1.5180 M

15. Volume of 0.02 M MnO_4^- solution required to oxidise 40.0 mL of 0.1 M Fe^{2+} solution is

(a) 200 mL (b) 100 mL (c) 40 mL (d) 20 mL

More than One Correct Option

16. 1 g equivalent of a substance is the weight of that amount of a substance which is equivalent to

(a) 0.25 mol O_2 (b) 8 g O_2

(c) 16 g O_2 (d) 0.50 mol O_2

17. Phenol can be distinguished from ethanol by the reactions with **[NCERT Exemplar]**

(a) Br_2/water (b) Na

(c) neutral $FeCl_3$ (d) All of these

18. $K_4[Fe(CN)_6]$ can be used to test

(a) Fe^{3+} (b) Zn^{2+}

(c) Cd^{2+} (d) Cr^{3+}

19. Compound '*A*' reacts with $CHCl_3$ and KOH gives offensive smelling compound. Compound '*A*' can be

(a) primary aliphatic amine

(b) primary aromatic amine

(c) secondary amine

(d) tertiary amine

20. Which of the following compounds may give blood red colouration while performing Lassaigne's test for nitrogen

(a) $(NH_2)_2C=O$

(b) $(NH_2)_2C=S$

(c) p—$NH_2C_6H_4SO_3H$

(d) $C_6H_5SO_3H$

Assertion and Reason

Directions (Q. Nos. 21 to 25) *Each of these questions contains two statements. Statement I (Assertion) and statement II (Reason). Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c), (d) given below* :

(a) Statement I is true, statement II is true ; statement II is a correct explanation for statement I

(b) Statement I is true, statement II is true, statement II is not a correct explanation for statement I.

(c) Statement I is true ; statement II is false

(d) Statement I is false ; statement II is true

21. Statement I $PbCl_2$ and Hg_2Cl_2 precipitates can be separated by hot water.

Statement II Hg_2Cl_2 is blackened by aq. NH_3.

22. Statement I Sodium carbonate extract of a salt containing sulphide gives a violet colour with appropriate reagent.

Statement II The appropriate reagent sodium nitroprusside gives violet colour due to the formation of sodium thionitroprusside.

23. Statement I Aldehydes and ketones both react with Tollen's reagent to form silver mirror.

Statement II Both aldehydes and ketones contain a carbonyl group. [**NCERT** Exemplar]

24. Statement I Coloured cations can be identified by borax bead test.

Statement II Transparent bead $(NaBO_2 + B_2O_3)$ forms coloured bead with coloured cation.

25. Statement I Phenolic compounds give characteristic colour with neutral $FeCl_3$ ·

Statement II It is the property of all the enolic compounds.

Comprehension Based Questions

Directions (Q. Nos. 26 to 28) p-amino-N, N-dimethyl aniline is added to a strongly acidic solution of X. The resulting solution is treated with a few drops of aqueous solution of Y to yield blue colouration due to the formation of an intense blue precipitate. The precipitate dissolves in excess of reagent. Similarly, treatment of the solution of Y with the solution of potassium hexacyanoferrate (III) leads to a brown colouration due to the formation of Z.

26. The compound X is

(a) $NaNO_3$ (b) $NaCl$

(c) Na_2SO_4 (d) Na_2S

27. The compound Y is

(a) $MgCl_2$ (b) $FeCl_2$

(c) $FeCl_3$ (d) $ZnCl_2$

28. The compound Z is

(a) $Mg_2[Fe(CN)_6]$ (b) $Fe[Fe(CN)_6]$

(c) $Fe_4[Fe(CN)_6]_3$ (d) $K_2Zn_3[Fe(CN)_6]_2$

Directions (Q. Nos. 29 to 31) Both $Cr_2O_7^-(aq)$ and $MnO_4^-(aq)$ can be used to titrate $Fe^{2+}(aq)$. You have been provided with 0.1 M solution of each and volumetric estimation is carried in acidic medium. Suppose for the given volume of Fe^{2+} solution,

V_1 = volume of MnO_4^-, V_2 = volume of $Cr_2O_7^{2-}$ required in the oxidation to Fe^{3+}

29. Select the correct alternate ; Fe^{2+} is equivalent to

(a) $\frac{1}{5}$ mol of MnO_4^-

(b) $\frac{1}{6}$ mol of $Cr_2O_7^{2-}$

(c) 1 equivalent each of MnO_4^- and $Cr_2O_7^{2-}$

(d) All of the above

30. Select the correct relation between V_1 and V_2 , if Fe^{2+} is 1M.

(a) $V_1 = V_2$

(b) $V_1 > V_2$

(c) $V_1 < V_2$

(d) nothing can be predicted

31. 24.50 mL of 0.1 M $Cr_2O_7^{2-}$ is required in the oxidation of given volume of 0.1 M Fe^{2+}. 0.1 M MnO_4^- required will be

(a) 29.40 mL (b) 24.50 mL

(c) 20.42 mL (d) 20.10 mL

Previous Years' Questions

32. The compound formed in the positive test for nitrogen with the Lassaigne solution of an organic compound is [AIEEE 2004]

(a) $Fe_4[Fe(CN)_6]_3$ (b) $Na_3[Fe(CN)_6]$
(c) $Fe(CN)_3$ (d) $Na_4[Fe(CN)_5NOS]$

33. If Fe^{3+} and Cr^{3+} both are present in group III of qualitative analysis, then distinction can be made by [AIEEE 2002]

(a) addition of NH_4OH in the presence of NH_4Cl when only $Fe(OH)_3$ is precipitated
(b) addition of NH_4OH in the presence of NH_4Cl when $Cr(OH)_3$ and $Fe(OH)_3$ both are precipitated and on adding Br_2 water and NaOH, $Cr(OH)_3$ dissolves
(c) precipitate of $Cr(OH)_3$ and $Fe(OH)_3$ as obtained in (b) are treated with conc HCl when only $Fe(OH)_3$ dissolves
(d) Both (b) and (c)

Answers

Round I

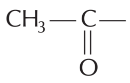
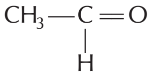
1. (c)	**2.** (c)	**3.** (b)	**4.** (c)	**5.** (c)	**6.** (c)	**7.** (c)	**8.** (d)	**9.** (a)	**10.** (b)
11. (c)	**12.** (b)	**13.** (b)	**14.** (a)	**15.** (d)	**16.** (a)	**17.** (b)	**18.** (a)	**19.** (b)	**20.** (d)
21. (b)	**22.** (b)	**23.** (b)	**24.** (c)	**25.** (a)	**26.** (c)	**27.** (b)	**28.** (b)	**29.** (b)	**30.** (b)
31. (b)	**32.** (b)	**33.** (c)	**34.** (b)						

Round II

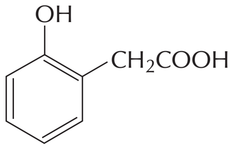
1. (b)	**2.** (c)	**3.** (a)	**4.** (b)	**5.** (d)	**6.** (b)	**7.** (c)	**8.** (b)	**9.** (a)	**10.** (d)
11. (d)	**12.** (d)	**13.** (a)	**14.** (a)	**15.** (c)	**16.** (a,b)	**17.** (a,c)	**18.** (a,b,c)	**19.** (a,b)	**20.** (b,c)
21. (b)	**22.** (a)	**23.** (d)	**24.** (a)	**25.** (a)	**26.** (d)	**27.** (c)	**28.** (b)	**29.** (d)	**30.** (b)
31. (a)	**32.** (a)	**33.** (d)							

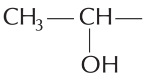
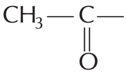
the Guidance

Round I

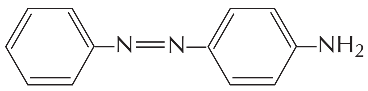
2. The compound which contains —CHO group, gives positive Tollen's test and the compound with  $CH_3-\underset{\underset{O}{\|}}{C}-$ group gives positive iodoform test. Thus, the structure of the compound should be  $CH_3-\underset{\underset{H}{|}}{C}=O$

3. The compound liberates CO_2 with $NaHCO_3$, so it contains —COOH group and it also gives colour with neutral $FeCl_3$ solution, so it also contains a —OH group directly attached to the benzene ring (*i.e*, phenol). Hence, the structure of the compound is



6. Formaldehyde cannot produce iodoform, as only those compound which contains either  $CH_3-\underset{\underset{OH}{|}}{CH}-$ group or  $CH_3-\underset{\underset{O}{\|}}{C}-$ group on reaction with iodine and sodium hydroxide (alkali) yield iodoform.

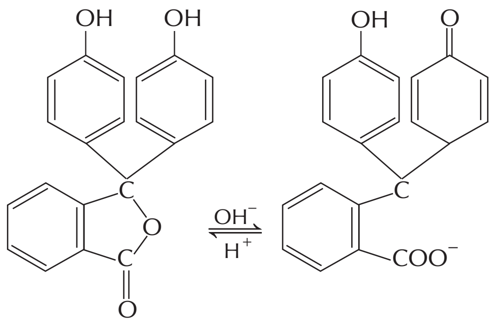
7.



aniline yellow
(*p*-amino azobenzene or 4-phenyl azoaniline)

It is a carcinogenic compound and a basic dye.

9. Phenolphthalein is colourless in acid solution (benzenoid form) and pink in alkali (basic) solution (quinonoid form).



colourless (acid medium)
benzenoid form

red (alkaline medium)
quinonoid form

10. In the titation of oxalic acid *vs* $KMnO_4$, $KMnO_4$ acts as a oxidant as well as a self indicator.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

$$5\begin{vmatrix} COOH \\ COOH \end{vmatrix} + 5[O] \longrightarrow 5H_2O + 10CO_2 \uparrow$$

11. Equivalent mass of $MnO_4^- = \dfrac{\text{molar mass}}{7-2} = \dfrac{\text{molar mass}}{5}$.

Equivalent mass of $C_2O_4^{2-} = \dfrac{\text{molar mass}}{2(4-3)} = \dfrac{\text{molar mass}}{2}$

Milliequivalent of $KMnO_4 = 50 \times 5 \times 0.04 = 10 =$ M eq. of $H_2C_2O_4 = 50 \times 2 \times 0.1 = 10$.

13. Let the amount of $K_2Cr_2O_7$ in the mixture be $x\ g$, then amount of $KMnO_4$ will be $(0.5 - x)g$

$$\therefore \quad \left(\frac{x}{49} + \frac{0.5 - x}{31.6}\right) = \frac{100 \times 0.15}{1000}$$

where, 49 is eq. wt. of $K_2Cr_2O_7$ and 3.16 is equivalent wt. of $KMnO_4$ on solving we get $x = 0.0732$ g percentage of

$$K_2Cr_2O_7 = \frac{0.0732 \times 100}{0.5} = 14.64\%$$

14. 126 g of oxalic acid $= 1$ mol of $H_2C_2O_4$

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

1 mole of oxalate ion require $= 2/5$ mol $KMnO_4$

$$Cr_2O_7^{2-} + 3C_2O_4^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 6CO_2 + 7H_2O$$

1 mole of oxalate ion require $= 1/3$ mol $K_2Cr_2O_7$

16. Eq. of $KMnO_4$ used $= \dfrac{50 \times 1}{1000 \times 10} = 0.005$

$\therefore$ Eq. of Mohr's salt reacted $= 0.005$

$\therefore$ Weight of Mohr's salt needed $= 0.005 \times 392 = 1.96$ g

Thus, percentage purity of Mohr's salt $= \dfrac{1.96}{3.92} \times 100 = 50\%$

18. Normality of oxalic acid $= \dfrac{6.3 \times 1000}{63 \times 250} = 0.4$

$$N_1V_1 = N_2V_2$$
$$V_1 \times 0.1 = 10 \times 0.4$$
$$V_1 = 40 \text{ mL}$$

19. The blue precipitate of Fe^{2+} ions with potassium ferricyanide is due to the formation of Turnbull's blue $K\overset{II}{Fe}[\overset{III}{Fe}(CN)_6]$

$$\underset{}{Fe^{2+}} + \underset{\text{potassium ferricyanide}}{K_3[Fe(CN)_6]} \longrightarrow \underset{\text{Turnbull's blue}}{K\overset{II}{Fe}[\overset{III}{Fe}(CN)_6]} + 2K^+$$

21. NaCl is a salt of strong acid and strong base, hence on dissolution will give neutral solution. As white ppt is obtained by the addition of $AgNO_3$ to the solution of Na salt, it can be of AgCl. Futher AgCl is also insoluble in HNO_3. Hence, the anion is Cl^-.

$$NaCl + AgNO_3 \longrightarrow AgCl \downarrow HNO_3$$

22. Ba^{2+} ion imparts green colour to the falme and Cl^- ion forms chromyl chloride (which is orange red in colour) when treated with $K_2Cr_2O_7$ and conc H_2SO_4. Thus, the reagent is

$$Ba^{2+} + 2Cl^- \longrightarrow BaCl_2$$

$$2BaCl_2 + K_2Cr_2O_7 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2BaSO_4 + \underset{\substack{\text{chromyl chloride} \\ \text{(orange red gas)}}}{2CrO_2Cl_2} + 3H_2O$$

26. As in cases (1), (2) and (4), the acids and bases taken are strong and the enthalpy of neutralisation of all strong acids with strong bases is same, *i. e*, –57.3 kJ.

27. During the fromation of egg albumin sol, hot water is not used because in hot water precipitation of egg albumin takes place whereas in cold water formation of precipitate does not occur.

28. In the given experiment following reaction occurs

$$H_2O_2 + 2I^- + 2H^+ \longrightarrow 2H_2O + I_2$$

Iodine liberated in this reaction reacts with sodium thiosulphate solution and is reduced to iodide ions.

$$I_2 + \underset{\text{thiosulphate ion}}{2S_2O_3^{2-}} \xrightarrow{\text{Fast}} \underset{\text{tetrathionate ion}}{S_4O_6^{2-}} + 2I^-$$

30. $KI + AgNO_3$ (slight excess) $\longrightarrow AgI + KNO_3$

$$AgNO_3 \longrightarrow Ag^+ + NO_3^-$$

$$AgI(s) + Ag^+ \longrightarrow \underset{\text{silver iodide sol}}{[AgI]\ Ag^+}$$

31. The main purpose of using leveling bulb is to assure that pressure within the reaction vessel is same as that in the room.

32. The enthalpy of ionisation of weak acid is given by

$$\Delta H_{\text{ion(HA)}} = \Delta H_{\text{N(weak acid/strong base)}} - \Delta H_{\text{N(strong acid/strong base)}}$$
$$= -56.1 - (-57.3) = 1.2 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{(ionisation)}} = 1.5 \text{ kJ mol}^{-1}$$

Hence, percentage ionisation in 1 M solution

$$= \frac{(1.5 - 1.2)}{1.5} \times 100 = 20$$

Round II

1. $FeS + H_2SO_4(\text{dilute}) \longrightarrow FeSO_4(aq) + H_2S(g)$

2. $\underset{\text{chloride salt}}{NaCl} + H_2SO_4 \longrightarrow NaHSO_4 + \underset{\text{colourless}}{HCl\uparrow}$

$\underset{\text{iodide salt}}{NaI} + H_2SO_4 \longrightarrow NaHSO_4 + HI$

$2HI + H_2SO_4 \longrightarrow \underset{\text{violet colur}}{I_2\uparrow} + SO_2 + 2H_2O$

3. **Brown ring test**

$NO_3^- + 3Fe^{2+} + 4H^+ \longrightarrow NO + 3Fe^{3+} + 2H_2O$

$[Fe(H_2O)_6]^{2+} + NO \longrightarrow \underset{\text{brown complex}}{[Fe(H_2O)_5(NO)]^{2+}} + H_2O$

In the ring test of NO_3^- ion, Fe^{2+} ion reduces nitrate ion to nitric oxide, which combines with Fe^{2+} (*aq*) ion to form brown complex.

4. On passing H_2S gas in the aqueous solution of salt in the presence of dilute. HCl, black ppt of CuS is formed.

$3CuS + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 3S + 4H_2O$

$Cu^{2+} + 4NH_4OH \longrightarrow \underset{\text{deep blue complex}}{[Cu(NH_3)_4]^{2+}} + 4H_2O$

5. $5C_2O_4^{2-} + \underset{\text{purple}}{2MnO_4^-} + 16H^+ \longrightarrow \underset{\substack{\text{colourless}\\ \text{(auto catalyst)}}}{2Mn^{2+}} + 8H_2O + 10CO_2$

6. Because $KMnO_4$ oxidises HCl into Cl_2 which is also an oxidising agent.

$2Cl^- \longrightarrow Cl_2 + 2e^-] \times 5$

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$

7. Benzaldehyde does not reduce Fehling's solution (a distinction from other aldehydes). Acetone (ketone) does not give any test with Fehling's solution.

8. Compound (b) contains both N and S, therefore it will form NaSCN which reacts with $FeCl_3$ to give ferric thiocyanate which is blood red in colour.

9. $Na_2[FeCN)_5NO] + Na_2S \longrightarrow Na_4[Fe(CN)_5NOS]$ violet colour, sulphur is confirmed.

10. Silver ion can easily pull out chlorine from $CH_2{=}CH{-}CH_2{-}Cl$ because $CH_2{=}CH{-}\overset{+}{C}H_2$ is allylic carbocation which is resonance stabilized.

11. $[HgI_4]^{2-} + NH_4Cl + 4OH^- \longrightarrow NH_2HgOHgI$

12. Nessler's reagent $K_2[HgI_4]$ in alkaline medium is used to detect NH_4^+ ion.

13. When 100 mL HCl is added to 35 mL NaOH, 35 mL HCl is utilized to neutralise NaOH, while 65 mL HCl remains as such. Hence, solution becomes acidic. In acid solution, the colour of methyl orange is red due to presence of Me^+ ions as

$$\underset{\substack{\text{methyl orange}\\ \text{(yellow)}}}{MeOH} \rightleftharpoons \underset{\text{red}}{Me^+} + OH^-$$

14. $5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

Note In a reaction (redox/neutralisation) number of equivalents of different reactants are same.

$$\text{Equivalents of } C_2O_4^{2-} = \text{eq. of } MnO_4^-$$

$$\text{eq. wt. of } C_2O_4^{2-} = \frac{\text{mol . wt}}{2}$$

$\therefore$ $$\text{molarity} = 2 \times \text{normality}$$

$$\text{eq. wt of } MnO_4^- = \frac{\text{mol. wt.}}{5}$$

$$\text{Molarity} = 5 \times \text{normality}$$

$$\text{Number of equivalents of } MnO_4^- = \frac{28.85 \times 5\, M_1}{1000}$$

$$\text{Number of equivalents of } Na_2C_2O_4^- = \frac{0.1467}{67}$$

$\therefore$ $$\frac{28.85 \times 5\, M_1}{1000} - \frac{0.1467}{67}$$

$$M_1 = 0.01518\ \text{M}$$

15. $MnO_4^- + 5Fe^{2+} \longrightarrow 5Fe^{3+} + Mn^{2+}$

$M_1V_1(MnO_4^-) = 5N_1V_1(MnO_4^-)$ milliequivalent

$M_2V_2(Fe^{2+}) = 5N_2V_2(Fe^{2+})$ milliequivalent

$N_1V_1(MnO_4^-) = N_2V_2(Fe^{2+})$

$5 \times 0.02 \times V_1 = 40 \times 0.1$

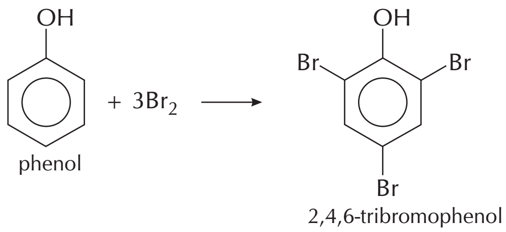
$V_1 = 40\ \text{mL}$

16. $O_2 + 4e^- \longrightarrow 2O^{2-}$

$4e^- \equiv 1\,\text{mol}\ O_2$

$0.25\ \text{mol} = 8\ \text{g}\ O_2$

17. Aqueous or alcoholic solution of phenol with excess of bromine water gives a yellowish white precipitate.



Phenols on treatment with neutral $FeCl_3$ form violet, red, blue or green coloured complexes.

18. (a) $4FeCl_3 + 3K_4[Fe(CN)_6] \longrightarrow \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3} + 12KCl$

(b) and (c) $M^{2+} + [Fe(CN)_6]^{4-} \xrightarrow[\text{of } CH_3COOH]{\text{In presence}} \underset{\text{bluish white ppt}}{M_2[Fe(CN)_6]\downarrow}$

$M = Zn^{2+}, Cd^{2+}$

19. $RNH_2 + CHCl_3 + 3KOH \longrightarrow RNC + 3KCl + 3H_2O$

(where, R may be alkyl or aryl group)

20. Only $(NH_2)_2C{=}S$ and $p-NH_2C_6H_4SO_3H$ contain both N and S which are required for observing blood red colouration in Lassaigne's test.

21. $PbCl_2$ is soluble in hot water while Hg_2Cl_2 is soluble in aquaregia.

$$Hg_2Cl_2 + 2NH_3 \longrightarrow HgNH_2Cl(\text{black}) + Hg + NH_4Cl$$

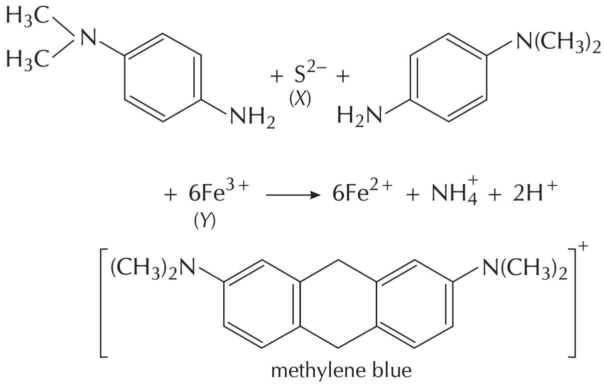
22. $Na_2S + \underset{\text{sodium nitroprusside}}{Na_2[Fe(NO)(CN)_5]} \longrightarrow \underset{\text{violet sodium thionitroprusside}}{Na_4[Fe(NOS)(CN)_5]}$

23. Tollen's reagent is not reduced by ketones.

24. Statement II is the correct explanation of statement I.

25. Statement II is the correct explanation of statement I.

26.



methylene blue

The compound X is Na_2S.

27. The compound Y is $FeCl_3$.

28. $Fe^{3+} + [Fe(CN)_6]^{3-} \longrightarrow \underset{(Z)}{Fe[Fe(CN)_6]}$ brown colouration

29. $6Fe^{2+} \longrightarrow 6Fe^{3+} + 6e^-$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

$$N(Cr_2O_7^{2-}) = 6 \times M(Cr_2O_7^{2-}) = 0.6\text{ N}$$

$$5Fe^{2+} \longrightarrow 5Fe^{3+} + 5e^-$$

$$N(MnO_4^-) = 5 \times M\,(MnO_4^-) = 0.5\text{ N}$$

$$\text{Volume of } Fe^{2+} = V \text{ mL (say)}$$

$$\text{Molarity of } Fe^{2+} = 1M \text{ (say)} = 1N$$

$$6Fe^{2+} \equiv Cr_2O_7^{2-} \text{ or } 1Fe^{2+} \equiv \frac{Cr_2O_7^{2-}}{6}$$

$$5Fe^{2+} \equiv MnO_4^- \text{ or } 1Fe^{2+} \equiv \frac{MnO_4^{2-}}{5}$$

In all cases, 1 equivalent of $x \equiv 1$ equivalent of y hence option (d) is correct.

30. $V \times 1 = 0.5 \times V_1$ (For MnO_4^-)

$$V_1 = 2V$$

$$V \times 1 = 0.6 \times V_2 \qquad (\text{For } Cr_2O_7^{2-})$$

$$V_2 = 1.33\text{ V}$$

Hence, option (b) is correct.

31. 24.5 of mL 0.1 M $Cr_2O_7^{2-} \equiv$ 24.5 mL of 0.6 N $Cr_2O_7^{2-}$

V mL of 0.1 M $MnO_4^- \equiv V$ mL of 0.5 N MnO_4^-

Thus, $24.5 \times 0.6 = V \times 0.5$

$$V = 29.4\text{ mL}$$

32. $Na + C + N \xrightarrow{\text{Fuse}} NaCN$

$$FeSO_4 + 6NaCN \longrightarrow Na_4[Fe(CN)_6] + Na_2SO_4$$

$$4FeCl_3 + 3Na_4[Fe(CN)_6] \longrightarrow Fe_4[Fe(CN)_6]_3 + 12NaCl$$

33. $2NaOH + Br_2 \longrightarrow NaOBr + NaBr + H_2O$

$NaOBr \longrightarrow NaBr + [O]$

$2Cr(OH)_3 + 4NaOH + 3[O] \longrightarrow \underset{\text{yellow solution}}{2Na_2CrO_4} + 5H_2O$

While $Fe(OH)_3$ is soluble in HCl.

Online Exam Held on 09-4-2013

JEE Main

Solved Paper 2013

Instructions

- This test consists of 30 questions.
- Each question is allotted 4 marks for correct response.
- Candidates will be awarded marks as stated above for correct response of each question. 1/4 mark will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
- There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted according as per instructions.

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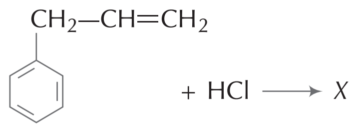
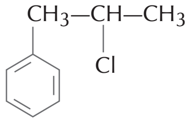
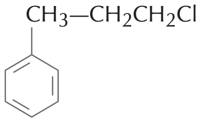
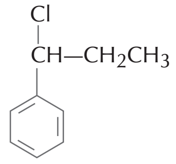
1. Given,

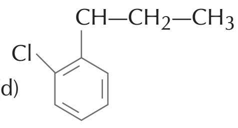


X is

(a)


(b)


(c)


(d)


2. Given, $x\,Na_2HAsO_3 + y\,NaBrO_3 + z\,HCl \longrightarrow$

$$NaBr + H_3AsO_4 + NaCl$$

The value of x, y and z in the above redox reaction are respectively.

(a) 2, 1, 2 (b) 2, 1, 3

(c) 3, 1, 6 (d) 3, 1, 4

3. The migration of dispersion medium under the influence of an electric potential is called

(a) cataphoresis (b) electroosmosis

(c) electrophoresis (d) sedimentation

4. The addition of HI in the presence of peroxide catalyst does not follow anti-Markownikoff's rule because

(a) HI is a strong reducing agent

(b) HI bond is too strong to be broken homolytically

(c) I atom combines with H atom to give back HI

(d) Iodine atom is not reactive enough to add across a double bond

5. In reaction $A + 2B \rightleftharpoons 2C + D$ initial concentration of B was 1.5 times of [A], but at equilibrium the concentrations of A and B became equal. The equilibrium constant for the reaction is

(a) 8 (b) 4 (c) 12 (d) 6

6. Trigonal bipyramidal geometry is shown by

(a) $XeOF_2$ (b) XeO_3F_2

(c) $FXeOSO_2F$ (d) $[XeF_8]^{2-}$

7. If a polythene sample contains two monodisperse fractions in the ratio 2 : 3 with degree of polymerization 100 and 200 respectively, then its weight average molecular weight will be

(a) 4900 (b) 4600 (c) 4300 (d) 5200

8. The instantaneous rate of disappearance of MnO_4^- ion in the following reaction is 4.56×10^{-3} Ms^{-1}

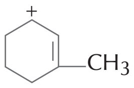
$$2MnO_4^- + 10\,I^- + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O$$

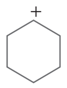
The rate of appearance I_2 is

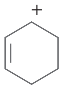
(a) 4.56×10^{-4} Ms^{-1} (b) 1.14×10^{-2} Ms^{-1}

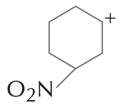
(c) 1.14×10^{-3} Ms^{-1} (d) 5.7×10^{-3} Ms^{-1}

9. Which one of the following is most stable?

(a) 

(b) 

(c) 

(d) 

10. In an atom how many orbital(s) will have the quantum numbers $n = 3$, $l = 2$ and $m_l = +2$?
(a) 5 (b) 3
(c) 1 (d) 7

11. Potassium dichromate when heated with concentrated sulphuric acid and a soluble chloride, gives brown-red vapours of
(a) CrO_3 (b) $CrCl_3$
(c) CrO_2Cl_2 (d) Cr_2O_3

12. Rate of dehydration of alcohols follows the order
(a) $2° > 1° < CH_3OH > 3°$
(b) $3° > 2° > 1° > CH_3OH$
(c) $2° > 3° > 1° > CH_3OH$
(d) $CH_3OH > 1° > 2° > 3°$

13. Given, (a) $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$

$$\Delta H°_{298\,K} = -285.9 \text{ kJmol}^{-1}$$

(b) $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(g)$;

$$\Delta H°_{298\,K} = -241.8 \text{ kJ mol}^{-1}$$

the molar enthalpy of vaporization of water will be
(a) 241.8 kJ mol^{-1} (b) 22.0 kJ mol^{-1}
(c) 44.1 kJ mol^{-1} (d) 527.7 kJ mol^{-1}

14. Calcination is the process in which
(a) removal of water takes place
(b) decomposition of carbonates takes place
(c) oxidation of sulphides takes place
(d) All of the above

15. Sodium carbonate cannot be used in place of $(NH_4)_2CO_3$ for the identification of Ca^{2+}, Ba^{2+} and Sr^{2+} ions (*in group V*) during mixture analysis because
(a) Mg^{2+} ions will be precipitated
(b) concentration of CO_3^{2-} ions is very low
(c) sodium ions will react with acid radicals
(d) Na^+ ions will interfere with the detection of Ca^{2+}, Ba^{2+}, Sr^{2+} ions

16. Which one of the following molecules is polar?
(a) XeF_4 (b) IF_5
(c) SbF_5 (d) CF_4

17. Type of isomerism which exists between $[Pd(C_6H_5)_2(SCN)_2]$ and $[Pd(C_6H_5)_2(NCS)_2]$ is
(a) linkage isomerism
(b) coordination isomerism
(c) ionisation isomerism
(d) solvate isomerism

18. In which of the following ionization processes the bond energy has increased and also the magnetic behaviour has changed from paramagnetic to diamagnetic?
(a) $NO \longrightarrow NO^+$ (b) $N_2 \longrightarrow N_2^+$
(c) $C_2 \longrightarrow C_2^+$ (d) $O_2 \longrightarrow O_2^+$

19. 12 g of a non-volatile solute dissolved in 108 g of water produces the relative lowering of vapour pressure of 0.1. The molecular mass of the solute is
(a) 80 (b) 60
(c) 20 (d) 40

20. Which of the following enzyme converts starch into maltose?
(a) Diastase (b) Maltase
(c) Zymase (d) Invertase

21. Electrode potentials ($E°$) are given below

$$Cu^+ / Cu = +0.52 \text{ V}$$
$$Fe^{3+} / Fe^{2+} = +0.77 \text{ V}$$
$$\frac{1}{2} I_2(s) / I^- = +0.54 \text{ V}$$
$$Ag^+ / Ag = +0.88 \text{ V}$$

Based on the above potentials strongest oxidizing agent will be
(a) Cu (b) Fe^{3+}
(c) Ag^+ (d) I_2

22. Aryl fluoride may be prepared from a diazonium chloride using
(a) HBF_4 / Δ (b) $HBF_4 / NaNO_2Cu, \Delta$
(c) CuF / HF (d) Cu / HF

23. An ether (A), $C_5H_{12}O$ when heated with excess of hot concentrated HI produced two alkyl halides which when treated with NaOH yielded compounds (B) and (C). Oxidation of (B) and (C) gave a propanone and an ethanoic acid respectively. The IUPAC name of the ether (A) is
(a) 2-ethoxypropane (b) ethoxypropane
(c) methoxybutane (d) 2-methoxybutane

24. Electron gain enthalpy with negative sign of fluorine is less than that of chlorine due to
(a) high ionization enthalpy of fluorine
(b) smaller size of chlorine atom
(c) smaller size of fluorine atom
(d) bigger size of 2p orbital of fluorine

25. Solid $Ba(NO_3)_2$ is gradually dissolved in a 1.0×10^{-4} M Na_2CO_3 solution. At which concentration of Ba^{2+}, precipitate of $BaCO_3$ begins to form? (K_{sp} for $BaCO_3 = 5.1 \times 10^{-9}$)

(a) 5.1×10^{-5} M (b) 7.1×10^{-5} M
(c) 4.1×10^{-5} M (d) 8.1×10^{-2} M

26. An element having an atomic radius of 0.14 nm crystallizes in an fcc unit cell. What is the length of a side of the cell?

(a) 0.56 nm (b) 0.24 nm
(c) 0.96 nm (d) 0.4 nm

27. Which of the following compounds is not expected to show 'Lassaignes' test for nitrogen?

(a) Propanenitrile
(b) Hydroxylamine hydrochloride
(c) Nitromethane
(d) Ethanamine

28. Formaldehyde can be distinguished from acetaldehyde by the use of

(a) Schiff's reagent
(b) Tollen's reagent
(c) I_2, Alkali
(d) Fehling's solution

29. By how many folds the temperature of a gas would increase when the root mean square velocity of the gas molecules in a container of fixed volume is increased by 5×10^4 cm/s to 10×10^4 cm/s?

(a) Two (b) Three
(c) Six (d) Four

30. The element with which of the following outer electron configuration may exhibit the largest number of oxidation states in its compounds

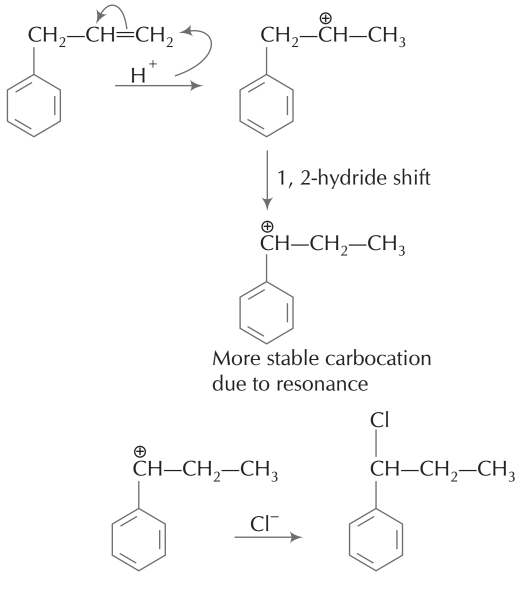
(a) $3d^5 4s^2$ (b) $3d^8 4s^2$
(c) $3d^7 4s^2$ (d) $3d^6 4s^2$

Answers

1. (c)	**2.** (c)	**3.** (b)	**4.** (c)	**5.** (b)	**6.** (b)	**7.** (a)	**8.** (b)	**9.** (a)	**10.** (c)
11. (c)	**12.** (b)	**13.** (c)	**14.** (b)	**15.** (a)	**16.** (b)	**17.** (a)	**18.** (a)	**19.** (c)	**20.** (a)
21. (c)	**22.** (a)	**23.** (a)	**24.** (c)	**25.** (a)	**26.** (d)	**27.** (b)	**28.** (c)	**29.** (d)	**30.** (a)

Hints and **Solutions**

1.



More stable carbocation due to resonance

2. $3Na_2HAsO_3 + NaBrO_3 + 6HCl \longrightarrow NaBr + 3H_3AsO_4 + 6NaCl$

3. Electroosmotic flow is caused by the coulomb force induced by an electric field on net mobile electric charge in a solution. When an electric field is applied to the fluid, the net charge in the electrical double layer (a layer of mobile ions forms in the region near the interface) is induced to move by the resulting coulomb force.

4. Addition of HI in the presence of peroxide catalyst does not follow anti Markownikoff's rule because iodine radicals have tendency to form I_2 molecule.

$$I^\bullet + I^\bullet \longrightarrow I_2$$

5. Let the degree of dissociation = x

	A	$+$	$2B$	$\rightleftharpoons$	$2C$	$+$	D
Initial concentration	1		1.5		0		0
At equilibrium	$(1-x)$		$(1.5-2x)$		$2x$		x

Given, $(1-x) = (1.5 - 2x)$

$$1 = 1.5 - 2x + x$$
$$1 = 1.5 - x$$
$$x = 1.5 - 1 = 0.5$$

Equilibrium constant for the reaction

$$K_C = \frac{[C]^2\,[D]}{[A]\,[B]^2} = \frac{(2x)^2\,(x)}{(1-x)\,(1.5-2x)^2}$$

$\because$ $x = 0.5$

$$K_C = \frac{(2\times 0.5)^2\,(0.5)}{(1-0.5)\,(1.5-2\times 0.5)^2}$$

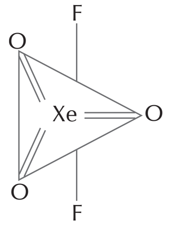
$$= \frac{(1)\times(0.5)}{(0.5)\,(0.5)^2} = \frac{0.5}{0.5\times 0.25} = \frac{0.5}{0.125} = 4$$

6. Trigonal bipyramidal geometry is shown by XeO_3F_2. Hybridization on Xe atom,

$$H = \frac{1}{2}(V + M - C + A) = \frac{1}{2}(8 + 2 - 0 + 0)$$

$$= \frac{10}{2} = 5 = sp^3d$$

Trigonal bipyramidal geometry.



7. Degree of polymerisation $= \dfrac{\overline{M}_n}{M_o}$

so $\overline{M}_w = 4900$

where, $\overline{M}_n$ = number average molecular weight

M_o = molecular weight of monomer

and $\overline{M}_w = \overline{M}_n$ for monodispersed sample

8. Rate of reaction $= -\dfrac{1}{2}[MnO_4] = \dfrac{1}{5}[I_2]$

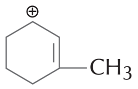
$\therefore$ Given, Rate of disappearance of MnO_4^-

$$= \frac{d\,[MnO_4^-]}{dt} = 4.56\times 10^{-3}$$

$\because$ Rate of appearance of $I_2 = \dfrac{5}{2}\times 4.56\times 10^{-3}$

$$= 11.4\times 10^{-3}$$

$$= 1.14\times 10^{-2}\ Ms^{-1}$$

9. Due to the presence of electron releasing group —CH_3 and resonance effect  is most stable.

10. Quantum numbers $n = 3, l = 2, m = +2$ represents only one orbital.

11. $$K_2Cr_2O_7 + 4NaCl + 3H_2SO_4 \xrightarrow{\Delta} \underset{\substack{\text{chromyl chloride}\\ \text{(red vapours)}}}{2CrO_2Cl_2} + K_2SO_4 + 2Na_2SO_4 + 3H_2O$$

12. Dehydration of alcohols takes place according to Saytzeff rule. In acid catalysed dehydration, formation of most stable carbocation takes place.

Thus, the order of dehydration of alcohols is

$$3° > 2° > 1° > CH_3OH$$

13. Molar enthalpy of vaporization = 285.9 − 241.8

$= 44.1\,kJ\ mol^{-1}$

14. Calcination is a thermal treatment in the presence of air to ores and other solid materials to bring about a thermal decomposition, phase transition or removal of volatile fractions.

$$M_2CO_3 \xrightarrow{\Delta} M_2O + CO_2$$

15. In fifth group, $(NH_4)_2CO_3$ is used in the presence of NH_4Cl. In presence of NH_4Cl dissociation of $(NH_4)_2CO_3$ decreases and due to low concentration of CO_3^{2-} ions only V group radical are precipitated out. If Na_2CO_3 is used, concentration of CO_3^{2-} ions will increase and Mg^{2+} ions will also be precipitated.

16. Only IF_5 is polar because of its unsymmetrical structure. Rest of the molecules have zero dipole moment.

17. Given compound shows linkage isomerism.

18. (a) $NO\,(7+8=15) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \pi^* 2p_x^1 \approx \pi 2p_y^0$

Bond order $= \dfrac{10-5}{2} = 2.5$

(Because of the presence of one unpaired electron, it is paramagnetic.

$NO^+\,(7+8-1=14) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2$

$$BO = \frac{10-4}{2} = 3$$

(it is diamagnetic as have no unpaired electron)

Bond energy $\propto$ BO

So $NO^+ > NO$ (Bond energy)

(b) $N_2(14)$, BO = 3 and diamagnetic

$N_2^+(13)$, BO $= \dfrac{9-4}{2} = 2.5$ and paramagnetic

(c) $C_2(12)$, BO $= \dfrac{8-4}{2} = 2$, diamagnetic

$C_2^+(6+6-1)$, BO $= \dfrac{7-4}{2} = 1.5$, paramagnetic

(d) $O_2(8+8=16)$, BO $= \dfrac{10-6}{2} = 2$, paramagnetic

$O_2^+\,(8+8-1=15)$, BO = 2.5, paramagnetic

Thus, only the $NO \longrightarrow NO^+$

transition involves increase in bond energy and change of magnetic character from paramagnetic to diamagnetic.

19. From Raoult's law

Relative lowering in vapour pressure

$$\Delta p = \frac{p^\circ - p}{p^\circ}$$

$$= \frac{n}{N} = \frac{w}{m} \times \frac{M}{W}$$

$w = 12$ g; $W = 108$ g, $m = ?$ $M = 18$ g, $\Delta p = 0.1$

$$\Delta p = \frac{w}{m} \times \frac{M}{W}$$

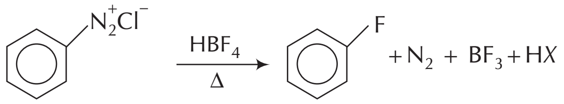
$$0.1 = \frac{12}{m} \times \frac{18}{108}$$

$$m = \frac{12 \times 18}{10.8} = 20$$

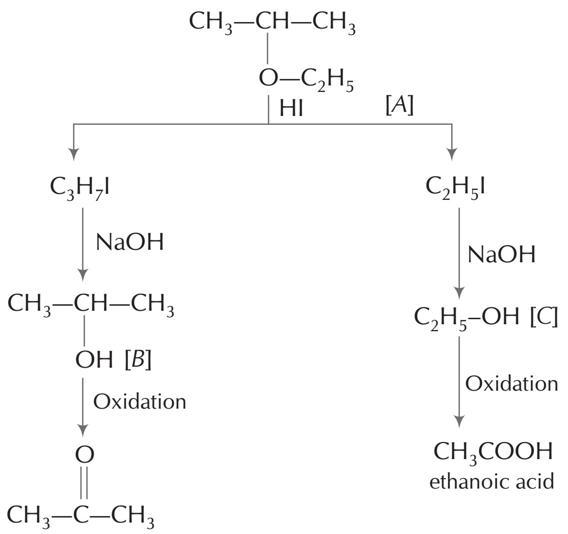
20. $\underset{\text{starch}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{Diastase}} \underset{\text{maltose}}{C_{12}H_{22}O_{11}}$

21. More positive value of electrode potential represents that Ag^+ is the strongest oxidizing agent.

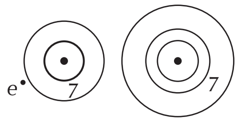
22.



23. Ether (*A*) is 2-ethoxypropane



24. Due to smaller size and high repulsive force within the outermost orbit of fluorine its electron gain enthalpy is less negative.



High repulsion

25. Concentration of CO_3^{2-} ions $= 1.0 \times 10^{-4}$ M

For precipitation $K_{sp} \le [Ba^{2+}][CO_3^{2-}]$

Given, $K_{sp} = 5.1 \times 10^{-9}$

Hence, minimum concentration of Ba^{2+} ions should be

$$= \frac{K_{sp}}{[CO_3^{2-}]} = \frac{5.1 \times 10^{-9}}{1.0 \times 10^{-4}} = 5.1 \times 10^{-5} \text{ M}$$

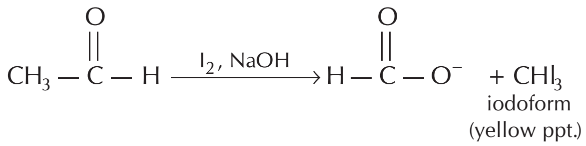
26. For fcc unit cell, $r = \frac{\sqrt{2}}{4}a$

$$0.14 = \frac{\sqrt{2}}{4}a$$

$$a = \frac{4 \times 0.14}{\sqrt{2}} = 0.396 \text{ nm} = 0.4 \text{ nm}$$

27. Hydroxylamine hydrochloride does not contain carbon, so in lassaigne's test does not result in the formation of NaCN. Hence, it does not give the test of nitrogen, for which formation of NaCN is essential.

28.



$$CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—H \xrightarrow{I_2,\ NaOH} H—\overset{\overset{\displaystyle O}{\|}}{C}—O^- + \underset{\substack{\text{iodoform}\\\text{(yellow ppt.)}}}{CHI_3}$$

Formaldehyde does not form iodoform.

29. Relation between root mean square velocity and temperature

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

$$v_{rms} \propto \sqrt{T}$$

$$T \propto v_{rms}^2$$

if *v* is doubled, *T* will be four times.

30. Due to the presence of maximum number of unpaired electrons, element having $3d^5, 4s^2$, configuration may exhibit the largest number of oxidation states in its compounds.

Online Exam Held on
22-4-2013

JEE Main

Solved Paper 2013

Instructions

- This test consists of 30 questions.
- Each question is allotted 4 marks for correct response.
- Candidates will be awarded marks as stated above for correct response of each question. 1/4 mark will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
- There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted according as per instructions.

---

1. Oxidation state of sulphur in anions SO_3^{2-}, $S_2O_4^{2-}$ and $S_2O_6^{2-}$ increases in the order

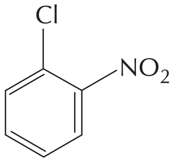
(a) $S_2O_6^{2-} < S_2O_4^{2-} < SO_3^{2-}$

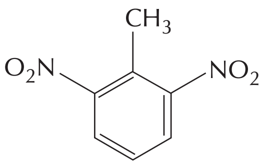
(b) $SO_3^{2-} < S_2O_4^{2-} < S_2O_6^{2-}$

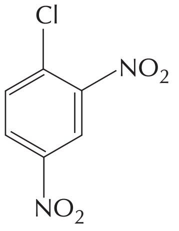
(c) $S_2O_4^{2-} < SO_3^{2-} < S_2O_6^{2-}$

(d) $S_2O_4^{2-} < S_2O_6^{2-} < SO_3^{2-}$

2. A major component of Borsch reagent is obtained by reacting hydrazine hydrate with which of the following?

(a)


(b)


(c)


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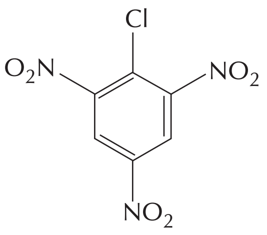


3. Given,

Reaction	Energy change (in kJ)
$Li(s) \longrightarrow Li(g)$	161
$Li(g) \longrightarrow Li^+(g)$	520
$\frac{1}{2}F_2(g) \longrightarrow F(g)$	77
$F(g) + e^- \longrightarrow F^-(g)$	(Electron gain enthalpy)
$Li^+(g) + F^-(g) \longrightarrow LiF(s)$	−1047
$Li(s) + \frac{1}{2}F_2(g) \longrightarrow LiF(s)$	−617

Bases on data provided, the value of electron gain enthalpy of fluorine would be

(a) -300 kJ mol^{-1} (b) -350 kJ mol^{-1}

(c) -328 kJ mol^{-1} (d) -228 kJ mol^{-1}

4. A molecule M associates in a given solvent according to the equation $M \rightleftharpoons (M)_n$. For a certain concentration of M, the van't Hoff factor was found to be 0.9 and the fraction of associated molecules was 0.2. The value of n is

(a) 3 (b) 5

(c) 2 (d) 4

5. The solubility order of alkali metal fluoride in water is
(a) LiF < RbF < KF < NaF
(b) RbF < KF < NaF < LiF
(c) LiF > NaF > KF > RbF
(d) LiF < NaF < KF < RbF

6. XeO_4 molecule is tetrahedral having
(a) two $p\pi - d\pi$ bonds (b) one $p\pi - d\pi$ bond
(c) four $p\pi - d\pi$ bonds (d) three $p\pi - d\pi$ bonds

7. The reaction, $X \longrightarrow Y$ is an exothermic reaction. Activation energy of the reaction for conversion of X into Y is 150 kJ mol^{-1}. Enthalpy is 135 kJ mol^{-1}. The activation energy for the reverse reaction, $Y \longrightarrow X$ will be
(a) 280 kJ mol^{-1} (b) 285 kJ mol^{-1}
(c) 270 kJ mol^{-1} (d) 15 kJ mol^{-1}

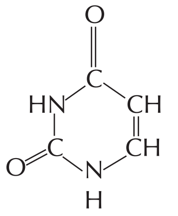
8. For which of the following compounds Kjeldahl method can be used to determine the percentage of nitrogen?
(a) Nitrobenzene (b) Pyridine
(c) Alanine (d) Diazomethane

9. Which of the following statements about aspirin is not true?
(a) It is effective in relieving pain
(b) It is a neurologically active drug
(c) It has antiblood clotting action
(d) It belongs to narcotic analgesics

10. The density of 3M solution of sodium chloride is 1.252 g mL^{-1}. The molality of the solution will be

(molar mass, NaCl = 58.5 g mol^{-1})
(a) 2.60 m (b) 2.18 m
(c) 2.79 m (d) 3.00 m

11. Which of the following structures represents thymine?

(a)


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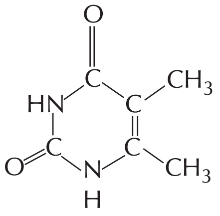

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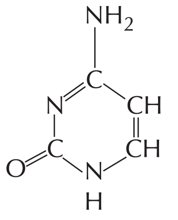
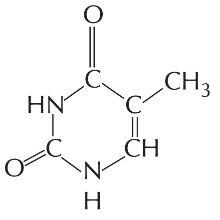


(d)


12. The polymer used for optical lenses is
(a) polypropylene
(b) polyvinyl chloride
(c) polythene
(d) polymethyl methacrylate

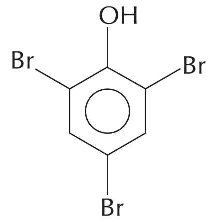
13. Which of the following is diamagnetic?
(a) $[Fe(CN)_6]^{3-}$ (b) $[Co(OX)_3]^{3-}$
(c) $[FeF_6]^{3-}$ (d) $[Co(F_6)]^{3-}$

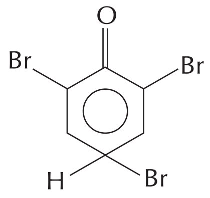
14. Bond order normally gives idea of stability of a molecular species. All the molecules *viz*. H_2, Li_2 and B_2 have the same bond order yet they are not equally stable. Their stability order is
(a) $H_2 > B_2 > Li_2$ (b) $Li_2 > H_2 > B_2$
(c) $Li_2 > B_2 > H_2$ (d) $B_2 > H_2 > Li_2$

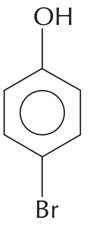
15. Which one of the following arrangements represents the correct order of solubilities of sparingly soluble salts Hg_2Cl_2, $Cr_2(SO_4)_3$, $BaSO_4$ and $CrCl_3$ respectively?
(a) $\left(\frac{K_{sp}}{108}\right)^{1/5}, \left(\frac{K_{sp}}{27}\right)^{1/4}, (K_{sp})^{1/2}, \left(\frac{K_{sp}}{4}\right)^{1/3}$
(b) $(K_{sp})^{1/2}, \left(\frac{K_{sp}}{4}\right)^{1/3}, \left(\frac{K_{sp}}{27}\right)^{1/4}, \left(\frac{K_{sp}}{108}\right)^{1/5}$
(c) $(K_{sp})^{1/2}, \left(\frac{K_{sp}}{108}\right)^{1/5}, \left(\frac{K_{sp}}{27}\right)^{1/4}, \left(\frac{K_{sp}}{4}\right)^{1/3}$
(d) $\left(\frac{K_{sp}}{4}\right)^{1/3}, \left(\frac{K_{sp}}{108}\right)^{1/5}, (K_{sp})^{1/2}, \left(\frac{K_{sp}}{27}\right)^{1/4}$

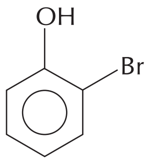
16. The wave number of the first emission line in the Balmer series of H—spectrum is (R = Rydberg constant)
(a) $\frac{5}{36}R$ (b) $\frac{9}{400}R$
(c) $\frac{7}{6}R$ (d) $\frac{3}{4}R$

17. What is the structure of the major product when phenol is treated with bromine water?

(a)


(b)


(c)


(d)


18. NaOH is a strong base. What will be pH of 5.0×10^{-2}M NaOH solution? (log 2 = 0.3)
(a) 14.00 (b) 13.70
(c) 13.00 (d) 12.70

19. Flocculation value of $BaCl_2$ is much less than that of KCl for sol *A* and flocculation value of Na_2SO_4 is much less than that of NaBr for sol *B*. The correct statement among the following is
(a) Both the sols *A* and *B* are negatively charged
(b) Sol *A* is positively charged and sol *B* is negatively charged
(c) Both the sols *A* and *B* are positively charged
(d) Sol *A* is negatively charged and sol *B* is positively charged

20. Amongst the following alcohols which would react fastest with conc. HCl and $ZnCl_2$?
(a) Pentanol (b) 2-methylbutanol
(c) 2-pentanol (d) 2-methylbutan-2-ol

21. Values of dissociation constant, K_a are given as follows

Acid	K_a
HCN	6.2×10^{-10}
HF	7.2×10^{-4}
HNO_2	4.0×10^{-4}

Correct order of increasing base strength of the base CN^-, F^- and NO_2^- will be
(a) $F^- < CN^- < NO_2^-$ (b) $NO_2^- < CN^- < F^-$
(c) $F^- < NO_2^- < CN^-$ (d) $NO_2^- < F^- < CN^-$

22. Clemmensen reduction of a ketone is carried out in the presence of
(a) $LiAlH_4$ (b) Zn–Hg with HCl
(c) glycol with KOH (d) H_2 with Pt as catalyst

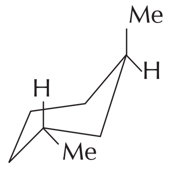
23. Which of the following statements is incorrect?
(a) Fe^{3+} ion also gives blood red colour with SCN^- ion
(b) Fe^{3+} ion gives red colour with SCN^- ion
(c) On passing H_2S into Na_2ZnO_2 solution, a white ppt of ZnS is formed
(d) Cupric ion reacts with excess of ammonia solution to give deep blue colour of $[Cu(NH_3)_4]^{2+}$ ion

24. The order of increasing sizes of atomic radii among the elements O, S, Se and As is
(a) As < S < O < Se (b) Se < S < As < O
(c) O < S < As < Se (d) O < S < Se < As

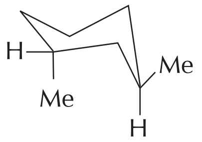
25. In Williamson synthesis of mixed ether having a primary and a tertiary alkyl group if tertiary halide is used, then
(a) rate of reaction will be slow due to slow cleavage of carbon halogen bond
(b) alkene will be the main product
(c) simple ether will form instead of mixed ether
(d) expected mixed ether will be formed

26. Which of the following would not give 2-phenylbutane as the major product in a Friedel-Crafts alkylation reaction?
(a) 1-butene + HF
(b) 2-butanol + H_2SO_4
(c) Butanoyl chloride + $AlCl_3$ then Zn, HCl
(d) Butyl chloride + $AlCl_3$

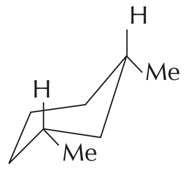
27. Arrange in the correct order of stability (decreasing order) for the following molecules



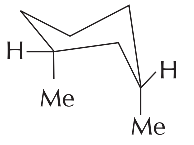
(I)



(II)



(III)



(IV)

(a) (I) > (II) > (III) > (IV)
(b) (IV) > (III) > (II) ≈ (I)
(c) (I) > (II) ≈ (III) > (IV)
(d) (III) > (I) ≈ (II) > (IV)

28. Which one of the following statements about packing in solids is incorrect?
(a) Coordination number in bcc mode of packing is 8
(b) Coordination number in hcp mode of packing is 12
(c) Void space in hcp mode of packing is 32%
(d) Void space in ccp mode of packing is 26%

29. The Wurtz-Fittig reaction involves condensation of
(a) two molecules of aryl halides
(b) one molecule of each of aryl-halide and alkyl-halide
(c) one molecule of each aryl-halide and phenol
(d) two molecules of a alkyl-halides

30. In Goldschmidt alumino thermic process which of the following reducing agent is used?
(a) Calcium (b) Coke
(c) Al powder (d) Sodium

Answers

1. (c)	**2.** (c)	**3.** (c)	**4.** (c)	**5.** (d)	**6.** (c)	**7.** (b)	**8.** (c)	**9.** (d)	**10.** (c)
11. (d)	**12.** (d)	**13.** (b)	**14.** (*)	**15.** (d)	**16.** (a)	**17.** (a)	**18.** (d)	**19.** (b)	**20.** (d)
21. (c)	**22.** (b)	**23.** (a)	**24.** (d)	**25.** (b)	**26.** (c)	**27.** (d)	**28.** (c)	**29.** (b)	**30.** (c)

(*) No option is correct.

Hints *and* Solutions

1. Let the oxidation state of S be x.

SO_3^{2-}

$$\begin{aligned} x + (-2) \times 3 &= -2 \\ x - 6 &= -2 \\ \therefore \quad x &= +4 \end{aligned}$$

$S_2O_4^{2-}$

$$\begin{aligned} 2 \times x + (-2)\,4 &= -2 \\ 2x - 8 &= -2 \\ 2x = 6 \text{ or } x &= +3 \end{aligned}$$

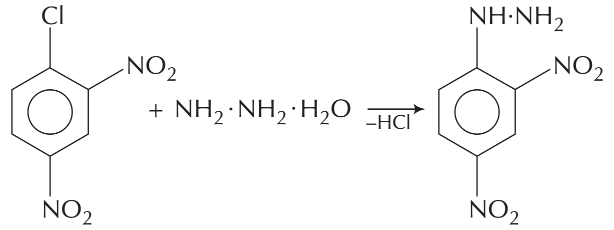
$S_2O_6^{2-}$

$$\begin{aligned} 2x + (-2)\,6 &= -2 \\ 2x &= 10 \\ x &= +5 \end{aligned}$$

$\therefore$ The increasing order of oxidation states is

$$S_2O_4^{2-} < SO_3^{2-} < S_2O_6^{2-}$$

2. Borsch reagent is 2, 4-dinitrophenyl hydrazine, thus, it is obtained by treating 2, 4-dinitrochlorobenzene with hydrazine hydrate.



2,4-dinitrochlorobenzene

2,4-dinitrophenyl hydrazine (Borsch reagent)

3. From Born-Haber cycle,

$$Q = S + I + D + \text{EA} + U$$

$$-617 = 161 + 520 + 77 + \text{EA} - 1047$$

[$\because$ Here, S = sublimation energy, I = ionisation energy, D = dissociation energy, EA = electron gain enthalpy and U = lattice energy.

$$\begin{aligned} \therefore \quad \text{EA} &= 289 - 617 \\ &= -328 \text{ kJ mol}^{-1} \end{aligned}$$

4. Let the degree of association be α.

$$\begin{array}{lll} M & \rightleftharpoons & (M)_n \\ 1 & 0 & \text{Initially} \\ 1-\alpha & \dfrac{\alpha}{n} & \text{At time } t \end{array}$$

$$\text{Total moles after association} = 1 - \alpha + \frac{\alpha}{n} = 1 + \left(\frac{1}{n} - 1\right)\alpha$$

$$i = \frac{\text{moles after association}}{\text{initial moles}}$$

$$i = \frac{1 + \left(\frac{1}{n} - 1\right)\alpha}{1}$$

$$\text{or} \qquad (i - 1) = \left(\frac{1}{n} - 1\right)\alpha$$

We have, $i = 0.9$ and $\alpha = 0.2$

On putting values,

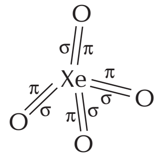
$$\begin{aligned} 0.9 - 1 &= \left(\frac{1}{n} - 1\right)0.2 \\ -0.1 &= -0.2 + \frac{0.2}{n} \\ -0.1 + 0.2 &= \frac{0.2}{n} \\ n &= \frac{0.2}{0.1} = 2 \end{aligned}$$

5. For a substance to dissolve, the hydration energy must be greater than lattice energy. Due to small size of Li^+ ion, the hydration energy of LiF is considerably high, but it has low solubility in water because of its higher lattice energy.

On moving down the group lattice energy decreases which results in increased solubility. Thus, the order of solubility for alkali metal fluorides in water is

$$\text{LiF} < \text{NaF} < \text{KF} < \text{RbF}$$

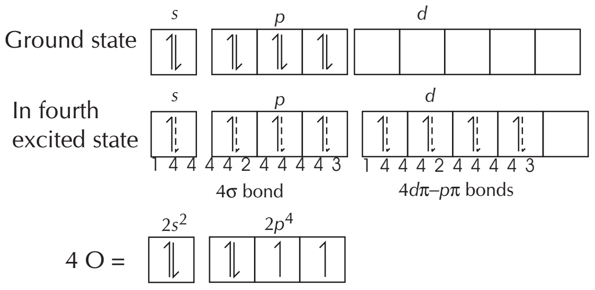
6. The structure of XeO_4 molecule is as



Thus, it contains four $p\pi$-$d\pi$ bonds.

Alternatively

$$\text{Xe} = 5s^2, 5p^6, 5d^0$$

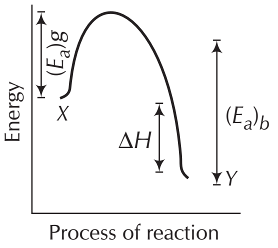


7. An exothermic reaction can be represented as

$$X \longrightarrow Y + \text{energy}$$

i.e., energy of $Y << X$

So, the energy profile diagram is



$$\therefore \quad (E_a)_f + \Delta H = (E_a)_b$$
$$150 + 135 = (E_a)_b$$
$$(E_a)_b = 285 \text{ kJ mol}^{-1}$$

8. Kjeldahl method can be used to determine nitrogen in nitro and azo groups and nitrogen present in the ring. Among the given, only alanine [$H_2N\,CH(CH_3)\,COOH$] have nitrogen in open chain and as amino group, so it can be estimated by using Kjeldahl method.

9. Aspirin is a non-narcotic (non habit forming) analgesic *i.e.*, give relief from pain and also it have antiblood clotting action. It is a neurologically active drug.

10. 3*M* solution means 3 moles of solute (NaCl) are present in 1000 L of solution.

Mass of solution = volume of solution × density

$$= 1000 \times 1.252$$
$$= 1252 \text{ g}$$

Mass of solute = No. of moles × molar mass of NaCl

$$= 3 \times 58.5 \text{ g} = 175.5 \text{ g}$$

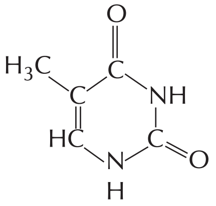
Mass of solvent = (1252 − 175.5) g

$$= 1076.5 \text{ g}$$
$$= 1.076 \text{ kg}$$

$$\text{Molality} = \frac{\text{moles of solute}}{\text{mass of solvent (in kg)}}$$

$$= \frac{3}{1.076} = 2.79 \text{ m}$$

11. The structure of thymine is

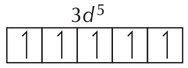


12. Polymethyl methacrylate (PMMA or plexi glass) is used as a substitute of glass so used to prepare optical lenses.

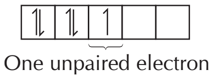
13. If there is no unpaired electrons, the species is diamagnetic.

Fe^{3+} and Co^{3+} both the ions have unpaired electrons in their ground state, but strong field ligands, like CN^-, OX if present, pair up the unpaired electrons resulting to reduce paramagnetism.

$Fe^{3+} = 3d^5 4s^0$

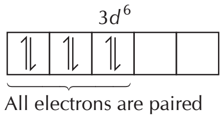


In $[Fe(CN^-)_6]^{3-}$,



$Co^{3+} = 3d^6 4s^0$

In $[Co(OX)_3]^{3-}$,



Thus, $[Co(OX)_3]^{3-}$ is a diamagnetic species as all the electrons are paired in it.

14. The MO configuration of the given species can be written as

$H_2\,(1 + 1 = 2) = \sigma\, 1s^2$

$Li_2\,(3 + 3 = 6) = \sigma\, 1s^2, \sigma^* 1s^2, \sigma\, 2s^2$

$B_2 (5 + 5 = 10) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2px^1 \approx \pi 2py^1$

As the number of antibonding electrons (σ^* or π^*) increases, energy increases and stability decreases. Thus, the correct order of stability is

$$H_2 > Li_2 > B_2$$

(*) No answer is found true.

15. (i) $\underset{s_1 \text{ mol L}^{-1}}{Hg_2Cl_2} \rightleftharpoons \underset{s_1}{Hg_2^{2+}} + \underset{2s_1}{2Cl^-}$

$$K_{sp} = [Hg_2^{2+}][Cl^-]^2$$
$$= (s_1)(2s_1)^2 = s_1 \cdot 4s_1^2 = 4s_1^3$$

$$\therefore \text{Solubility, } s_1 = \left(\frac{K_{sp}}{4}\right)^{1/3}$$

(ii) $\underset{s_2 \text{ mol L}^{-1}}{Cr_2(SO_4)_3} \rightleftharpoons \underset{2s_2}{2Cr^{3+}} + \underset{3s_2}{3SO_4^{2-}}$

$$K_{sp} = [Cr^{3+}]^2 [SO_4^{2-}]^3 = (2s_2)^2 (3s_2)^3$$
$$= 4s_2^2 \times 27s_2^3 = 108 s_2^5$$

$$\therefore \text{Solubility, } s_2 = \left(\frac{K_{sp}}{108}\right)^{1/5}$$

(iii) $\underset{s_3 \text{ mol L}^{-1}}{BaSO_4} \rightleftharpoons \underset{s_3}{Ba^{2+}} + \underset{s_3}{SO_4^{2-}}$

$$K_{sp} = [Ba^{2+}][SO_4^{2-}] = (s_3)^2$$

$\therefore$ Solubility, $s_3 = (K_{sp})^{1/2}$

(iv) $\underset{s_4 \text{ mol L}^{-1}}{CrCl_3} \rightleftharpoons \underset{s_4}{Cr^{3+}} + \underset{3s_4}{3Cl^-}$

$$\begin{aligned} K_{sp} &= [Cr^{3+}][Cl^-]^3 \\ &= (s_4)(3s_4)^3 \\ &= 27s_4^4 \end{aligned}$$

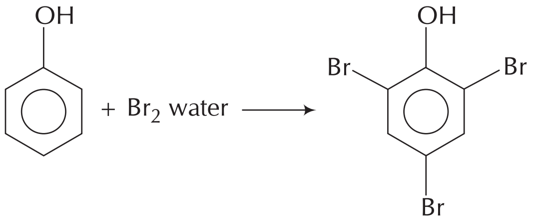
$\therefore$ Solubility, $s_4 = \left(\dfrac{K_{sp}}{27}\right)^{1/4}$

16. For Balmer series, $n_1 = 2$ and $n_2 = (n_1 + 1)$ for first emission line $= (2 + 1) = 3$

We know that,

$$\begin{aligned} \text{wave number, } \bar{v} &= R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \\ &= R\left(\frac{1}{(2)^2} - \frac{1}{(3)^2}\right) \\ &= R\left(\frac{1}{4} - \frac{1}{9}\right) \\ &= \frac{5R}{36} \end{aligned}$$

17. When phenol reacts with bromine water, it results in the formation of white crystalline precipitate of 2,4,6-tribromophenol because of the generation of highly reactive phenoxide ion.



2, 4, 6-tribromo phenol

18. 5.0×10^{-2} M NaOH $\equiv [OH^-] = 5 \times 10^{-2}$M

$$\begin{aligned} [H^+][OH^-] &= 1 \times 10^{-14} \\ [H^+] \cdot 5 \times 10^{-2} &= 1 \times 10^{-14} \\ [H^+] &= \frac{1 \times 10^{-14}}{5 \times 10^{-2}} = 2 \times 10^{-13} \\ pH &= -\log[H^+] \\ &= -\log(2 \times 10^{-13}) \\ &= 12.69 \approx 12.70 \end{aligned}$$

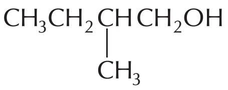
19. Flocculation value of $BaCl_2$ is less than that of KCl so sol *A* must not be negatively charged. It should be positively charged.

Similarly, flocculation value of Na_2SO_4 is much less than that of NaBr, it means sol *A* must not be positively charged. It should be negatively charged.

20. Conc. HCl and $ZnCl_2$ is Lucas reagent and 3° alcohols (alcohols having $\rightarrow$C—OH group) react fastest with it.

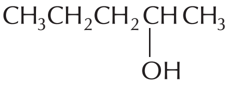
The structures of the given alcohols are as

$CH_3CH_2CH_2CH_2CH_2OH$
pentanol (1° alcohol)



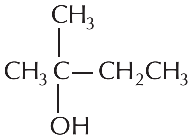
$\underset{\displaystyle CH_3}{CH_3CH_2\underset{|}{C}HCH_2OH}$

2-methylbutanol
(1° alcohol)



$CH_3CH_2CH_2\underset{\underset{\displaystyle OH}{|}}{C}HCH_3$

2-pentanol
(2° alcohol)



$CH_3\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_2CH_3$

2-methylbutan-2-ol
(3° alcohol)

Hence, 2-methylbutan-2-ol reacts fastest with the given reagent.

21. We know that acidic strength $\propto K_a$ value.

Thus, on the basis of K_a value, order of acidic strength is

$$HCN < HNO_2 < HF$$

Conjugate base of a strong acid is weak.

Therefore, the order of base strength of conjugate base is

$$F^- < NO_2^- < CN^-$$

22. Zn—Hg with HCl is called Clemmensen reagent. It reduces the $>C=O$ group of a ketone into $>CH_2$ group. Thus, the reaction.

$$>C=O \xrightarrow[\text{Conc. HCl}]{\text{Zn—Hg}} >CH_2$$

is called Clemmensen reduction.

23. $Fe^{3+} + SCN^- \longrightarrow [Fe(SCN)]^{2+}$
red colour, not
blood red colour

All other given statements are correct.

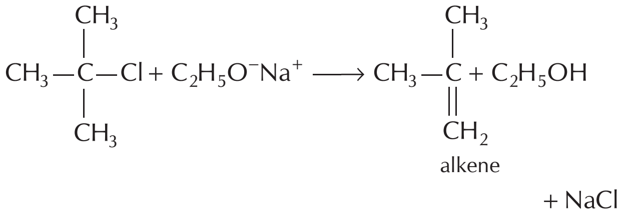
24. Atomic radii decreases along a period due to increase in effective nuclear charge and increases on moving down a group.

Therefore, atomic radii of element of group 15, *i.e.*, As is greater than the elements of group 16.

Hence, the correct order of atomic radii is

$$O < S < Se < As.$$

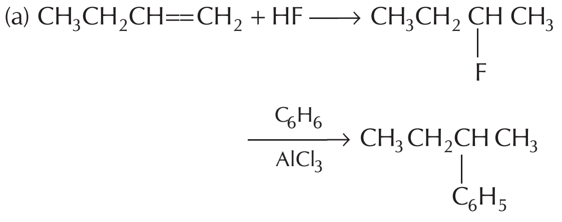
25. Tertiary (3°) halides are more reactive towards elimination than substitution in the presence of a base like alkoxide ion. That's why in Williamson synthesis, if tertiary halide is taken, alkene will be the major product.



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Cl + C_2H_5O^-Na^+ \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_2}{\|}}{C}} + C_2H_5OH + NaCl$$

alkene

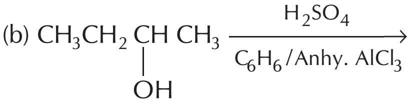
26. (a)



$$CH_3CH_2CH{=\!=}CH_2 + HF \longrightarrow CH_3CH_2\underset{\underset{F}{|}}{CH}CH_3 \xrightarrow[AlCl_3]{C_6H_6} CH_3CH_2\underset{\underset{C_6H_5}{|}}{CH}CH_3$$

2-phenylbutane

(b)

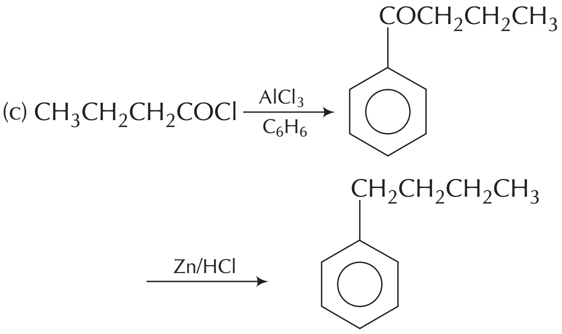


$$CH_3CH_2\underset{\underset{OH}{|}}{CH}CH_3 \xrightarrow[C_6H_6/\text{Anhy. }AlCl_3]{H_2SO_4}$$

$CH_3CH_2CH(C_6H_5)CH_3$

2-phenylbutane

(c)



1-phenyl butane

(d) $CH_3CH_2CH_2CH_2Cl \xrightarrow[\substack{\text{Anhy }AlCl_3\\ \text{(involves}\\ \text{rearrangement)}}]{C_6H_6}$

$CH_3CH_2CH(CH_6H_5)CH_3$

2-phenyl butane

27. The structure in which bulkier groups (which is Me group here) occupy equatorial positions is more stable than the one in which bulkier group are at axial positions. Here, the order of stability is

$$\text{III} > \text{I} \approx \text{II} > \text{IV}$$

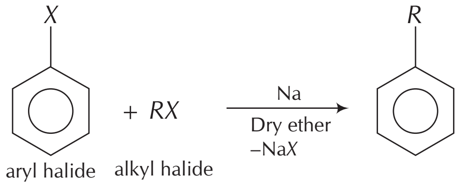
28. For hcp and ccp packing both packing fraction is 74%.

$\therefore$ Fraction of free space or void $= 100 - 74$

$= 26\%$

Coordination number in bcc packing is 8 and in hcp packing is 12.

29. When one molecule of alkyl halide undergoes condensation with one molecule of aryl halide in the presence of Na in dry ether, the reaction is called Wurtz–Fittig reaction *e.g.*,



30. In Goldschmidt aluminothermic process, oxides of Cr, Fe etc., are treated with Al powder which reduces these oxides into crude metal. Thus, acts as reducing agent here.

$$Fe_2O_3 + \underset{\text{reducing agent}}{2Al} \longrightarrow Al_2O_3 + 2Fe$$

Online Exam Held on
23-4-2013

JEE Main

Solved Paper 2013

Instructions

- This test consists of 30 questions.
- Each question is allotted 4 marks for correct response.
- Candidates will be awarded marks as stated above for correct response of each question. 1/4 mark will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
- There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted according as per instructions.

---

1. Which of the following polymer is a polyamide?
(a) Terylene (b) Nylon
(c) Rubber (d) Vulcanised rubber

2. The magnetic moment of the complex anion $[Cr(NO)(NH_3)(CN)_4]^{2-}$ is
(a) 5.91 BM (b) 3.87 BM
(c) 1.73 BM (d) 2.82 BM

3. Glycosidic linkage is actually an
(a) carbonyl bond (b) ether bond
(c) ester bond (d) amide bond

4. Equimolar solutions of the following compounds are prepared separately in water. Which will have the lowest pH value ?
(a) $BeCl_2$ (b) $SrCl_2$
(c) $CaCl_2$ (d) $MgCl_2$

5. The number of protons, electrons and neutrons in a molecule of heavy water are respectively
(a) 8, 10, 11 (b) 10, 10, 10
(c) 10, 11, 10 (d) 11, 10,10

6. Number of atoms in the following samples of substances is the largest in
(a) 4.0 g of hydrogen (b) 70.0g of chlorine
(c) 127.0 g of iodine (d) 48.0 g of magnesium

7. Which has trigonal bipyramidal shape?
(a) $XeOF_4$ (b) XeO_3
(c) XeO_3F_2 (d) $XeOF_2$

8. Which is the correct order of second ionization potential of C, N, O and F in the following?
(a) $O > N > F > C$ (b) $O > F > N > C$
(c) $F > O > N > C$ (d) $C > N > O > F$

9. Natural glucose is termed D-glucose because
(a) —OH on the second carbon is on the right side in the Fischer projection
(b) —OH on the sixth carbon is on the right side in the Fischer projection
(c) —OH on the fifth carbon is on the right side in Fischer projection
(d) It is dextrorotatory

10. The shape of IF_6^- is
(a) trigonally distorted octahedron
(b) pyramidal
(c) octahedral
(d) square antiprism

11.
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g), K_1 \quad \ldots(i)$$
$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g), K_2 \quad \ldots(ii)$$
$$H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(g), K_3 \quad \ldots(iii)$$

The equation for the equilibrium constant of the reaction $2NH_3(g) + \frac{5}{2}O_2(g) \rightleftharpoons 2NO(g) + 3H_2O(g)$, (K_4) in terms of K_1, K_2 and K_3 is
(a) $\frac{K_1K_2}{K_3}$ (b) $\frac{K_1K_3^2}{K_2}$
(c) $K_1K_2K_3$ (d) $\frac{K_2K_3^3}{K_1}$

12. H_1-receptor antagonists is a term associated with
(a) antiseptics (b) antihistamines
(c) antacids (d) analgesics

13. The correct order of viscosity of the following liquids will be
(a) water < methyl alcohol < dimethyl ether < glycerol
(b) methyl alcohol < glycerol < water < dimethyl ether
(c) dimethyl ether < methyl alcohol < water < glycerol
(d) glycerol < dimethyl ether < water < methyl alcohol

14. What is the pH of a 10^{-4} M OH^- solution at 330K, if K_w at 330 K is $10^{-13.6}$?
(a) 4 (b) 9.0 (c) 10 (d) 9.6

15. The order of reactivity of the given haloalkanes towards nucleophile is
(a) $RI > RBr > RCl$ (b) $RCl > RBr > RI$
(c) $RBr > RCl > RI$ (d) $RBr > RI > RCl$

16. Identify the incorrect statement.
(a) In $(Si_3O_9)^{6-}$, tetrahedral SiO_4 units share two oxygen atoms
(b) Trialkyl chlorosilane on hydrolysis gives R_3SiOH
(c) $SiCl_4$ undergoes hydrolysis to give H_4SiO_4
(d) $(Si_3O_9)^{6-}$ has cyclic structure

17. When a small amount of $KMnO_4$ is added to concentrated H_2SO_4, a green oily compound is obtained which is highly explosive in nature. Compound may be
(a) $MnSO_4$ (b) Mn_2O_7
(c) MnO_2 (d) Mn_2O_3

18. The reaction of phenol with benzoyl chloride to give phenyl benzoate is known as
(a) Claisen reaction
(b) Schotten-Baumann reaction
(c) Reimer-Tiemann reaction
(d) Gatterman-Koch reaction

19. Identify the incorrect statement.
(a) Cu_2O is colourless
(b) Copper (I) compounds are colourless except where colour results from charge transfer.
(c) Copper (I) compounds are diamagnetic
(d) Cu_2S is black

20. Vapour pressure of pure benzene is 119 torr and that of toluene is 37.0 torr at the same temperature. Mole fraction of toluene in vapour phase which is in equilibrium with a solution of benzene and toluene having a mole fraction of toluene 0.50, will be
(a) 0.137 (b) 0.237
(c) 0.435 (d) 0.205

21. In a face centred cubic lattice, atoms of *A* form the corner points and atoms of *B* form the face centered points. If two atoms of *A* are missing from the corner points, the formula of the ionic compound is
(a) AB_3 (b) AB_4 (c) A_2B_5 (d) AB_2

22. The de-Broglie wavelength of a car of mass 1000 kg and velocity 36 km/h is
($h = 6.63 \times 10^{-34}$ Js)
(a) 6.626×10^{-34} m (b) 6.626×10^{-38} m
(c) 6.626×10^{-31} m (d) 6.626×10^{-30} m

23. Given, $E^0_{\frac{1}{2}Cl_2/Cl} = 1.36$ V, $E^0_{Cr^{3+}/Cr} = -0.74$ V,

$E^0_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33$ V, $E^0_{MnO_4^-/Mn^{2+}} = 1.51$ V

The correct order of reducing power of the species (Cr, Cr^{3+}, Mn^{2+} and Cl^-) will be
(a) $Mn^{2+} < Cl^- < Cr^{3+} < Cr$
(b) $Mn^{2+} < Cr^{3+} < Cl^- < Cr$
(c) $Cr^{3+} < Cl^- < Mn^{2+} < Cr$
(d) $Cr^{3+} < Cl^- < Cr < Mn^{2+}$

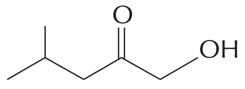
24. Smoke is an example of
(a) solid dispersed in solid (b) gas dispersed in liquid
(c) solid dispersed in gas (d) gas dispersed in solid

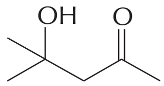
25. Which of the following statements/relationships is not correct in thermodynamic changes?
(a) $\Delta U = 0$ (isothermal reversible expansion of a gas)
(b) $W = -nRT \ln\frac{V_2}{V_1}$ (isothermal reversible expansion of an ideal gas)
(c) $q = -nRT \ln\frac{V_2}{V_1}$ (isothermal reversible expansion of an ideal gas)
(d) For a system, at constant volume, heat involved completely changes to internal energy

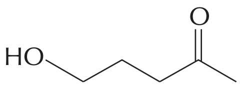
26. Bond distance in HF is 9.17×10^{-11} m. Dipole moment of HF is 6.104×10^{-30} Cm. The per cent ionic character in HF will be (electron charge $= 1.60 \times 10^{-19}$ C)
(a) 61.0% (b) 38.0%
(c) 35.5% (d) 41.5%

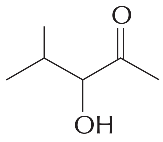
27. The rate constant of a zero order reaction is 2.0×10^{-2} mol L^{-1} s^{-1}. If the concentration of the reactant after 25 s is 0.5 M, what is the initial concentration?
(a) 0.5 M (b) 1.25 M
(c) 12.5 M (d) 1.0 M

28. Which of the following is the product of aldol condensation?

(a)


(b)


(c)


(d)


29. The order of basicity of amines in gaseous state is
(a) $1° > 2° > 3° > NH_3$
(b) $3° > 2° > NH_3 > 1°$
(c) $3° > 2° > 1° > NH_3$
(d) $NH_3 > 1° > 2° > 3°$

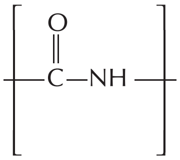
30. Monocarboxylic acids are functional isomers of
(a) ethers
(b) amines
(c) esters
(d) alcohols

Answers

1. (b)	**2.** (c)	**3.** (b)	**4.** (a)	**5.** (b)	**6.** (a)	**7.** (c)	**8.** (b)	**9.** (c)	**10.** (a)
11. (d)	**12.** (b)	**13.** (c)	**14.** (d)	**15.** (a)	**16.** (b)	**17.** (b)	**18.** (b)	**19.** (a)	**20.** (b)
21. (b)	**22.** (b)	**23.** (a)	**24.** (c)	**25.** (c)	**26.** (d)	**27.** (d)	**28.** (b)	**29.** (c)	**30.** (c)

Hints *and* Solutions

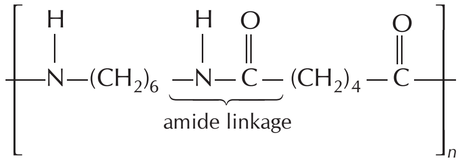
1. Among the given polymers, only nylon contains



$$\left[\overset{\displaystyle O}{\overset{\|}{C}}—NH \right]$$

or amide linkage, so it is also called a polyamide *e.g.*, nylon-66

$$\underset{\text{hexamethylene diamine}}{nH_2N(CH_2)_6NH_2} + \underset{\text{adipic acid}}{nHOOC(CH_2)_4COOH} \xrightarrow[-H_2O]{}$$



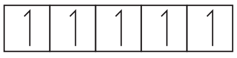
$$\left[\overset{\displaystyle H}{\overset{|}{N}}—(CH_2)_6\underbrace{—\overset{\displaystyle H}{\overset{|}{N}}—\overset{\displaystyle O}{\overset{\|}{C}}—}_{\text{amide linkage}}(CH_2)_4—\overset{\displaystyle O}{\overset{\|}{C}} \right]_n$$

nylon-66

2. In $[Cr(NO)(NH_3)(CN)_4]^{2-}$,

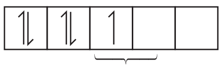
Let the oxidation state of Cr is x.

$$\therefore \quad x + (+1) + (0) + (-1)4 = -2$$
$$x - 3 = -2$$
$$x = 1$$
$$Cr^+ = [Ar]\,3d^5\,4s^0$$



But CN^- and NO being strong field ligands pair up the unpaired electrons of Cr^+.

$$[Cr(NO)(NH_3)(CN)_4]^{2-}$$

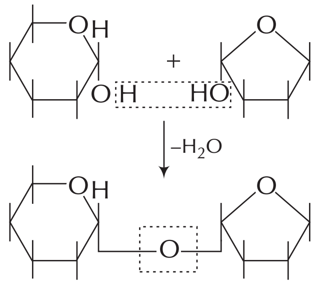
[Ar] =


One unpaired electron

$$\therefore \quad n = 1$$

Magnetic moment, $\mu = \sqrt{n(n+2)}$
$$= \sqrt{1(1+2)} = \sqrt{3} = 1.73 \text{ BM}$$

3. A linkage between two monosaccharide units through oxygen atom is called glycosidic linkage *e.g.*,



glycosidic linkage

Thus, glycosidic linkage (*R*—O—*R*) is actually an ether bond.

4. Alkaline earth metal chlorides form strong acid HCl and base $M(OH)_2$ (where, M = alkaline earth metal) when dissolved in water. On moving down the group, the strength of $M(OH)_2$ increases, hence, it neutralises the acid more and reduces the acidity of solution or increases the pH of solution. (as pH varies inversely with acidity) Thus, the solution of $BeCl_2$ because of the less basic nature of $Be(OH)_2$ is most acidic and hence, have lowest pH value.

5. Heavy water is D_2O.

In it,

Number of $p^+ = 1 \times 2 + 8 = 10$

Number of $e^- = 1 \times 2 + 8 = 10$

Number of $n^0 = 1 \times 2 + 8 = 10$

(∵ D have 1 n^0 because it is actually, ${}_1H^2$.)

6. $$\text{Number of atoms} = \frac{\text{weight}}{\text{atomic weight}} \times N_A \times \text{species}$$

∴ In 4 g of hydrogen,

$$\text{Number of atoms} = \frac{4}{2} \times N_A \times 2 = 4N_A$$

[Here species = 2 because hydrogen is present as H_2]

In 71 g of chlorine, $= 2N_A$

$$\text{Number of atoms} = \frac{71}{71} \times N_A \times 2 = 2\,N_A$$

In 127 g of iodine,

$$\text{Number of atoms} = \frac{127}{127} \times N_A \times 2 = 2N_A$$

In 48 g of magnesium,

$$\text{Number of atoms} = \frac{48}{24} \times N_A \times 1 = 2N_A$$

[Here Mg is present as Mg so species = 1]

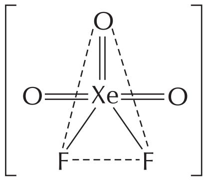
Thus, the number of atoms are largest in 4 g of hydrogen.

7. The shape is trigonal bipyramidal, if a compound have 5 bond pairs and 0 lone pairs.

$XeOF_4 = 5bp + 1lp$ = square pyramidal shape

$XeO_3 = 3bp + 1lp$ = pyramidal shape

$XeO_3F_2 = 5bp + 0lp$ = trigonal bipyramidal shape



$XeOF_2 = 3bp + 2lp$ = T-shape

8. Second ionisation potential represents the amount of energy required to remove an electron from a unipositive ion. The electronic configuration of unipositive ions of given atoms is as

$$C^+(6-1=5) = 1s^2, 2s^2, 2p^1$$

$$N^+(7-1=6) = 1s^2, 2s^2, 2p^2$$

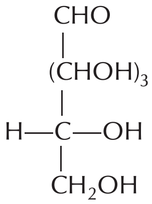
$$O^+(8-1=7) = 1s^2, 2s^2, 2p^3$$

$$F^+(9-1=8) = 1s^2, 2s^2, 2p^4$$

From the electronic configuration, it is clear that the second IP of O is highest because here the electron which is to be removed belongs to half-filled (so more stable) *p* orbital. Moreover, along a period, as the number of electrons increases, size decreases, effective nuclear charge increases and hence, IP increases. Thus, the correct order of second IP is

$$O > F > N > C$$

9. Depending upon the configuration of glyceraldehyde (where the configuration is D if —OH present at the C attached to CH_2OH group is on right side), glucose is called D-glucose, if the —OH group present at the C bearing —CH_2OH group (which is fifth carbon here) is on the right hand side, *i.e.*,



$$\begin{array}{c} CHO \\ | \\ (CHOH)_3 \\ | \\ H{-}C{-}OH \\ | \\ CH_2OH \end{array}$$

right hand side

10. Number of hybrid orbital,

$$H = \frac{1}{2}[V - C + A + M]$$

[Here V = valence e^- of central atom, C and A = positive and negative charge respectively, M = monovalent atoms]

In IF_6^-,

$$H = \frac{1}{2}[7 - 0 + 1 + 6] = 7$$

So, the hybridisation is sp^3d^3 and structure should be pentagonal bipyramidal.

But it contains one lone pair, so bond pair = 6

Hence, its actual geometry is trigonally distorted octahedron.

11. In the required equation NH_3 is on LHS, so invert the equation (i)

$$2NH_3(q) \rightleftharpoons N_2(g) + 3H_2(g);\ K_5 = \frac{1}{K_1} \qquad \text{...(iv)}$$

Moreover, there are three moles of H_2O, so multiply Eq. (iii) by 3

$$3H_2(g) + \frac{3}{2}O_2(g) \rightleftharpoons 3H_2O(g);\ K_6 = K_3^3 \qquad \text{...(v)}$$

(because when a reaction is multiplied by n, K becomes K^n).

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO\,(g),\ K_2$$

On adding Eqs. (iv), (ii) and (v) we get

$$2NH_3(g) + \frac{5}{2}O_2(g) \rightleftharpoons 2NO(g) + 3H_2O(g)$$

$$K_4 = K_2 \times K_5 \times K_6$$

[because equilibrium constants are multiplied, when two or more reactions are added.]

On putting the values of K_5 and K_6, we get

$$K_4 = K_2 \cdot \frac{1}{K_1} \cdot K_3^3$$

$$= \frac{K_2K_3^3}{K_1}$$

12. The term antihistamine refers only to compounds not have inhibit action at the H_1-receptor so the term H_1-receptor antagonists is related with antihistamines.

13. Viscosity shows the rate of flow of a liquid. It is actually the measure of frictional resistance, and frictional resistance is more, when bonding is strong. In glycerol, there is excessive H-bonding because of the presence of three —OH groups, so it is highly viscous. H-bonding is least in dimethyl ether, so it is least viscous.

Hence, the order of viscosity is

$$\underset{(\text{no —OH})}{\text{dimethylether}} < \underset{\text{One —OH}}{\text{methyl alcohol}} < \underset{(2\text{ —OH})}{H_2O} < \underset{(3\text{ —OH})}{\text{glycerol}}$$

14. At 330 K,

$$[H^+][OH^-] = K_w = 1\times10^{-13.6}$$
$$[H^+](10^{-4}\text{ M}) = 1\times10^{-13.6}$$
$$[H^+] = \frac{1\times10^{-13.6}}{10^{-4}}$$
$$= 10^{-9.6}$$
$$\text{pH} = -\log[H^+]$$
$$= -\log(10^{-9.6})$$
$$= 9.6$$

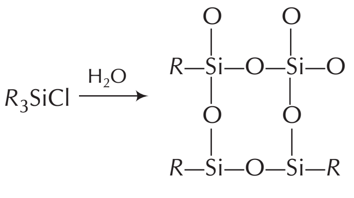
15. As the size of halogen atom increases, R—X bond length increases and hence, R—X bond becomes weak. Thus, reactivity increases. Hence, the order of reactivity is

$$R\text{—}\underbrace{\text{I}}_{\text{larger}} > R\text{—Br} > R\text{—}\underbrace{\text{Cl}}_{\text{small}}$$

16. When two oxygen per SiO_4 tetrahedron are shared,cyclic silicates containing $Si_3O_9^{6-}$ or $Si_6O_{15}^{12-}$ units may be obtained.

$SiCl_4$ when subjected to hydrolysis results in the formation of silicic acid, $Si(OH)_4$ or H_4SiO_4.

Hydrolysis of trialkyl chlorosilane gives very complex cross-linked polymer.

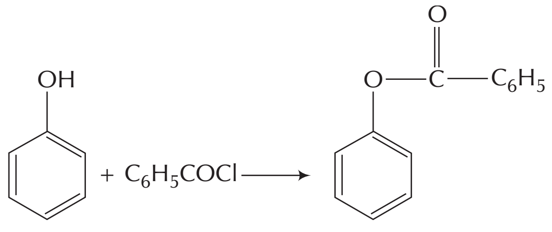


17. When a small amount of $KMnO_4$ is added to concentrated H_2SO_4, manganese heptoxide is obtained, which on warming decomposes with a mild explosion into MnO_2 and O_2.

$$2KMnO_4 + H_2SO_4 \longrightarrow \underset{\text{green liquid}}{Mn_2O_7} + K_2SO_4 + H_2O$$

$$2Mn_2O_7 \longrightarrow 4MnO_2 + 3O_2$$

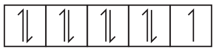
18. The reaction of phenol with benzoyl chloride to give phenyl benzoate is also known as Schotten-Baumann reaction.



phenyl benzoate

19. Cu_2O is not colourless, it is coloured because of the presence of one unpaired electron, which makes d-d transition possible.

$Cu^{2+} = [Ar]\,3d^9$



All other given statements are correct.

20. From Raoult's law, for ideal solution,

$$p = p_B^0 x_B + p_T^0 x_T$$
$$[B = \text{Benzene}, T = \text{Toluene}]$$
$$= 119\times0.5 + 37\times0.5 \qquad (\because x_B = 1 - x_T)$$
$$= 59.5 + 18.5$$
$$= 78\text{ torr}$$

Mole fraction of toluene in vapour phase

$$(x_T)_v = \frac{p_T^o x_T}{p}$$
$$= \frac{18.5}{78}$$
$$= 0.237$$

21. While solving such problems always remember that each corner atom is shared by 8 unit cells and each face centre atom is shared by 2 unit cells.

$\therefore$ Number of A atoms per unit cell $= (8-2)\times\frac{1}{8} = \frac{6}{8} = \frac{3}{4}$

Number of B atoms per unit cell $= 6\times\frac{1}{2} = 3$

$$A : B = \frac{3}{4} : 3 = 1 : 4$$

$\therefore$ Formula of the ionic compound is AB_4.

22. de-Broglie equation is

$$\lambda = \frac{h}{mv}$$

Given, $m = 1000$ kg and $v = 36$ km/h

$$= \frac{36\times1000}{60\times60} = 10\text{ m/s}$$

On putting values,

$$\lambda = \frac{6.63 \times 10^{-34}}{1000 \times 10}$$

$$= 6.63 \times 10^{-38} \text{ m}$$

23. More the negative value of reduction potential, higher the reducing power. Thus, the correct order of reducing tendency is

$$\underset{(1.51\text{ V})}{\text{Mn}^{2+}} < \underset{(1.36\text{ V})}{\text{Cl}^{-}} < \underset{(1.33\text{ V})}{\text{Cr}^{3+}} < \underset{(-0.74\text{ V})}{\text{Cr}}$$

24. Smoke is a colloid in which dispersed phase is solid and dispersion medium is gas or in other words, in smoke, a solid is dispersed in a gas.

25. For isothermal process, $\Delta U = 0$

From first law of thermodynamics

$$\Delta U = q + W$$

At constant volume, $\Delta V = 0$

$\therefore \quad W = 0$

so, $\quad \Delta U = q$

i.e., heat involved completely changes to internal energy.

If $\quad \Delta U = 0$

$$q = -W$$

$$= -\left(-nRT \ln \frac{V_2}{V_1}\right)\left[\because W_{\text{rev}} = -nRT \ln \frac{V_2}{V_1}\right]$$

$$= nRT \ln \frac{V_2}{V_1}$$

26. $$\% \text{ ionic character} = \frac{\mu_{\text{observed}}}{\mu_{\text{calculated}}} \times 100$$

$$\mu_{\text{observed}} = 6.104 \times 10^{-30} \text{ Cm}$$

$$\mu_{\text{calculated}} = e \times d$$

$$= 1.6 \times 10^{-19} \text{ C} \times 9.17 \times 10^{-11} \text{ m}$$

$$= 1.467 \times 10^{-29} \text{ Cm}$$

$$\therefore \% \text{ ionic character} = \frac{6.104 \times 10^{-30}}{1.467 \times 10^{-29}} \times 100$$

$$= 41.6\%$$

27. For zero order reaction,

$$\text{rate } = \frac{dx}{dt} = k$$

$$= \frac{x_1 - x_2}{dt}$$

$$= 2.0 \times 10^{-2}$$

$$\frac{x_1 - 0.5}{25} = 2.0 \times 10^{-2}$$

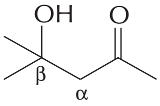
(Here, $x_1 =$ initial concentration)

$$x_1 - 0.5 = 0.5$$

$$x_1 = 0.5 + 0.5$$

$$= 1.0 \text{ M}$$

28. When two aldehydes or ketones (or carbonyl compounds) having α-hydrogen atoms react in the presence of a base, they result in the formation of β-hydroxy aldehyde or ketone, called the aldol or ketol and the reaction is called aldol condensation.

Thus, 

is the product of aldol condensation.

29. In gaseous state, as the number of alkyl group increases, electron density and hence, the availability of electrons for donation increases, thus, basicity increases.
Hence, the correct order of basicity of amines in gaseous state is

$$3° > 2° > 1° > \text{NH}_3$$

30. Monocarboxylic acids and esters have the same general formula but different functional groups, so these are called functional isomers. *e.g.*, $C_3H_6O_2$ can be CH_3CH_2COOH or CH_3COOCH_3.

Online Exam Held on
25-4-2013

JEE Main

Solved Paper 2013

Instructions

- This test consists of 30 questions.
- Each question is allotted 4 marks for correct response.
- Candidates will be awarded marks as stated above for correct response of each question. 1/4 mark will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
- There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted according as per instructions.

---

1. The catenation tendency of C, Si and Ge is in the order Ge < Si < C. The bond energies (in kJ mol^{-1}) of C—C, Si—Si and Ge—Ge bonds are respectively

(a) 348, 297, 260 (b) 297, 348, 260
(c) 348, 260, 297 (d) 260, 297, 348

2. In which of the following exothermic reactions, the heat liberated per mole is the highest ?

(a) $CaO + H_2O \longrightarrow Ca(OH)_2$
(b) $SrO + H_2O \longrightarrow Sr(OH)_2$
(c) $BaO + H_2O \longrightarrow Ba(OH)_2$
(d) $MgO + H_2O \longrightarrow Mg(OH)_2$

3. Given,

(i) $n = 5, m_l = +1$
(ii) $n = 2, l = 1, m_l = -1, m_s = -1/2$

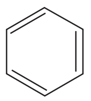
The maximum number of electron(s) in an atom that can have the quantum numbers as given in (i) and (ii) are respectively

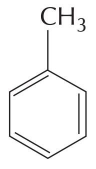
(a) 25 and 1 (b) 8 and 1
(c) 2 and 4 (d) 4 and 1

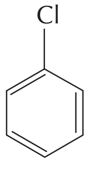
4. Which one of the following cannot function as an oxidising agent?

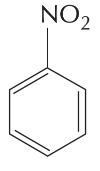
(a) I^- (b) $S(s)$
(c) $NO_3^-(aq)$ (d) $Cr_2O_7^{2-}$

5. Given,

(i) 

(ii) 

(iii) 

(iv) 

In the above compounds correct order of reactivity in electrophilic substitution reactions will be

(a) (ii) > (i) > (iii) > (iv)
(b) (iv) > (iii) > (ii) > (i)
(c) (i) > (ii) > (iii) > (iv)
(d) (ii) > (iii) > (i) > (iv)

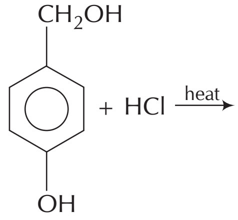
6. Which one of the following is the wrong assumption of kinetic theory of gases ?

(a) Momentum and energy always remain conserved
(b) Pressure is the result of elastic collision of molecules with the container's wall
(c) Molecules are separated by great distances compared to their sizes
(d) All the molecules move in straight line between collision and with same velocity

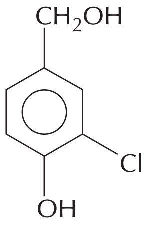
7. A radioactive isotope having a half-life period of 3 days was received after 12 days. If 3 g of the isotope is left in the container, what would be the initial mass of the isotope ?
(a) 12 g (b) 36 g
(c) 48 g (d) 24 g

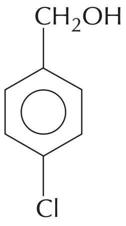
8. Which of the following statement is not correct ?
(a) Amylopectin is a branched polymer of α-glucose
(b) Cellulose is linear polymer of β-glucose
(c) Glycogen is the food reserve of plants
(d) All proteins are polymers of α-amino acids

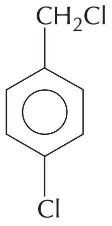
9. The major product in the following reaction

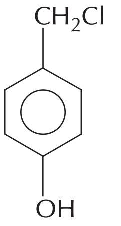


is

(a)


(b)


(c)


(d)


10. The ratio $\frac{K_p}{K_c}$ for the reaction,

$$CO(g) + \frac{1}{2}O_2(g) \rightleftharpoons CO_2(g) \text{ is}$$

(a) $\frac{1}{\sqrt{RT}}$ (b) $(RT)^{1/2}$
(c) RT (d) 1

11. Copper crystallises in fcc with a unit length of 361 pm. What is the radius of copper atom?
(a) 157 pm (b) 128 pm
(c) 108 pm (d) 181 pm

12. In which of the following sets, all the given species are isostructural ?
(a) CO_2, NO_2, ClO_2, SiO_2 (b) PCl_3, $AlCl_3$, BCl_3, $SbCl_3$
(c) BF_3, NF_3, PF_3, AlF_3 (d) BF_4^-, CCl_4, NH_4^+, PCl_4^+

13. Given that
(i) $\Delta_f H°$ of N_2O is 82 kJ mol^{-1}
(ii) Bond energies of $N{\equiv}N$, $N{=}N$, $O{=}O$ and $N{=}O$ are 946, 418, 498 and 607 kJ mol^{-1} respectively. The resonance energy of N_2O is
(a) -88 kJ (b) -66 kJ
(c) -62 kJ (d) -44 kJ

14. What would be the pH of a solution obtained by mixing 5 g of acetic acid and 7.5 g of sodium acetate and making the volume equal to 500 mL?
($K_a = 1.75 \times 10^{-5}$, $pK_a = 4.76$)
(a) pH = 4.70
(b) pH < 4.70
(c) pH of solution will be equal to pH of acetic acid
(d) 4.76 < pH < 5.0

15. 6 L of an alkene require 27 L of oxygen at constant temperature and pressure for complete combustion. The alkene is
(a) ethene (b) propene
(c) 1-butene (d) 2-butene

16. Bakelite is obtained from phenol by reacting with
(a) acetal
(b) CH_3CHO
(c) HCHO
(d) chlorobenzene

17. How many grams of methyl alcohol should be added to 10 L tank of water to prevent its freezing at 268 K?
(K_f for water is 1.86 K kg mol^{-1})
(a) 880.07 g (b) 899.04 g
(c) 886.02 g (d) 868.06 g

18. In which of the following octahedral complex species the magnitude of Δ_o will be maximum?
(a) $[Co(H_2O)_6]^{2+}$ (b) $[Co(CN)_6]^{3-}$
(c) $[Co(C_2O_4)_3]^{3-}$ (d) $[Co(NH_3)_6]^{3+}$

19. In nucleophilic substitution reaction, order of halogens as incoming (attacking) nucleophile is

$$I^- > Br^- > Cl^-$$

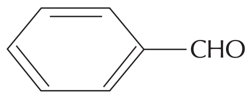
The order of halogens as departing nucleophile should be
(a) $Br^- > I^- > Cl^-$ (b) $I^- > Br^- > Cl^-$
(c) $Cl^- > Br^- > I^-$ (d) $Cl^- > I^- > Br^-$

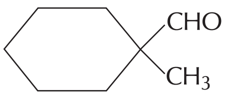
20. The Gibbs energy for the decomposition of Al_2O_3 at 500°C is as follows

$$\frac{2}{3}Al_2O_3 \longrightarrow \frac{4}{3}Al + O_2, \ \Delta_r G = +940 \text{ kJ mol}^{-1}$$

The potential difference needed for the electrolytic reduction of aluminium oxide at 500°C should be atleast
(a) 4.5 V (b) 3.0 V
(c) 5.0 V (d) 2.5 V

21. Cannizzaro's reaction is not given by

(a) 

(b) 

(c) CH_3CHO (d) HCHO

22. Phenol on heating with $CHCl_3$ and NaOH gives salicylaldehyde. The reaction is called
(a) Reimer-Tiemann reaction
(b) Claisen reaction
(c) Cannizzaro's reaction
(d) Hell-Volhard-Zelinsky reaction

23. The internuclear distances in O—O bonds for O_2^+, O_2, O_2^- and O_2^{2-} respectively are
(a) 1.30 Å, 1.49 Å, 1.12 Å, 1.21 Å
(b) 1.49 Å, 1.21 Å, 1.12 Å, 1.30 Å
(c) 1.21 Å, 1.12 Å, 1.49 Å, 1.30 Å
(d) 1.12 Å, 1.21 Å, 1.30 Å, 1.49 Å

24. Among the following vitamins the one whose deficiency causes rickets (bone deficiency) is
(a) vitamin A (b) vitamin B
(c) vitamin D (d) vitamin C

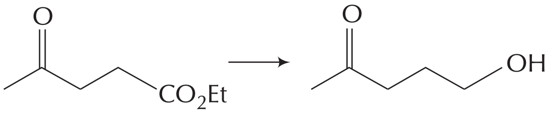
25. Which one of the following arrangements represents the correct order of the proton affinity of the given species?
(a) $I^- < F^- < HS^- < NH_2^-$ (b) $HS^- < NH_2^- < F^- < I^-$
(c) $F^- < I^- < NH_2^- < HS^-$ (d) $NH_2^- < HS^- < I^- < F^-$

26. Carbylamine forms from aliphatic or aromatic primary amine *via* which of the following intermediates?
(a) Carbanion (b) Carbene
(c) Carbocation (d) Carbon radical

27. 10 mL of 2M NaOH solution is added to 200 mL of 0.5 L M of NaOH solution. What is the final concentration?
(a) 0.57 M (b) 5.7 M
(c) 11.4 M (d) 1.14 M

28. The structure of which of the following chloro species can be explained on the basis of dsp^2 hybridization?
(a) $PdCl_4^{2-}$ (b) $FeCl_4^{2-}$
(c) $CoCl_4^{2-}$ (d) $NiCl_4^{2-}$

29. Which of the following reagent(s) used for the conversion?



(a) glycol/$LiAlH_4/H_3O^+$ (b) glycol/NaH/H_3O^+
(c) $LiAlH_4$ (d) $NaBH_4$

30. A solution of copper sulphate ($CuSO_4$) is electrolysed for 10 min with a current of 1.5 A. The mass of copper deposited at the cathode (atomic mass of Cu = 63 u) is
(a) 0.3892 g (b) 0.2938 g
(c) 0.2398 g (d) 0.3928 g

Answers

1. (a)	**2.** (d)	**3.** (b)	**4.** (a)	**5.** (a)	**6.** (d)	**7.** (c)	**8.** (c)	**9.** (d)	**10.** (a)
11. (b)	**12.** (d)	**13.** (a)	**14.** (d)	**15.** (b)	**16.** (c)	**17.** (c)	**18.** (b)	**19.** (b)	**20.** (d)
21. (c)	**22.** (a)	**23.** (d)	**24.** (c)	**25.** (a)	**26.** (b)	**27.** (a)	**28.** (a)	**29.** (a)	**30.** (b)

Hints and **Solutions**

1. Higher the catenation tendency, higher is the bond energy.
∴ The bond energies of C—C, Si—Si and Ge—Ge bonds are respectively 348, 297 and 260 kJ mol^{-1}.

2. Higher the stability of oxide, more will be the heat liberated per mole. On moving down the group, stability of oxides decreases, thus, MgO is most stable among the given and hence, heat liberated is highest in case of MgO.

3. (i) When $n = 5$

$l = 0, 1, 2, 3, 4$

When $l = 0, m_l = 0$

When $l = 1, m_l = 0, +1, -1$ (two e^-)

When $l = 2, m_l = 0, \pm 1, \pm 2$ (two e^-)

When $l = 3, m_l = 0, \pm 1, \pm 2, \pm 3$ (two e^-)

When $l = 4, m_l = 0, \pm 1, \pm 2, \pm 3, \pm 4$ (two e^-)

(because each orbital can accommodate a maximum of two electrons.)

∴ Total electrons having $n = 5$

and $m_l = \pm 1$

$= 2 + 2 + 2 + 2$
$= 8$

(ii) Only one electron is associated with $n = 2, l = 1$, $m_l = -1$ and $m_s = -1/2$ because Pauli's principle states that no two electrons can have same value for all the four quantum numbers.

4. In I^-, iodine is present in its lowest possible oxidation state. Further reduction in oxidation state is not possible. That's why its further reduction is not possible. Hence, it cannot function as oxidising agent.

5. Presence of electron releasing groups, (like—R) increases the electron density over benzene nucleus and makes it more reactive towards electrophile.
Electron withdrawing groups (like Cl^-, NO_2^-; NO_2^- is more electron withdrawing than Cl^-) make the benzene nucleus electrons deficient and hence, decrease its reactivity towards electrophile.
Hence, the correct order of reactivity towards electrophilic substitution reaction will be

$$\text{(ii)} > \text{(i)} > \text{(iii)} > \text{(iv)}$$

6. According to kinetic theory of gases, the gaseous molecules are so far apart that the actual volume of the molecules is negligible as compared to the total volume of the gas.
The gaseous molecules move in straight lines with uniform speed and change direction on collision with other molecules or the walls of container.
All the collisions are perfectly elastic, hence there is no loss of kinetic energy during the collision. The pressure of the gas is caused by the hits recorded by molecules on the walls of the container.

7. We know that,
total time, $t = n \times t_{1/2} \Rightarrow 12 = n \times 3$

$$\therefore \quad n = 4 \quad \text{and} \quad N = N_0 \times \left(\frac{1}{2}\right)^n$$

[where, N = amount left and N_0 = initial amount]

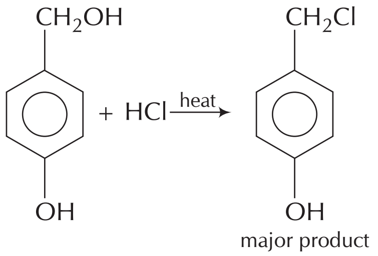
$$3 = N_0 \left(\frac{1}{2}\right)^4$$

$$3 = N_0 \frac{1}{16}$$

$$N_0 = 3 \times 16 = 48 \text{ g}$$

8. Glycogen serves as the reserve food for animals and is stored in the liver and muscles (hence known as animal starch).
All other given statements are true.

9.



Only aliphatic —OH is substituted by Cl^-. In phenol the C—O bond is stabilised by resonance.

10. We know that,

$$K_p = K_c (RT)^{\Delta n_g}$$

where, Δn_g = No. of moles of gaseous products – No. of moles of gaseous reactants
For the given reaction,

$$\Delta n_g = 1 - \left(1 + \frac{1}{2}\right) = -0.5$$

On putting the value of Δn_g,

$$K_p = K_c (RT)^{-0.5}$$

$$K_p = \frac{K_c}{\sqrt{RT}}$$

$$\frac{K_p}{K_c} = \frac{1}{\sqrt{RT}}$$

11. For fcc unit cell,

$$\text{Radius, } r = \frac{\sqrt{2} \times a}{4} = \frac{\sqrt{2} \times 361}{4} \text{ pm} = 128 \text{ pm}$$

12. Species having the same number of bond pairs and lone pairs are generally isostructural.
BF_4^-, CCl_4, NH_4^+ and PCl_4^+ all have four bond pairs and zero lone pairs, so all of these are isostructural.

> **Note :** In set (a) structure of CO_2 is quite different from NO_2, SiO_2 etc. Similarly in set (b) PCl_3 and $SbCl_3$ have a lone pair but BCl_3 and $AlCl_3$ do not, so they have different structures. In set (c) also NF_3 and PF_3 have lone pair, but remaining two do not have.

13. $N_2 + \frac{1}{2} O_2 \longrightarrow N_2O$

$$\text{or} \quad N{\equiv}N + \frac{1}{2} O{=}O \longrightarrow N{=}N{=}O$$

$$\therefore \quad \Delta H = BE_{N\equiv N} + \frac{1}{2} BE_{O=O} - [BE_{N=N} + BE_{N=O}]$$

$$= 946 + \frac{1}{2} \times 498 - [418 + 607]$$

$$= 1195 - 1025 = +170$$

Resonance energy = Experimental value – calculated value

$$= 82 - 170 = -88 \text{ kJ}$$

14. Concentration $= \dfrac{\text{mass}}{\text{molar mass} \times V\ (\text{mL})}$

$$\therefore \quad [CH_3COOH] = \frac{5 \times 1000}{60 \times 500}$$

[Molar mass of $CH_3COOH = 60 \text{ g mol}^{-1}$]

$$= 0.166 \text{ M}$$

Similarly, $[CH_3COONa] = \frac{7.5 \times 1000}{82 \times 500}$

$= 0.183\ M$

For the buffer of $CH_3COOH—CH_3COONa$,

$$pH = pK_a + \log \frac{[CH_3COONa]}{[CH_3COOH]}$$

$$= 4.76 + \log\left[\frac{0.183}{0.166}\right]$$

$$= 4.76 + \log (1.10)$$

$$= 4.76 + 0.042$$

$$= 4.80$$

$\therefore \qquad 4.76 < pH < 5.0$

15. General reaction for the combustion of alkene is

$$C_nH_{2n} + \frac{3n}{2}O_2 \longrightarrow nCO_2 + nH_2O$$

Given, 6 L alkene require $O_2 = 27\ L$

$\therefore$ 1 L alkene will require $O_2 = \frac{27}{6}\ L$

$= 4.5\ L$ or $\frac{9}{2}\ L$

On comparing the amount of O_2,

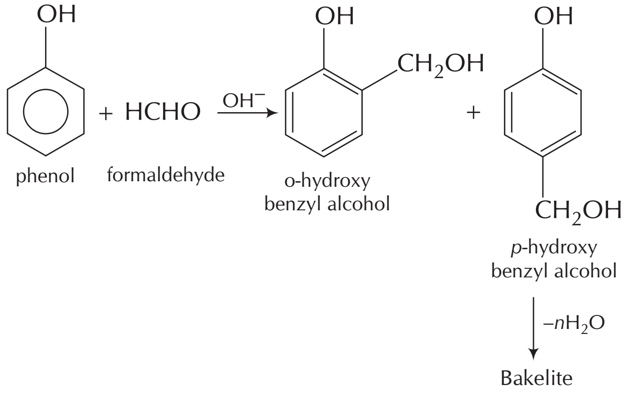
$$\frac{3n}{2} = \frac{9}{2}$$

$\therefore \qquad 3n = 9$

or $\qquad n = 3$

On putting the value of n in general formula of alkene, we get $C_3H_{2\times 3} = C_3H_6$. Hence, the alkene is propene ($CH_3CH{=}CH_2$).

16. When phenol reacts with formaldehyde in the presence of a base, a mixture of *o*- and *p*- benzoyl phenol is obtained, which further undergo condensation polymerisation to give a highly cross-linked polymer, called bakelite.



17. Normal freezing point of water = 273.15 K. In order to prevent freezing at 268 K, let the amount of methanol added be x g.

$\therefore$ Molality, $\qquad m = \frac{x}{32 \times 10} = \frac{x}{320}$

[$\because$ Molar mass of $CH_3OH{=}32\ g\ mol^{-1}$ and mass of $H_2O = V$ of H_2O because density of water $\simeq 1\ g\ mL^{-1}$]

Lowering in freezing point $= K_f \cdot m$

$$273 \cdot 15 - 268 = 1.86 \times \frac{x}{320}$$

$$5.15 = \frac{1.86x}{320}$$

or $\qquad x = \frac{5.15 \times 320}{1.86} = 886.02\ g$

18. Δ_o magnitude depends upon the charge of central metal atom and strength of ligand. Among the given, CN^- is the strongest field ligand and in the complex $[Co(CN)_6]^{3-}$, Co is present as Co^{3+}. So, this complex will exhibit the maximum value of Δ_o.

19. The order of departing nature of halides is

$$I^- > Br^- > Cl^-$$

This is because of large size and low electronegativity and nucleophilicity of I^-.

20. $\frac{2}{3}Al_2O_3 \longrightarrow \frac{4}{3}Al + O_2;\ \Delta_rG = +940\ kJ\ mol^{-1}$

Half cell reactions are $\frac{2}{3}Al_2^{3+} + 4e^- \longrightarrow \frac{4}{3}Al$

$$2O^{2-} \longrightarrow O_2 + 4e^-$$

$$\frac{2}{3}Al_2^{3+} + 2O^{2-} \longrightarrow \frac{4}{3}Al + O_2$$

Number of electrons involved, $n = 4$

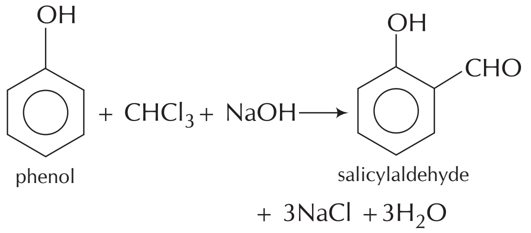
We know that, $\Delta_rG = nFE_{cell}$

$$E_{cell} = \frac{\Delta_rG}{nF} = \frac{940 \times 10^3\ J\ mol^{-1}}{4 \times 96500} = 2.5\ V$$

21. Only those aldehydes undergo Cannizzaro reaction in the presence of concentrated base, which have lack of α-H atom.

CH_3CHO contains three α-H atoms, that's why it does not undergo Cannizzaro's reaction, rather it undergoes aldol condensation.

22. When phenol is treated with chloroform in the presence of alkali, it results in the formation of salicylaldehyde. This reaction is known as Reimer-Tiemann reaction.



23. Internuclear distances in O—O bonds *i.e*, O—O bond length increases as the bond order decreases.

$$O_2(8+8=16) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \pi^* 2p_x^1 \approx \pi^* 2p_y^1$$

Bond order, $BO = \frac{10-6}{2} = 2$

$O_2^+(8+8-1=15)$,

$$BO = \frac{10-5}{2} = 2.5$$

$O_2^-(8+8+1=17)$,

$$BO = \frac{10-7}{2} = 1.5$$

$O_2^{2-}(8+8+2=18)$,

$$BO = \frac{10-8}{2} = 1$$

∴ The order of BO is

$$O_2^{2-} < O_2^- < O_2 < O_2^+$$

and the order of O—O bond length or internuclear distances in O—O bonds is

$$O_2^+ < O_2 < O_2^- < O_2^{2-}$$

Thus, the bond lengths corresponds to

$$1.12 < 1.21 < 1.30 < 1.49$$

24. Rickets is because of the deficiency of vitamin D.

> **Note :** Vitamin D is the only vitamin which is synthesised in the human body.

25. Proton affinity means basicity and the conjugate base of a strong acid is weak and *vice-versa*.

The order of acidity of acids of given base is

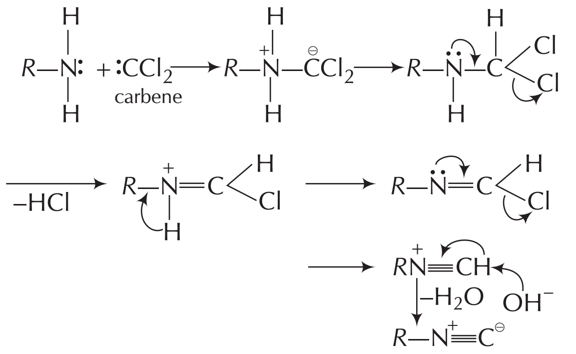
$$NH_3 < H_2S < HF < HI$$

∴ The order of proton affinity (or basicity) is

$$I^- < F^- < HS^- < NH_2^-$$

26. The mechanism of carbylamine reaction is given below

$$CHCl_3 \xrightarrow[\alpha\text{-elimination}]{OH^-} \underset{\text{dichlorocarbene}}{:CCl_2}$$



27. Final concentration, $M = \frac{M_1V_1 + M_2V_2}{V_1 + V_2}$

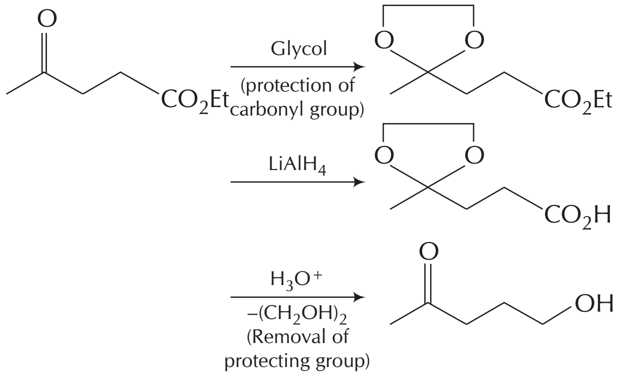
$$= \frac{10 \times 2 + 200 \times 0.5}{200 + 10} = \frac{20 + 100}{210}$$

$$= \frac{120}{210} = 0.57\,M$$

28. Although Cl^- is a weak field ligand but in case of $[PdCl_4]^{2-}$, it pair up the electrons of Pd and results in dsp^2-hybridisation because of the large size of Pd^{2+}.

In all other pairing is not possible, so hybridisation is sp^3 with tetrahedral structure.

29.



30. From Faraday's first law,

Mass of Cu deposited,

$$w = Z\,it = \frac{E}{96500} \cdot i \cdot t = \frac{63}{2 \times 96500} \times 1.5\text{ A} \times 10 \times 60\text{ s}$$

$$= 0.2938\text{ g}$$

JEE Main

Solved Paper 2013

Instructions

- This test consists of 30 questions.
- Each question is allotted 4 marks for correct response.
- Candidates will be awarded marks as stated above for correct response of each question. 1/4 mark will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
- There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted according as per instructions.

---

1. Which of the following complex species is not expected to exhibit optical isomerism?

(a) $[Co(en)_3]^{3+}$ (b) $[Co(en)_2Cl_2]^+$
(c) $[Co(NH_3)_3Cl_3]$ (d) $[Co(en)(NH_3)Cl_2]^+$

2. Which one of the following molecules is expected to exhibit diamagnetic behaviour?

(a) C_2 (b) N_2 (c) O_2 (d) S_2

3. A solution of $(-l)$ 1-chloro-1-phenylethane in toluene racemises slowly in the presence of a small amount of $SbCl_5$, due to the formation of

(a) carbanion (b) carbene
(c) carbocation (d) free radical

4. Given, $E^\circ_{Cr^{3+}/Cr} = -0.74$ V; $E^\circ_{MnO_4^-/Mn^{2+}} = 1.51$ V

$E^\circ_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33$ V; $E^\circ_{Cl/Cl^-} = 1.36$ V

Based on the data given above strongest oxidising agent will be

(a) Cl (b) Cr^{3+}
(c) Mn^{2+} (d) MnO_4^-

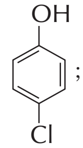
5. A piston filled with 0.04 mole of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of q and W for the process will be ($R = 8.314$ J / mol K log 7.5 = 2.01)

(a) $q = +208$ J, $W = -208$ J
(b) $q = -208$ J, $W = -208$ J
(c) $q = -208$ J, $W = +208$ J
(d) $q = +208$ J, $W = +208$ J

6. The molarity of a solution obtained by mixing 750 mL of 0.5 (M) HCl with 250 mL of 2(M) HCl will be

(a) 0.875 M (b) 1.00 M
(c) 1.75 M (d) 0.0975 M

7. Arrange the following compounds in the order of decreasing acidity



(I)

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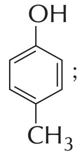

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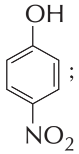

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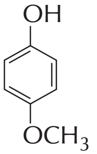


(IV)

(a) II > IV > I > III (b) I > II > III > IV
(c) III > I > II > IV (d) IV > III > I > II

8. For gaseous state, if most probable speed is denoted by C^*, average speed by $\overline{C}$ and mean square speed by C, then for a large number of molecules, the ratios of these speeds are

(a) $C^* : \overline{C} : C = 1.225 : 1.128 : 1$
(b) $C^* : \overline{C} : C = 1.128 : 1.225 : 1$
(c) $C^* : \overline{C} : C = 1 : 1.128 : 1.225$
(d) $C^* : \overline{C} : C = 1 : 1.225 : 1.128$

9. The rate of a reaction double when its temperature changes from 300 K to 310 K. Activation energy of such a reaction will be ($R = 8.314$ JK^{-1} mol^{-1} and log 2 = 0.301)

(a) 53.6 kJ mol^{-1} (b) 48.6 kJ mol^{-1}
(c) 58.5 kJ mol^{-1} (d) 60.5 kJ mol^{-1}

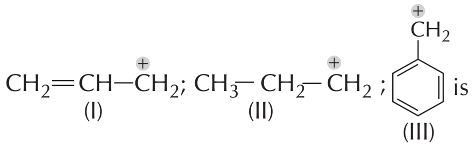
10. A compound with molecular mass 180 is acylated with CH_3COCl to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is

(a) 2 (b) 5 (c) 4 (d) 6

11. Which of the following arrangements does not represent the correct order of the property stated against it?

(a) $V^{2+} < Cr^{2+} < Mn^{2+} < Fe^{2+}$: paramagnetic behaviour
(b) $Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+}$: ionic size
(c) $Co^{3+} < Fe^{3+} < Cr^{3+} < Sc^{3+}$: stability in aqueous solution
(d) Sc < Ti < Cr < Mn : number of oxidation states

12. The order of stability of the following carbocations



$CH_2{=}CH{-}\overset{+}{C}H_2$; $CH_3{-}CH_2{-}\overset{+}{C}H_2$; is
(I) (II) (III)

(a) III > II > I (b) II > III > I
(c) I > II > III (d) III > I > II

13. Consider the following reaction,

$$xMnO_4^- + yC_2O_4^{2-} + zH^+ \longrightarrow xMn^{2+} + 2\,y\,CO_2 + \frac{z}{2}H_2O$$

The values of x, y and z in the reaction are, respectively

(a) 5, 2 and 16 (b) 2, 5 and 8
(c) 2, 5 and 16 (d) 5, 2 and 8

14. Which of the following is the wrong statement?

(a) ONCl and ONO^- are not isoelectronic
(b) O_3 molecule is bent
(c) Ozone is violet-black in solid state
(d) Ozone is diamagnetic gas

15. A gaseous hydrocarbon gives upon combustion 0.72 g of water and 3.08 g of CO_2. The empirical formula of the hydrocarbon is

(a) C_2H_4 (b) C_3H_4
(c) C_6H_5 (d) C_7H_8

16. In which of the following pairs of molecules/ions both the species are not likely to exist?

(a) H_2^+, He_2^{2-} (b) H_2^-, He_2^{2-}
(c) H_2^{2+}, He_2 (d) H_2^-, He_2^{2+}

17. Which of the following exists as covalent crystals in the solid state?

(a) Iodine (b) Silicon
(c) Sulphur (d) Phosphorus

18. Synthesis of each molecule of glucose in photosynthesis involves

(a) 18 molecules of ATP
(b) 10 molecules of ATP
(c) 8 molecules of ATP
(d) 6 molecules of ATP

19. The coagulating power of electrolytes having ions Na^+, Al^{3+} and Ba^{2+} for arsenic sulphide sol increases in the order

(a) $Al^{3+} < Ba^{2+} < Na^+$
(b) $Na^+ < Ba^{2+} < Al^{3+}$
(c) $Ba^{2+} < Na^{2+} < Al^{3+}$
(d) $Al^{3+} < Na^+ < Ba^{2+}$

20. Which of the following represents the correct order of increasing first ionization enthalpy for Ca, Ba, S, Se and Ar

(a) Ca < S < Ba < Se < Ar
(b) S < Se < Ca < Ba < Ar
(c) Ba < Ca < Se < S < Ar
(d) Ca < Ba < S < Se < Ar

21. Energy of an electron is given by

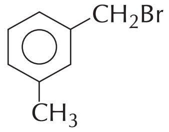
$$E = -\,2.178 \times 10^{-18}\ \text{J}\left(\frac{Z^2}{n^2}\right)$$

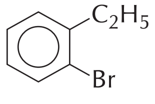
Wavelength of light required to excite an electron in an hydrogen atom from level $n = 1$ to $n = 2$ will be

($h = 6.62 \times 10^{-34}$ Js and $c = 3.0 \times 10^8$ ms^{-1})

(a) 1.214×10^{-7} m
(b) 2.816×10^{-7} m
(c) 6.500×10^{-7} m
(d) 8.500×10^{-7} m

22. Compound (A), C_8H_9Br gives a white precipitate when warmed with alcoholic $AgNO_3$. Oxidation of (A) gives an acid (B), $C_8H_6O_4$. (B) easily forms anyhydride on heating. Identify the compound (A).

(a)


(b)


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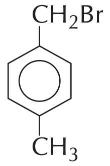

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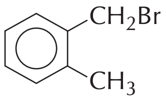


23. Four successive members of the first row transition elements listed below with atomic numbers. Which one of them is expected to have the highest $E^{\circ}_{M^{3+}/M^{2+}}$ value?

(a) Cr (Z = 24) (b) Mn (Z = 25)
(c) Fe (Z = 26) (d) Co (Z = 27)

24. How many litres of water must be added to 1 L of an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2?

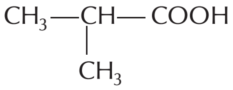
(a) 0.1 L (b) 0.9 L
(c) 2.0 L (d) 9.0 L

25. The first ionisation potential of Na is 5.1 eV. The value of electron gain enthalpy of Na^+ will be

(a) − 2.55 eV (b) − 5.1 eV
(c) − 10.2 eV (d) + 2.55 eV

26. An organic compound *A* upon reacting with NH_3 gives *B*. On heating, *B* gives *C*. *C* in the presence of KOH reacts with Br_2 to give $CH_3CH_2NH_2$. *A* is

(a) CH_3COOH (b) $CH_3CH_2CH_2COOH$

(c) 
$CH_3—\underset{\substack{|\\ CH_3}}{CH}—COOH$
(d) CH_3CH_2COOH

27. Stability of the species Li_2, Li_2^- and Li_2^+ increases in the order of

(a) $Li_2 < Li_2^+ < Li_2^-$ (b) $Li_2^- < Li_2^+ < Li_2$
(c) $Li_2 < Li_2^- < Li_2^+$ (d) $Li_2^- < Li_2 < Li_2^+$

28. An unknown alcohol is treated with the "Lucas reagent" to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism?

(a) Secondary alcohol by S_N1
(b) Tertiary alcohol by S_N1
(c) Secondary alcohol by S_N2
(d) Tertiary alcohol by S_N2

29. The gas leaked from a storage tank of the Union Carbide plant in Bhopal gas tragedy was

(a) Methylisocyanate (b) Methylamine
(c) Ammonia (d) Phosgene

30. Experimentally it was found that a metal oxide has formula $M_{0.98}O$. Metal *M*, present as M^{2+} and M^{3+} in its oxide. Fraction of the metal which exists as M^{3+} would be

(a) 7.01% (b) 4.08%
(c) 6.05% (d) 5.08%

Answers

1. (c)	**2.** (a,b)	**3.** (c)	**4.** (d)	**5.** (a)	**6.** (a)	**7.** (c)	**8.** (c)	**9.** (a)	**10.** (b)
11. (a)	**12.** (d)	**13.** (c)	**14.** (*)	**15.** (d)	**16.** (c)	**17.** (b)	**18.** (a)	**19.** (b)	**20.** (c)
21. (a)	**22.** (d)	**23.** (d)	**24.** (d)	**25.** (b)	**26.** (d)	**27.** (b)	**28.** (b)	**29.** (a)	**30.** (b)

* No option is correct.

Hints and **Solutions**

1. Optical isomerism is exhibited by only those complexes which lacks elements of symmetry.

$[Co(NH_3)_3Cl_3]$ shows facial as well as meridional isomerism. But both the forms contain plane of symmetry. Thus, this complex does not exhibit optical isomerism.

2. $C_2\ (6+6=12) = \sigma 1s^2, \overset{*}{\sigma}\ 1s^2, \sigma 2s^2, \overset{*}{\sigma}\ 2s^2,\ \pi 2p_x^2 \approx \pi 2p_y^2$

Since, all the electrons are paired, it is a diamagnetic species.

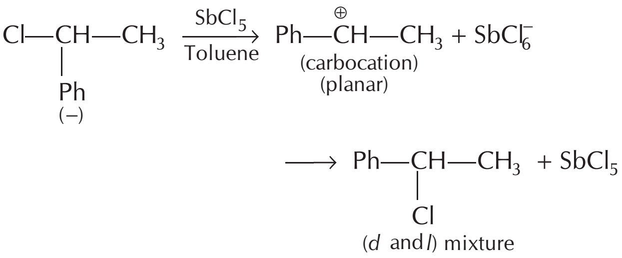
$N_2\ (7+7=14) = \sigma 1s^2, \overset{*}{\sigma}\ 1s^2, \sigma 2s^2,$
$\overset{*}{\sigma} 2s^2,\ \pi 2p_x^2 \approx \pi 2p_y^2, \sigma 2p_z^2$

It is also a diamagnetic species because of the absence of unpaired electrons.

$O_2\ (8+8=16)$

or $S_2 = \sigma 1s^2, \overset{*}{\sigma}\ 1s^2, \sigma 2s^2, \overset{*}{\sigma}\ 2s^2,\ \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2$
$\overset{*}{\pi}\ 2p_x^1 \approx \overset{*}{\pi}\ 2p_y^1$

Due to the presence of two unpaired electrons O_2 and S_2 both are paramagnetic molecules.

3. 
$$Cl—\underset{\substack{|\\ Ph\\ (-)}}{CH}—CH_3 \xrightarrow[\text{Toluene}]{SbCl_5} \underset{\substack{\text{(carbocation)}\\ \text{(planar)}}}{Ph—\overset{\oplus}{C}H—CH_3} + SbCl_6^-$$
$$\longrightarrow \underset{(d\text{ and }l)\text{ mixture}}{Ph—\underset{\substack{|\\ Cl}}{CH}—CH_3} + SbCl_5$$

4. Higher the SRP, better is oxidising agent. Among the given $E^{\circ}_{MnO_4^-/Mn^{2+}}$ is highest, hence MnO_4^- is the strongest oxidising agent.

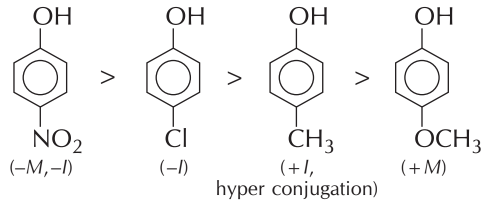
5. The process is isothermal expansion, hence

$$q = -W.$$
$$\Delta E = 0$$
$$q = +208\ J$$
$$W = -208\ J \quad (\textit{expansion work})$$

6. $M_f = \dfrac{M_1V_1 + M_2V_2}{V_1 + V_2} = \dfrac{750 \times 0.5 + 250 \times 2}{750 + 250} = \dfrac{875}{1000}$

$= 0.875\ M$

7.



Electron releasing group decreases while electron withdrawing group increases acidic strength by destabilising and stabilising the phenoxide ion formed respectively.

8. $C^* =$ most probable speed $= \sqrt{\dfrac{2RT}{M}}$

$\overline{C} =$ average speed $= \sqrt{\dfrac{8RT}{\pi M}}$

C = Mean square speed corrected as

$$\text{rms} = \sqrt{\frac{3RT}{M}},$$

$$\overset{*}{C} < \overline{C} < C$$

$$\overset{*}{C} : \overline{C} : C = 1 : \sqrt{\frac{4}{\pi}} : \sqrt{\frac{3}{2}}$$

$$= 1 : 1.128 : 1.225$$

As no option correspond to mean square speed, it is understood as misprint. It should be root mean square speed.

9. From Arrehenius equation,

$$\log \frac{k_2}{k_1} = \frac{-E_a}{2.303\,R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Given, $\dfrac{k_2}{k_1} = 2$; $T_2 = 310$ K, $T_1 = 300$ K

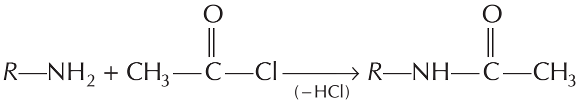
On putting values,

$$\Rightarrow \qquad \log 2 = \frac{-E_a}{2.303 \times 8.314}\left(\frac{1}{310} - \frac{1}{300}\right)$$

$$\Rightarrow \qquad E_a = 53598.6\ J/mol$$

$$= 53.6\ kJ/mol$$

10.



$$R\text{—}NH_2 + CH_3\text{—}\overset{O}{\overset{\|}{C}}\text{—}Cl \xrightarrow[(-HCl)]{} R\text{—}NH\text{—}\overset{O}{\overset{\|}{C}}\text{—}CH_3$$

Since each —$COCH_3$ group displace one H atom in the reaction of one mole of $CH_3\text{—}\overset{O}{\overset{\|}{C}}\text{—}Cl$ with one —NH_2 group, the molecular mass increases with 42 unit. Since the mass increases by $(390 - 180) = 210$ hence the number of —NH_2 group is $\dfrac{210}{42} = 5$.

11. (a) $V^{2+} = 3$ unpaired electrons

$Cr^{2+} = 4$ unpaired electrons

$Mn^{2+} = 5$ unpaired electrons

$Fe^{2+} = 4$ unpaired electrons

Hence, the order of paramagnetic behaviour should be $V^{2+} < Cr^{2+} = Fe^{2+} < Mn^{2+}$

(b) Ionic size decreases from left to right in the same period.

(c) (As per data from NCERT)

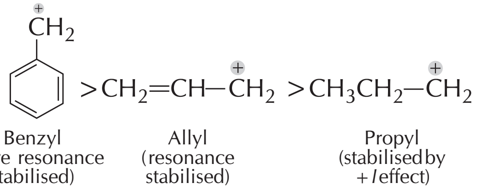
$Co^{3+}/Co^{2+} = 1.97$; $Fe^{3+}/Fe^{2+} = 0.77$;

$Cr^{3+}/Cr^{2+} = -0.41$

Sc^{3+} is highly stable (It does not show + 2).

(d) The oxidation states increases as we go from group 3 to group 7 in the same period.

12. The order of stability of carbocation will be



13. The half equations of the reaction are

$$MnO_4^- \longrightarrow Mn^{2+}$$
$$C_2O_4^{2-} \longrightarrow CO_2$$

The balanced half equations are

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$
$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$$

On equating number of electrons we get

$$2MnO_4^- + 16\,H^+ + 10e^- \longrightarrow 2Mn^{2+} + 8H_2O$$
$$5C_2O_4^{2-} \longrightarrow 10CO_2 + 10e^-$$

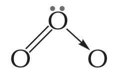
On adding both the equations we get

$$2MnO_4^- + 5C_2O_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 2 \times 5CO_2 + \frac{16}{2}H_2O$$

Thus x, y and z are 2, 5 and 16 respectively.

14. (a) $ONCl = 8 + 7 + 17 = 32e^-$

$ONO^- = 8 + 7 + 8 + 1 = 24e^-$ (correct)

(b) 

Central O atom is sp^2 hybridised with 1 lone pair, so bent shape (correct).

(c) In solid state, ozone is violet-black. (correct).

(d) O_3 has no unpaired electrons, so diamagnetic (correct).

(*) No option is correct.

15. 18 g H_2O contains 2 g H

$\therefore$ 0.72 g H_2O contains 0.08 g H.

44 g CO_2 contains 12 g C

$\therefore$ 3.08 g CO_2 contains 0.84 g C

$$\therefore \quad C : H = \frac{0.84}{12} : \frac{0.08}{1} = 0.07 : 0.08 = 7 : 8$$

$\therefore$ Empirical formula = C_7H_8

16. Species having zero or negative bond order do not exist.

$$H_2^{2+} (1 + 1 - 2 = 0) = \sigma 1s^0$$

Bond order = 0

$$He_2 \ (2 + 2 = 4) = \sigma 1s^2, \overset{*}{\sigma} 1s^2$$

$$\text{Bond order } = \frac{N_b - N_a}{2} = \frac{2-2}{2} = 0$$

So, both H_2^{2+} and He_2 do not exist.

17. Silicon exists as covalent crystal in solid state. (Network like structure, like diamond).

18. $6CO_2 + 12NADPH + 18\ ATP \longrightarrow C_6H_{12}O_6 + 12NADP + 18\ ADP$

19. According to Hardy Schulze rule, greater the charge on oppositely charged ion, greater is its coagulating power. Since arsenic sulphide is a negatively charged sol, thus, the order of coagulating power is $Na^+ < Ba^{2+} < Al^{3+}$.

20. Ionisation energy increases along a period from left to right and decreases down a group. The position of given elements in the Periodic Table is as

2	16	18
Ca	S	Ar
Ba	Se	

Thus, the order of increasing ΔH_{IE_1} is

Ba< Ca< Se< S< Ar

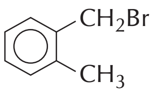
21. $$\Delta E = 2.178 \times 10^{-18} \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = \frac{hc}{\lambda}$$

$$2.178 \times 10^{-18} \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = \frac{6.62 \times 10^{-34} \times 3.0 \times 10^8}{\lambda}$$

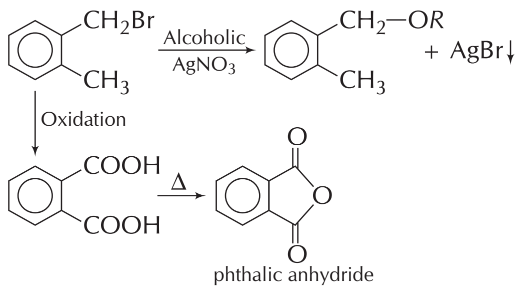
$$\therefore \quad \lambda \approx 1.21 \times 10^{-7} \text{ m}$$

22. Compound *A* gives a precipitate with alcoholic $AgNO_3$ (here white is misprinting because the colour of ppt is light yellow), so it must contains Br in side chain. On oxidation, it gives $C_8H_6O_4$, which shows the presence of two alkyl chains attached directly with the benzene nucleus.

Since compound *B* gives anhydride on heating, the two alkyl substituent must occupy adjacent (1, 2) positions. Thus, *A* must be



and the reactions are as follows



23. SRP value normally increases from left to right in the period of *d*-block elements. Some SRP value are exceptionally higher due to stability of product ion. *e.g.*,

$$E^\circ_{Mn^{3+}/Mn^{2+}} = +1.57 \text{ V}; \ E^\circ_{Co^{3+}/Co^{2+}} = +\ 1.97 \text{ V}.$$

Thus, $E^\circ_{M^{3+}/M^{2+}}$ is highest for Co.

24. $pH = 1 \ \therefore \ [H^+] = 10^{-1} = 0.1$ M

$pH = 2 \ \therefore \ [H^+] = 10^{-2} = 0.01$ M

For dilution of HCl, $M_1V_1 = M_2V_2$

$$0.1 \times 1 = 0.01 \times V_2$$

$$V_2 = 10 \text{ L}$$

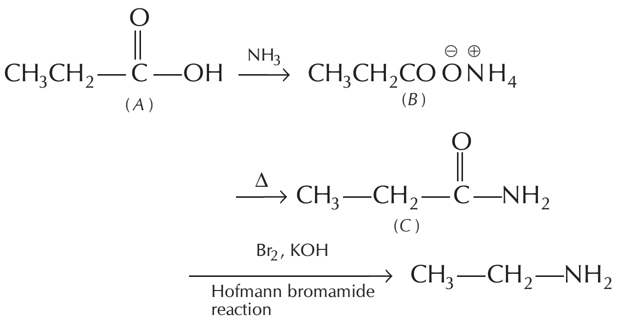
Volume of water to be added = 10 − 1 = 9 L

25. $Na \longrightarrow Na^+ + e^-$ (First IE)

$Na^+ + e^- \longrightarrow Na$ (Electron gain enthalpy of Na^+)

Because reaction is reverse so,

$$\Delta H(e_g) = -\ 5.1 \text{ eV}$$

26. 

$$\underset{(A)}{CH_3CH_2-\overset{\overset{\large O}{\|}}{C}-OH} \xrightarrow{NH_3} \underset{(B)}{CH_3CH_2CO\overset{\ominus}{O}\overset{\oplus}{N}H_4}$$

$$\xrightarrow{\Delta} \underset{(C)}{CH_3-CH_2-\overset{\overset{\large O}{\|}}{C}-NH_2}$$

$$\xrightarrow[\text{Hofmann bromamide reaction}]{Br_2,\ KOH} CH_3-CH_2-NH_2$$

27. Li_2 $(3+3=6)=\sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{4-2}{2} = 1$$

Li_2^+ $(3+3-1=5)=\sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^1$

$$\text{Bond order} = \frac{3-2}{2} = \frac{1}{2} = 0.5$$

Li_2^- $(3+3+1=7)=\sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2 \; \overset{*}{\sigma} 2s^1$

$$\text{Bond order} = \frac{4-3}{2} = \frac{1}{2} = 0.5$$

Stability order is $Li_2 > Li_2^+ > Li_2^-$ (because Li_2^- have more number of electrons in antibonding orbitals which destabilises the species).

28. The reaction of alcohol with Lucas reagent is mostly an S_N1 reaction and the rate of reaction is directly proportional to the stability of carbocation formed in the reaction. Since 3° R—OH forms 3° carbocation (most stable) hence it will react fastest.

29. Methyl isocyanate $CH_3—N═C═O$ (MIC gas) gas was leaked from the storage tank of the Union Carbide plant in Bhopal gas tragedy.

30. $M_{0.98}O$

Consider one mole of the oxide.

Moles of $M = 0.98$ moles of $O^{2-} = 1$

Let moles of $M^{3+} = x$

$\Rightarrow$ Moles of $M^{2+} = 0.98 - x$

$\Rightarrow$ On balancing charge,

$$(0.98 - x) \times 2 + 3x - 2 = 0$$

$$\Rightarrow \quad 1.96 - 2x + 3x - 2 = 0$$

$$\Rightarrow \quad x = 0.04$$

$$\Rightarrow \text{Percentage of } M^{3+} = \frac{0.04}{0.98} \times 100$$

$$= 4.08\%$$

Solved Paper 2014

JEE Main

Joint Entrance Examination

Instructions

- This test consists of 30 questions.
- Each question is allotted 4 marks for correct response.
- Candidates will be awarded marks as stated above for correct response of each question. 1/4 mark will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
- There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted according as per instructions.

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1. The correct set of four quantum numbers for the valence electrons of rubidium atom $(Z = 37)$ is

(a) $5, 0, 0, +\frac{1}{2}$ (b) $5, 1, 0, +\frac{1}{2}$

(c) $5, 1, ,1, +\frac{1}{2}$ (d) $5, 0, 1, +\frac{1}{2}$

2. If Z is a compressibility factor, van der Waals' equation at low pressure can be written as

(a) $Z = 1 + \frac{RT}{pb}$ (b) $Z = 1 - \frac{a}{VRT}$

(c) $Z = 1 - \frac{pb}{RT}$ (d) $Z = 1 + \frac{pb}{RT}$

3. CsCl crystallises in body centred cubic lattice. If a its edge length, then which of the following expressions is correct?

(a) $r_{\text{Cs}^+} + r_{\text{Cl}^-} = 3a$

(b) $r_{\text{Cs}^+} + r_{\text{Cl}^-} = \frac{3a}{2}$

(c) $r_{\text{Cs}^+} + r_{\text{Cl}^-} = \frac{\sqrt{3}}{2}a$

(d) $r_{\text{Cs}^+} + r_{\text{Cl}^-} = \sqrt{3}a$

4. For the estimation of nitrogen, 1.4 g of an organic compound was digested by Kjeldahl's method and the evolved ammonia was absorbed in 60 mL of $\frac{M}{10}$ sulphuric acid. The unreacted acid required 20 mL of $M/10$ sodium hydroxide for complete neutralisation. The percentage of nitrogen in the compound is

(a) 6% (b) 10% (c) 3% (d) 5%

5. Resistance of 0.2 M solution of an electrolyte is 50 Ω. The specific conductance of the solution of 0.5 M solution of same electrolyte is 1.4 S m^{-1} and resistance of same solution of the same electrolyte is 280 Ω. The molar conductivity of 0.5 M solution of the electrolyte in $\text{Sm}^2\text{mol}^{-1}$ is

(a) 5×10^{-4} (b) 5×10^{-3} (c) 5×10^{3} (d) 5×10^{2}

6. For the complete combustion of ethanol, $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$, the amount of heat produced as measured in bomb calorimeter, is 1364.47 kJ mol^{-1} at 25°C. Assuming ideality of the enthalpy of combustion, $\Delta_C H$, for the reaction will be $(R = 8.314 \text{ JK}^{-1}\text{mol}^{-1})$

(a) $-1366.95 \text{kJ mol}^{-1}$ (b) $-1361.95 \text{kJ mol}^{-1}$

(c) $-1460.50 \text{kJ mol}^{-1}$ (d) $-1350.50 \text{kJ mol}^{-1}$

7. The equivalent conductance of NaCl at concentration C and at infinite dilution are λ_C and λ_∞, respectively. The correct relationship between λ_C and λ_∞ is given as (where, the constant B is positive)

(a) $\lambda_C = \lambda_\infty + (B)C$
(b) $\lambda_C = \lambda_\infty - (B)C$
(c) $\lambda_C = \lambda_\infty - (B)\sqrt{C}$
(d) $\lambda_C = \lambda_\infty + (B)\sqrt{C}$

8. Consider separate solution of 0.500 M $C_2H_5OH\,(aq)$, 0.100 M $Mg_3(PO_4)_2\,(aq)$, 0.250 M $KBr(aq)$ and 0.125 M $Na_3PO_4\,(aq)$ at 25°C. Which statement is true about these solution, assuming all salts to be strong electrolytes?

(a) They all have the same osmotic pressure
(b) 0.100 M $Mg_3(PO_4)_2(aq)$ has the highest osmotic pressure
(c) 0.125 M $Na_3PO_4(aq)$ has the highest osmotic pressure
(d) 0.500 M $C_2H_5OH\,(aq)$ has the highest osmotic pressure

9. For the reaction,

$$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$$

if $K_p = K_C(RT)^x$

where the symbols have usual meaning, then the value of x is (assuming ideality)

(a) -1
(b) $-\frac{1}{2}$
(c) $\frac{1}{2}$
(d) 1

10. For the non-stoichiometric reaction $2A + B \rightarrow C + D$, the following kinetic data were obtained in three separate experiments, all at 298 K.

	Initial concentration (A)	Initial concentration (B)	Initial rate of formation of C (mol $L^{-1}S^{-1}$)
(i)	0.1 M	0.1 M	1.2×10^{-3}
(ii)	0.1 M	0.2 M	1.2×10^{-3}
(iii)	0.2 M	0.1 M	2.4×10^{-3}

The rate law for the formation of C is

(a) $\frac{dc}{dt} = k[A]\,[B]$
(b) $\frac{dc}{dt} = k[A]^2[B]$
(c) $\frac{dc}{dt} = k[A][B]^2$
(d) $\frac{dc}{dt} = k[A]$

11. Among the following oxoacids, the correct decreasing order of acid strength is

(a) $HOCl > HClO_2 > HClO_3 > HClO_4$
(b) $HClO_4 > HOCl > HClO_2 > HClO_3$
(c) $HClO_4 > HClO_3 > HClO_2 > HOCl$
(d) $HClO_2 > HClO_4 > HClO_3 > HOCl$

12. The metal that can not be obtained by electrolysis of an aqueous solution of its salts is

(a) Ag
(b) Ca
(c) Cu
(d) Cr

13. The octahedral complex of a metal ion M^{3+} with four monodentate ligands L_1, L_2, L_3 and L_4 absorb wavelengths in the region of red, green, yellow and blue, respectively. The increasing order of ligand strength of the four ligands is

(a) $L_4 < L_3 < L_2 < L_1$
(b) $L_1 < L_3 < L_2 < L_4$
(c) $L_3 < L_2 < L_4 < L_1$
(d) $L_1 < L_2 < L_4 < L_3$

14. Which of the following properties is not shown by NO?

(a) It is diamagnetic in gaseous state
(b) It is a neutral oxide
(c) It combines with oxygen to form nitrogen dioxide
(d) It is bond order is 2.5

15. In which of the following reactions H_2O_2 acts as a reducing agent?

I. $H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$
II. $H_2O_2 - 2e^- \longrightarrow O_2 + 2H^+$
III. $H_2O_2 + 2e^- \longrightarrow 2OH^-$
IV. $H_2O_2 + 2OH^- - 2e^- \longrightarrow O_2 + 2H_2O$

(a) I and II
(b) III and IV
(c) I and III
(d) II and IV

16. The correct statement for the molecule CsI_3 is

(a) it is a covalent molecule
(b) it contains Cs^+ and I_3^-
(c) it contains Cs^{3+} and I^- ions
(d) it contains Cs^+, I^- and lattice I_2 molecule

17. The ratio of masses of oxygen and nitrogen of a particular gaseous mixture is 1 : 4. The ratio of number of their molecule is

(a) 1 : 4
(b) 7 : 32
(c) 1 : 8
(d) 3 : 16

18. Given below are the half-cell reactions

$$Mn^{2+} + 2e^- \longrightarrow Mn\,; \quad E^\circ = -1.18 \text{ eV}$$

$$2\,(Mn^{3+} + e^- \longrightarrow Mn^{2+})\,; \quad E^\circ = +1.51 \text{eV}$$

The E° for $3Mn^{2+} \longrightarrow Mn + 2Mn^{3+}$ will be

(a) -2.69 V; the reaction will not occur
(b) -2.69 V; the reaction will occur
(c) -0.33 V; the reaction will not occur
(d) -0.33 V; the reaction will occur

19. Which series of reactions correctly represents chemical relations related to iron and its compound?

(a) $Fe \xrightarrow{\text{Dil } H_2SO_4} FeSO_4 \xrightarrow{H_2SO_4,\,O_2} Fe_2(SO_4)_3 \xrightarrow{\text{Heat}} Fe$
(b) $Fe \xrightarrow{O_2,\text{ Heat}} FeO \xrightarrow{\text{Dil } H_2SO_4} FeSO_4 \xrightarrow{\text{Heat}} Fe$
(c) $Fe \xrightarrow{Cl_2,\text{ Heat}} FeCl_3 \xrightarrow{\text{Heat, air}} FeCl_2 \xrightarrow{Zn} Fe$
(d) $Fe \xrightarrow{O_2,\text{ Heat}} Fe_3O_4 \xrightarrow{CO,\ 600^\circ C} FeO \xrightarrow{CO,\ 700^\circ C} Fe$

20. The equation which is balanced and represents the correct product(s) is

(a) $Li_2O + 2KCl \longrightarrow 2LiCl + K_2O$

(b) $[CoCl(NH_3)_5]^+ + 5H^+ \longrightarrow Co^{2+} + 5NH_4^+ + Cl^-$

(c) $[Mg(H_2O)_6]^{2+} + (EDTA)^{4-} \xrightarrow{\text{Excess NaOH}} [Mg(EDTA)]^{2+} + 6H_2O$

(d) $CuSO_4 + 4KCN \longrightarrow K_2[Cu(CN)_4] + K_2SO_4$

21. In S_N2 reactions, the correct order of reactivity for the following compounds $CH_3Cl, CH_3CH_2Cl, (CH_3)_2CHCl$ and $(CH_3)_3CCl$ is

(a) $CH_3Cl > (CH_3)_2CHCl > CH_3CH_2Cl > (CH_3)_3CCl$

(b) $CH_3Cl > CH_3CH_2Cl > (CH_3)_2CHCl > (CH_3)_3CCl$

(c) $CH_3CH_2Cl > CH_3Cl > (CH_3)_2CHCl > (CH_3)_3CCl$

(d) $(CH_3)_2CHCl > CH_3CH_2Cl > CH_3Cl > (CH_3)_3CCl$

22. On heating an aliphatic primary amine with chloroform and ethanolic potassium hydroxide, the organic compound formed is

(a) an alkanol

(b) an alkanediol

(c) an alkyl cyanide

(d) an alkyl isocyanide

23. The most suitable reagent for the conversion of $R—CH_2—OH \longrightarrow R—CHO$ is

(a) $KMnO_4$

(b) $K_2Cr_2O_7$

(c) CrO_3

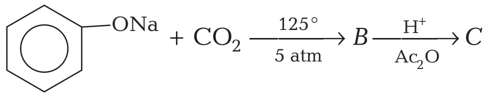
(d) PCC (pyridinium chlorochromate)

24. The major organic compound formed by the reaction of 1,1,1-trichloroethane with silver powder is

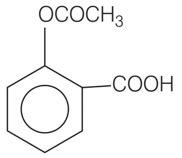
(a) acetylene (b) ethene

(c) 2-butyne (d) 2-butene

25. Sodium phenoxide when heated with CO_2 under pressure at 125°C yields a product which on acetylation produces *C*.



The major product *C* would be

(a)


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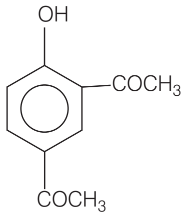
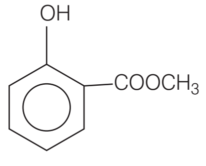
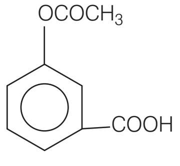


(c)


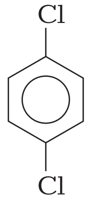
(d)


26. Considering the basic strength of amines in aqueous solution, which one has the smallest pK_b value?

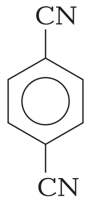
(a) $(CH_3)_2NH$ (b) CH_3NH_2

(c) $(CH_3)_3N$ (d) $C_6H_5NH_2$

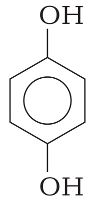
27. For which of the following molecule significant $\mu \neq 0$?



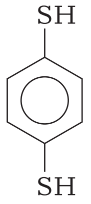
I



II



III



IV

(a) Only I (b) I and II (c) Only III (d) III and IV

28. Which one is classified as a condensation polymer?

(a) Dacron (b) Neoprene (c) Teflon (d) Acrylonitrile

29. Which one of the following bases is not present in DNA?

(a) Quinoline (b) Adenine (c) Cytosine (d) Thymine

30. In the reaction,

$$CH_3COOH \xrightarrow{LiAlH_4} A \xrightarrow{PCl_5} B \xrightarrow{\text{Alc. KOH}} C$$

The product *C* is

(a) acetaldehyde (b) acetylene

(c) ethylene (d) acetyl chloride

Answers

1. (a) **2.** (b) **3.** (c) **4.** (b) **5.** (a) **6.** (a) **7.** (c) **8.** (a) **9.** (b) **10.** (d)
11. (c) **12.** (b) **13.** (b) **14.** (a) **15.** (d) **16.** (b) **17.** (b) **18.** (a) **19.** (d) **20.** (b)
21. (b) **22.** (d) **23.** (d) **24.** (c) **25.** (a) **26.** (a) **27.** (d) **28.** (a) **29.** (a) **30.** (c)

Solutions

1. Given, Atomic number of Rb, $Z = 37$

Thus, its electronic configuration is $[\mathrm{Kr}]\,5s^1$. Since the last electron or valence electron enter in $5s$ subshell.

So, the quantum numbers are

$$n = 5,$$
$$l = 0 \text{ (from } s \text{ orbital)},$$
$$m = 0 \; (\because m = +l \text{ to } -l),$$
$$s = +\frac{1}{2} \text{ or } -\frac{1}{2}$$

2. *To solve this problem, the stepwise approach required i.e.,*

(i) Write the van der Waals' equation, then apply the condition that at low pressure, volume become high, i.e.,

$$V - b \simeq V$$

(ii) Now calculate the value of compressibility factor (Z).
$[Z = pV / RT]$

According to van der Waals' equation,

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

At low pressure, $\left(p + \frac{a}{V^2}\right)V = RT$

$$pV + \frac{a}{V} = RT$$
$$pV = RT - \frac{a}{V}$$

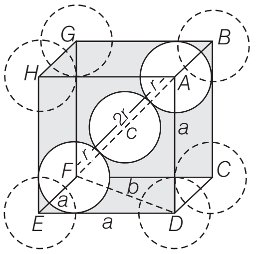
Divide both sides by RT, $\frac{pV}{RT} = 1 - \frac{a}{RTV}$

3. In CsCl, Cl^- lie at corners of simple cube and Cs^+ at the body centre, Hence, along the body diagonal, Cs^+ and Cl^- touch each other so,

$$r_{Cs^+} + r_{Cl^-} = 2r$$

Calculation of *r*

In ΔEDF,



Body centred cubic unit cell

$$FD = b = \sqrt{a^2 + a^2} = \sqrt{2}\,a$$

In ΔAFD,

$$c^2 = a^2 + b^2 = a^2 + (\sqrt{2}\,a)^2$$
$$= a^2 + 2a^2$$
$$c^2 = 3a^2$$
$$c = \sqrt{3}\,a$$

As Δ AFD is an equilateral triangle

$$\sqrt{3}\,a = 4r \;\Rightarrow\; r = \frac{\sqrt{3}\,a}{4}$$

$$\therefore \quad r_{Cs^+} + r_{Cl} = 2r = 2 \times \frac{\sqrt{3}}{4}a = \frac{\sqrt{3}}{2}a$$

4. *This problem is based on the estimation of percentage of* N *in organic compound using Kjeldahl's method. Use the concept of stoichiometry and follow the steps given below to solve the problem.*

(i) Write the balanced chemical reaction for the conversion of N *present in organic compound to ammonia, ammonia to ammonium sulphate and ammonium sulphate to sodium sulphate.*

(ii) Calculate millimoles (m moles) of N *present in organic compound followed by mass of* N *present in organic compound using the concept of stoichiometry.*

(iii) At last, calculate % of N *present in organic compound using formula*

$$\%\text{ of N} = \frac{\text{Mass of N} \times 100}{\text{Mass of organic compound}}$$

Mass of organic compound = 1.4 g

Let it contain x mmole of N atom.

$$\text{Organic compound} \longrightarrow \underset{x \text{ m mole}}{NH_3}$$

$$2NH_3 + \underset{\substack{6 \text{ m mole} \\ \text{initially taken}}}{H_2SO_4} \longrightarrow (NH_4)_2SO_4 \qquad \text{...(i)}$$

$$H_2SO_4 + 2\,NaOH \longrightarrow Na_2SO_4 + 2H_2O \qquad \text{...(ii)}$$

2 mmole NaOH reacted.

Hence, mmoles of H_2SO_4 reacted in Eq. (ii) = 1

$\Rightarrow$ mmoles of H_2SO_4 reacted from Eq. (i) = 6 − 1 = 5 mmoles

$\Rightarrow$ mmoles of NH_3 in Eq. (i) = 2 × 5 = 10 mmoles

$\Rightarrow$ mmoles of N atom in the organic compound = 10 mmoles

$\Rightarrow$ Mass of N = $10 \times 10^{-3} \times 14 = 0.14$ g

$$\%\text{ of N} = \frac{\text{Mass of N present in organic compound}}{\text{Mass of organic compound}} \times 100$$

$$\Rightarrow \quad \%\text{ of N} = \frac{0.14}{1.4} \times 100 = 10\%$$

5. *In order to solve the problem, calculate the value of cell constant of the first solution and then use this value of cell constant to calculate the value of k of second solution. Afterwards, finally calculate molar conductivity using value of k and m.*

For first solution, $\quad k = 1.4\ \mathrm{Sm^{-1}},\ R = 50\,\Omega,\ M = 0.2$

Specific conductance $(\kappa) = \frac{1}{R} \times \frac{l}{A}$

$$1.4\ \mathrm{S\,m^{-1}} = \frac{1}{50} \times \frac{l}{A}$$
$$\frac{l}{A} = 50 \times 1.4\ \mathrm{m^{-1}}$$

For second solution, $\quad R = 280,\ \frac{l}{A} = 50 \times 1.4\ \mathrm{m^{-1}}$

$$\kappa = \frac{1}{280} \times 1.4 \times 50 = \frac{1}{4}$$

Now, molar conductivity

$$\lambda_m = \frac{\kappa}{1000 \times m}$$
$$= \frac{1/4}{1000 \times 0.5} = \frac{1}{2000}$$
$$= 5 \times 10^{-4}\ \mathrm{Sm^2mol^{-1}}$$

6. $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$

$$\Delta U = -1364.47 \text{ kJ/mol}$$
$$\Delta H = \Delta U + \Delta n_g RT$$
$$\Delta n_g = -1$$
$$\Delta H = -1364.47 + \frac{-1 \times 8.314 \times 298}{1000}$$

[Here, value of R in unit of J must be converted into kJ]

$$= -1364.47 - 2.4776$$
$$= -1366.94 \text{ kJ/mol}$$

During solving such problem, students are advised to give much importance to unit conversion. As here, value of R (8.314 $J K^{-1} mol^{-1}$) in $JK^{-1}mol^{-1}$ must be converted into kJ by dividing the unit by 1000.

7. According to Debye Huckel Onsager equation,

$$\lambda_C = \lambda_\infty - B\sqrt{C}$$

where, λ_C = limiting equivalent conductivity at concentration C
λ_∞ = limiting equivalent conductivity at infinite dilution
C = concentration

8. *This problem includes concept of colligative properties (osmotic pressure here) and van't Hoff factor. Calculate the effective molarity of each solution.*
i.e., effective molarity = van't Hoff factor × molarity

0.5 M $C_2H_5OH\,(aq)$ $i = 1$
Effective molarity = 0.5

0.25 M KBr (aq) $i = 2$
Effective molarity = 0.5 M

0.1 M $Mg_3(PO_4)_2(aq)$ $i = 5$
Effective molarity = 0.5 M

0.125 M $Na_3PO_4(aq)$ $i = 4$
Effective molarity = 0.5 M

Hence, all colligative properties are same.

Note *This equation is solved by assuming that the examiner has taken* $Mg_3(PO_4)_2$ *to be completely soluble. However, the fact is that it is insoluble (sparingly soluble).*

9. For the given reaction, $\Delta n_g = n_p - n_R$

where, n_p = number of moles of products
n_R = number of moles of reactants

$$K_p = K_c(RT)^{\Delta n_g}$$
$$\Delta n_g = -\frac{1}{2}$$

10. *This problem can be solved by determining the order of reaction wrt each reactant and then writing rate law equation of the given equation accordingly as*

$$r = \frac{dc}{dt} = k[A]^x[B]^y$$

where, x = order of reaction wrt A
y = order of reaction wrt B

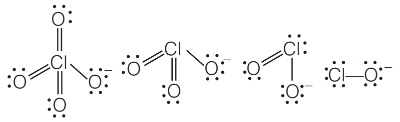
$$1.2 \times 10^{-3} = k(0.1)^x(0.1)^y$$
$$1.2 \times 10^{-3} = k(0.1)^x(0.2)^y$$
$$2.4 \times 10^{-3} = k(0.2)^x(0.1)^y$$
$$R = k[A]^1[B]^0$$

As shown above, rate of reaction remains constant as the concentration of reactant (B) changes from 0.1 M to 0.2 M and becomes double when concentration of A change from 0.1 to 0.2 (*i.e.,* doubled).

11. **Decreasing order of strength of oxoacids**

$$HClO_4 > HClO_3 > HClO_2 > HOCl$$

Reason Consider the structures of conjugate bases of each oxoacids of chlorine.



Negative charge is more delocalised on ClO_4^- due to resonance, hence, ClO_4^- is more stable (and less basic).

Hence, we can say as the number of oxygen atom(s) around Cl-atom increases as oxidation number of Cl-atom increases and thus, the ability of loose the H^+ increases.

12. Higher the position of element in the electrochemical series, more difficult is the reduction of its cations.

If $Ca^{2+}(aq)$ is electrolysed, water is reduced in preference to it. Hence, it cannot be reduced electrolytically from their aqueous solution.

$$Ca^{2+}(aq) + H_2O \longrightarrow Ca^{2+} + OH^- + H_2\uparrow$$

13. *Arrange the complex formed by different ligands L_1, L_2, L_3 and L_4 according to wavelength of their absorbed light, then use the following relation to answer the question.*

Ligand field strength ∝ Energy of light absorbed

$$\propto \frac{1}{\text{Wavelength of light absorbed}}$$

λ	L_1	L_2	L_3	L_4
Absorbed light	Red	Green	Yellow	Blue

Wavelength of absorbed light decreases

∴ Increasing order of energy of wavelengths absorbed reflect greater extent of crystal-field splitting. Hence, higher field strength of the ligand.

Energy Blue (L_4) > green (L_2) > yellow (L_3) > red (L_1)

∴ $L_4 > L_2 > L_3 > L_1$ in field strength of ligands.

14. NO is paramagnetic in gaseous state because in gaseous state, it has one unpaired electron.

Total number of electron present = $7 + 8 = 15\ e^-$.

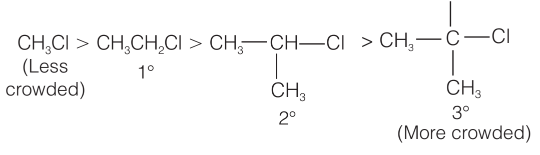
Hence, there must be the presence of unpaired electron in gaseous state while in liquid state, it dimerises due to unpaired electron.

15. Release of electron is known as reduction. So, H_2O_2 acts as reducing agent when it releases electrons.

Here, in reaction (II) and (IV), H_2O_2 releases two electrons, hence reaction (II) and (IV) is known as reduction.

In reaction (I) and (III), two electrons are being added so (I) and (III) represents oxidation.

16. I_3^- is an ion made up of I_2 and I^- which has linear shape.



$$CH_3Cl > CH_3CH_2Cl > CH_3-\underset{\underset{CH_3}{|}}{CH}-Cl > CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Cl$$

while Cs^+ is an alkali metal cation.

17.
$$\frac{n_{O_2}}{n_{N_2}} = \frac{\dfrac{(m_{O_2})}{(M_{O_2})}}{\dfrac{(m_{N_2})}{(M_{N_2})}}$$

where, m_{O_2} = given mass of O_2
m_{N_2} = given mass of N_2
M_{O_2} = molecular mass of O_2
M_{N_2} = molecular mass of N_2
n_{O_2} = number of moles of O_2
n_{N_2} = number of moles of N_2

$$= \left[\frac{m_{O_2}}{m_{N_2}}\right]\frac{28}{32} = \frac{1}{4} \times \frac{28}{32} = \frac{7}{32}$$

18. Standard electrode potential of reaction $[E^0]$ can be calculated as

$$E^0_{\text{cell}} = E_R - E_P$$

where, E_R = SRP of reactant
E_P = SRP of product

If E^0_{cell} = +ve, then reaction is spontaneous, otherwise non-spontaneous.

$$Mn^{3+} \xrightarrow{E_1^\circ = 1.51\,V} Mn^{2+}$$
$$Mn^{2+} \xrightarrow{E_2^\circ = -1.18\,V} Mn$$

$\therefore$ For Mn^{2+} disproportionation,

$$E^\circ = -1.51\,V - 1.18\,V = -2.69\,V < 0$$

19. *Analyse each reaction given in the question and choose the correct answer on the basis of oxidation state and stability of iron compounds. Use the concept of Ellingham diagram to solve this problem.*

The correct reactions are as follows

(a) $Fe + dil.H_2SO_4 \longrightarrow FeSO_4 + H_2$

$$H_2SO_4 + 2FeSO_4 + \frac{1}{2}O_2 \longrightarrow Fe_2(SO_4)_3 + H_2O$$
$$Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3\,(s) + 3SO_3\uparrow$$

The given reaction is incorrect in question.

(b) $Fe \xrightarrow{O_2} FeO$ (It could also be Fe_2O_3 or Fe_3O_4)

$$FeO + H_2SO_4 \xrightarrow{\Delta} FeSO_4 + H_2O$$
$$2FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2 + SO_3$$

(c) $Fe \xrightarrow[Cl_2]{\Delta} FeCl_3 \xrightarrow[Air]{\Delta}$ No reaction (It cannot give $FeCl_2$)

(d) $Fe \xrightarrow[\Delta]{O_2} Fe_3O_4 \xrightarrow[600°C]{CO} FeO \xrightarrow[700°C]{CO} Fe$

This is correct reaction.

20. *This problem is based on conceptual mixing of properties of lithium oxide and preparation, properties of coordination compounds. To answer this question, keep in mind that on adding acid ammine complexes get destroyed.*

(a) $Li_2O + KCl \longrightarrow 2LiCl + K_2O$

This is wrong equation, since a stronger base K_2O cannot be generated by a weaker base Li_2O.

(b) $[CoCl(NH_3)_5]^+ + 5H^+ \longrightarrow Co^{2+}(aq) + 5NH_4^+ + Cl^-$

This is correct. All ammine complexes can be destroyed by adding $H^\oplus$. Hence, on adding acid to $[CoCl(NH_3)_5]$, it gets converted to Co^{2+} (*aq*), NH_4^+ and Cl^-.

(c) $[Mg(H_2O)_6]^{2+} + EDTA^{4-} \xrightarrow[\text{excess}]{OH^-} [Mg(EDTA)]^{2+} + 6H_2O$

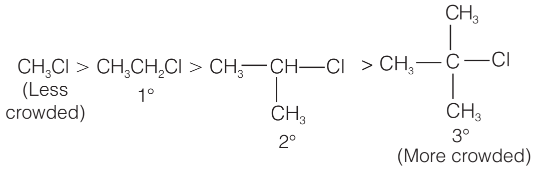
This is wrong, since the formula of complex must be $[Mg(EDTA)]^{2+}$ as EDT.

(d) The 4th reaction is incorrect. It can be correctly represented as

$$2CuSO_4 + 10KCN \longrightarrow 2K_3[Cu(CN)_4] + 2K_2SO_4 + (CN)_2\uparrow$$

21. *Steric hindrance (crowding) is the basis of S_N2 reaction, by using which we can arrange the reactant in correct order of their reactivity towards S_N2 reaction.*

$$\text{Rate of } S_N2 \propto \frac{1}{\text{Steric crowding of 'C'}}$$



$$CH_3Cl > CH_3CH_2Cl > CH_3-CH(CH_3)-Cl > CH_3-C(CH_3)_2-Cl$$

(Less crowded) 1° 2° 3° (More crowded)

As steric hinderance (crowding) increases, rate of S_N2 reaction decreases.

Note *The order of reactivity towards S_N2 reaction for alkyl halides is*

Primary halides (1°) > Secondary halides (2°) > Tertiary halides (3°)

22. This reaction is an example of carbylamine reaction which includes conversion of amine to isocyanide.

$$\underset{1°\text{ amine}}{R-\ddot{N}H_2} + CHCl_3 \xrightarrow[KOH]{C_2H_5OH} \underset{\text{Alkyl isocyanide}}{R-\overset{+}{N}\equiv\overset{-}{C}:}$$

Note *This reaction include rearrangement reaction of nitrene in which migration of alkyl group from carbon to nitrogen takes place.*

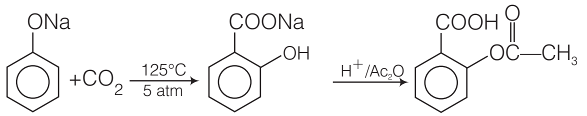
23. $R-CH_2OH \xrightarrow{PCC} R-CH=O$

Pyridinium chlorochromate is the mild oxidising agent which causes conversion of alcohol to aldehyde stage. While others causes conversion of alcohol to acid.

24. The reaction is

$$2CH_3-CCl_3 \xrightarrow[\Delta]{6Ag} \underset{\text{But-2-yne}}{CH_3-C\equiv C-CH_3} + 6AgCl$$

25. It is a Kolbe Schmidt reaction.



Aspirin (pain killer)

The second step of the reaction is an example of acetylation reaction.

26. *This problem can be solved by using the concept of effect of steric hindrance, hydration and H-bonding in basic strength of amines.*

Order of basic strength of aliphatic amine in aqueous solution is as follows (order of K_b)

$$(CH_3)_2\ddot{N}H > CH_3\ddot{N}H_2 > (CH_3)_3\ddot{N} > C_6H_5\ddot{N}H_2$$

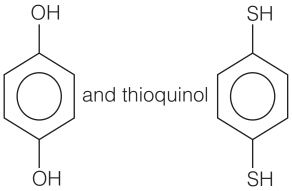
As we know, $pK_b = -\log K_b$

So, $(CH_3)_2\ddot{N}H$ will have smallest pK_b value.

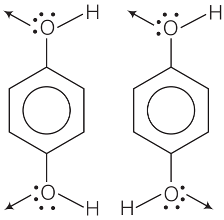
In case of phenyl amine, N is attached to sp^2 hybridised carbon. Hence, it has highest pK_b and least basic strength.

27. *Draw the structures of organic compounds indicating net dipole moment which includes lone pair and bond angle also.*

In the quinol and thioquinol

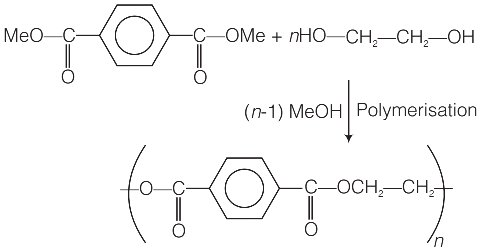


—OH groups and —SH groups do not cancel their dipole moment as they exist in different confirmation.



same as in thioquinol.

28. Dacron is a condensation polymer of ethylene glycol and methyl terepthalate. Formation of dacron can be shown as



Dacron

Here, elimination of MeOH occurs as a by product. So, this reaction is known as condensation polymerisation.

29. Quinoline is an alkaloid. It is not present in DNA. DNA has four nitrogen bases in adenine, guanine, cytosine and thymine.

30. *This problem is based on successive reduction, chlorination and elimination reaction. To solve such problem, use the function of the given reagents.*

(i) $LiAlH_4$ *causes reduction* (ii) PCl_5 *causes chlorination*

(iii) Alc.KOH *causes elimination reaction*

$$\underset{}{CH_3COOH} \xrightarrow{LiAlH_4} \underset{(A)}{CH_3CH_2OH} \xrightarrow{PCl_5} \underset{(B)}{CH_3CH_2Cl} \xrightarrow[-HCl]{Alc.KOH} \underset{\substack{(C)\\ \text{Ethylene}}}{CH_2{=}CH_2}$$

Solved Paper 2015

JEE Main

Joint Entrance Examination

Instructions

- This test consists of 30 questions.
- Each question is allotted 4 marks for correct response.
- Candidates will be awarded marks as stated above for correct response of each question. 1 mark will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
- There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted according as per instructions.

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1. The molecular formula of a commercial resin used for exchanging ions in water softening is $C_8H_7SO_3Na$ (mol. wt. = 206). What would be the maximum uptake of Ca^{2+} ions by the resin when expressed in mole per gram resin?

(a) $\frac{1}{103}$ (b) $\frac{1}{206}$ (c) $\frac{2}{309}$ (d) $\frac{1}{412}$

2. Sodium metal crystallises in a body centred cubic lattice with a unit cell edge of 4.29 Å. The radius of sodium atom is approximately

(a) 1.86 Å (b) 3.22 Å (c) 5.72 Å (d) 0.93 Å

3. Which of the following is the energy of a possible excited state of hydrogen?

(a) + 13.6 eV (b) – 6.8 eV
(c) – 3.4 eV (d) + 6.8 eV

4. The intermolecular interaction that is dependent on the inverse cube of distance between the molecules is

(a) ion-ion interaction (b) ion-dipole interaction
(c) London force (d) hydrogen bond

5. The following reaction is performed at 298K

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

The standard free energy of formation of NO (g) is 86.6 kJ/mol at 298 K. What is the standard free energy of formation of $NO_2(g)$ at 298 K? $(K_p = 1.6 \times 10^{12})$

(a) $R(298)\ \ln\ (1.6 \times 10^{12}) - 86600$

(b) $86600 + R(298)\ \ln\ (1.6 \times 10^{12})$

(c) $86600 - \frac{\ln\ (1.6 \times 10^{12})}{R(298)}$

(d) $0.5\ [2 \times 86600 - R(298)\ \ln\ (1.6 \times 10^{12})]$

6. The vapour pressure of acetone at 20°C is 185 torr. When 1.2 g of a non-volatile substance was dissolved in 100 g of acetone at 20°C, its vapour pressure was 183 torr. The molar mass $(g\ mol^{-1})$ of the substance is

(a) 32 (b) 64
(c) 128 (d) 488

7. The standard Gibbs energy change at 300K for the reaction, $2A \rightleftharpoons B + C$ is 2494. 2 J. At a given time, the composition of the reaction mixture is $[A] = \frac{1}{2}$, $[B] = 2$ and $[C] = \frac{1}{2}$. The reaction proceeds in the $[R = 8.314\ JK/mol, e = 2.718]$

(a) forward direction because $Q > K_c$
(b) reverse direction because $Q > K_c$
(c) forward direction because $Q < K_c$
(d) reverse direction because $Q < K_c$

8. Two Faraday of electricity is passed through a solution of $CuSO_4$. The mass of copper deposited at the cathode is (at. mass of Cu = 63.5 u)

(a) 0g (b) 63.5g
(c) 2g (d) 127g

9. Higher order (>3) reactions are rare due to

(a) low probability of simultaneous collision of all the reacting species
(b) increase in entropy and activation energy as more molecules are involved
(c) shifting of equilibrium towards reactants due to elastic collisions
(d) loss of active species on collision

10. 3 g of activated charcoal was added to 50 mL of acetic acid solution (0.06 N) in a flask. After an hour it was filtered and the strength of the filtrate was found to be 0.042 N. The amount of acetic acid adsorbed (per gram of charcoal) is

(a) 18 mg (b) 36 mg
(c) 42 mg (d) 54 mg

11. The ionic radii (in Å) of N^{3-}, O^{2-} and F^- respectively are

(a) 1.36, 1.40 and 1.71 (b) 1.36, 1.71 and 1.40
(c) 1.71, 1.40 and 1.36 (d) 1.71, 1.36 and 1.40

12. In the context of the Hall-Heroult process for the extraction of Al, which of the following statements is false?

(a) CO and CO_2 are produced in this process
(b) Al_2O_3 is mixed with CaF_2 which lowers the melting point of the mixture and brings conductivity
(c) Al^{3+} is reduced at the cathode to form Al
(d) Na_3AlF_6 serves as the electrolyte

13. From the following statements regarding H_2O_2, choose the incorrect statement.

(a) It can act only as an oxidising agent
(b) It decomposed on exposure to light
(c) It has to be stored in plastic or wax lined glass bottles in dark
(d) It has to be kept away from dust

14. Which one of the following alkaline earth metal sulphates has its hydration enthalpy greater than its lattice enthalpy?

(a) $CaSO_4$ (b) $BeSO_4$
(c) $BaSO_4$ (d) $SrSO_4$

15. Which among the following is the most reactive?

(a) Cl_2 (b) Br_2
(c) I_2 (d) ICl

16. Match the catalysts to the correct processes.

Catalyst	Process
(A) $TiCl_3$	(i) Wacker process
(B) $PdCl_2$	(ii) Ziegler- Natta polymerisation
(C) $CuCl_2$	(iii) Contact process
(D) V_2O_5	(iv) Deacon's process

(a) (A)- (iii), (B) - (ii), (C) - (iv), (D) - (i)
(b) (A)- (ii), (B) - (i), (C) - (iv), (D) - (iii)
(c) (A)- (ii), (B) - (iii), (C) - (iv), (D) - (i)
(d) (A)- (iii), (B) - (i), (C) - (ii), (D) - (iv)

17. Which one has the highest boiling point?

(a) He (b) Ne
(c) Kr (d) Xe

18. The number of geometric isomers that can exist for square planar $[Pt(Cl)(py)(NH_3)(NH_2OH)]^+$ is (py = pyridine)

(a) 2 (b) 3
(c) 4 (d) 6

19. The colour of $KMnO_4$ is due to

(a) $M \to L$ charge transfer transition
(b) $d - d$ transition
(c) $L \to M$ charge transfer transition
(d) $\sigma - \overset{*}{\sigma}$ transition

20. **Assertion (A)** Nitrogen and oxygen are the main components in the atmosphere but these do not react to form oxides of nitrogen.

Reason (R) The reaction between nitrogen and oxygen requires high temperature.

(a) Both Assertion and Reason are correct and the reason is the correct explanation for the Assertion.
(b) Both Assertion and Reason are correct but the reason is not the correct explanation for the Assertion.
(c) The Assertion is incorrect but the Reason is correct.
(d) Both the Assertion and Reason are incorrect.

21. In Carius method of estimation of halogens, 250 mg of an organic compound gave 141 mg of AgBr. The percentage of bromine in the compound is

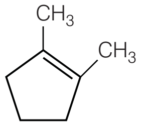
(at. mass Ag = 108, Br = 80)

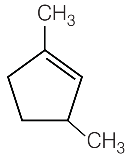
(a) 24 (b) 36 (c) 48 (d) 60

22. Which of the following compound will exhibit geometrical isomerism?

(a) 1-phenyl-2-butene
(b) 3-phenyl-1-butene
(c) 2-phenyl-1-butene
(d) 1, 1-diphenyl-1-propane

23. Which compound would give 5-keto-2-methyl hexanal upon ozonolysis?

(a)


(b)


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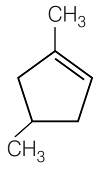
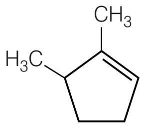


(d)


24. The synthesis of alkyl fluorides is best accomplished by

(a) free radical fluorination (b) Sandmeyer's reaction
(c) Finkelstein reaction (d) Swarts reaction

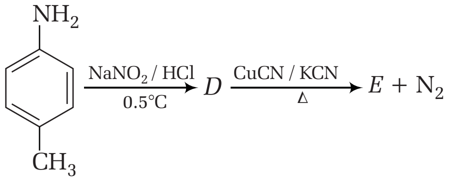
25. In the following sequence of reaction,

$$\text{Toluene} \xrightarrow{KMnO_4} A \xrightarrow{SOCl_2} B \xrightarrow[BaSO_4]{H_2/Pd} C$$

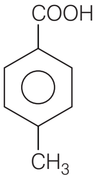
The product C is

(a) C_6H_5COOH
(b) $C_6H_5CH_3$
(c) $C_6H_5CH_2OH$
(d) C_6H_5CHO

26. In the reaction,



The product E is

(a)


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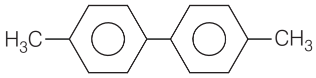
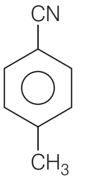
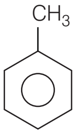


(c)


(d)


27. Which polymer is used in the manufacture of paints and lacquers?

(a) Bakelite
(b) Glyptal
(c) Polypropene
(d) Polyvinyl chloride

28. Which of the vitamins given below is water soluble?

(a) Vitamin C
(b) Vitamin D
(c) Vitamin E
(d) Vitamin K

29. Which of the following compounds is not an antacid?

(a) Aluminium hydroxide
(b) Cimetidine
(c) Phenelzine
(d) Ranitidine

30. Which of the following compounds is not coloured yellow?

(a) $Zn_2[Fe(CN)_6]$
(b) $K_3[Co(NO_2)_6]$
(c) $(NH_4)_3[As(Mo_3O_{10})_4]$
(d) $BaCrO_4$

Answer *with* Explanations

1. *(d)* We know the molecular weight of $C_8H_7SO_3Na$

$$= 12 \times 8 + 1 \times 7 + 32 + 16 \times 3 + 23 = 206$$

We have to find, mole per gram of resin.

$\therefore$ 1 g of $C_8H_7SO_3Na$ has number of mole

$$= \frac{\text{Weight of given resin}}{\text{Molecular weight of resin}} = \frac{1}{206} \text{ mol}$$

Now, reaction looks like

$$2C_8H_7SO_3Na + Ca^{2+} \longrightarrow (C_8H_7SO_3)_2Ca + 2Na^+$$

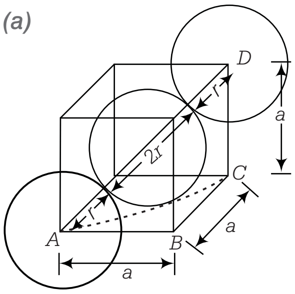
$\because$ 2 moles of $C_8H_7SO_3Na$ combines with 1 mol Ca^{2+}

$\therefore$ 1 mole of $C_8H_7SO_3Na$ will combine with $\frac{1}{2}$ mol Ca^{2+}

$\therefore \frac{1}{206}$ mole of $C_8H_7SO_3Na$ will combine with $\frac{1}{2} \times \frac{1}{206}$ mol Ca^{2+}

$$= \frac{1}{412} \text{ mol } Ca^{2+}$$

2. *(a)*



From this figure ,

$$(AC)^2 = (AB)^2 + (BC)^2$$
$$(AC)^2 = a^2 + a^2 = 2a^2$$

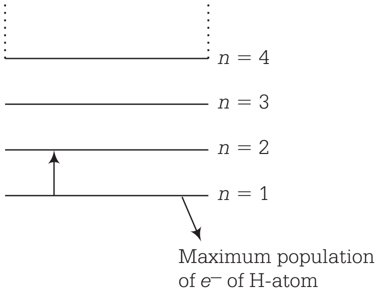
Also, $$(AD)^2 = (AC)^2 + (DC)^2$$
$$(4r)^2 = 2a^2 + a^2$$
$$16r^2 = 3a^2$$
$$r = \frac{\sqrt{3}}{4}a$$

Now, when Na metal crystallises in bcc unit cell with unit cell edge, $a = 4.29 \text{Å}$

We have the formula for radius,

i.e. $$r = \frac{\sqrt{3}}{4} \times 4.29 \text{ Å} = 1.86 \text{Å}$$

3. *(c)*



Since, at $n = 1$, the population of electrons is maximum *i.e.* at ground state. So, maximum excitation will take place from $n = 1$ to $n = 2$.

Hence, $n = 2$ is the possible excited state.

Now, we have the formula for energy of H-atom

$$(E_n)_H = -13.6 \frac{Z^2}{n^2} \text{eV}$$

where, Z = atomic number

Z for H-atom $= 1$

$$\therefore \quad (E_n)_{\text{H}} = -13.6 \times \frac{1}{2^2}\,\text{eV} = -\frac{13.6}{4}\,\text{eV} = -3.4\text{ eV}$$

4. *(b)* Ion-ion interaction is dependent on the square of distance, i.e. ion-ion interaction $\propto \dfrac{1}{r^2}$

Similarly,

$$\text{ion-dipole interaction} \propto \frac{1}{r^3}$$

$$\text{London forces} \propto \frac{1}{r^6}$$

$$\text{and dipole-dipole interactions} \propto \frac{1}{r^3}$$

Superficially it seems as both ion dipole interaction and hydrogen bonding vary with the inverse cube of distance between the molecules but when we look at the exact expressions of field (force) created in two situations it comes as

$$|\mathbf{E}| \text{or } |\mathbf{F}| = \frac{2|\mathbf{P}|}{4\pi\varepsilon_0 r^3} \qquad \text{(In case of ion-dipole interaction)}$$

$$\text{and} \qquad F = \frac{2q^2 r - 4q^2 a}{4\pi\varepsilon_0 r^3} \quad \text{(In case of dipole-dipole interaction)}$$

From the above it is very clear, the ion-dipole interaction is the better answer as compared to dipole-dipole interaction i.e. hydrogen bonding.

5. *(d)* For the given reaction,

$$2\text{NO}(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}_2(g)$$

Given, $\Delta G_f^\circ\,(\text{NO}) = 86.6\text{ kJ/mol}$

$\Delta G_f^\circ\,(\text{NO}_2) = ?$

$K_p = 1.6 \times 10^{12}$

Now, we have,

$$\Delta G_f^\circ = 2\Delta G^\circ_{f(\text{NO}_2)} - [2\Delta G^\circ_{f(\text{NO})} + \Delta G^\circ_{f(\text{O}_2)}]$$

$$= -RT\ln K_p = 2\Delta G^\circ_{f(\text{NO}_2)} - [2 \times 86{,}600 + 0]$$

$$\Delta G^\circ_{f(\text{NO}_2)} = \frac{1}{2}[2 \times 86{,}600 - R \times 298 \ln(1.6 \times 10^{12})]$$

$$\Delta G^\circ_{f(\text{NO}_2)} = 0.5\,[2 \times 86{,}600 - R \times (298)\ln(1.6 \times 10^{12})]$$

6. *(b)* Given,

$p_o = 185$ torr at 20°C

$p_s = 183$ torr at 20°C

Mass of non-volatile substance, $m = 1.2$ g

Mass of acetone taken $= 100$ g

$M = ?$

As , we have

$$\frac{p_o - p_s}{p_s} = \frac{n}{N}$$

Putting the values, we get,

$$\frac{185 - 183}{183} = \frac{\dfrac{1.2}{M}}{\dfrac{100}{58}} \Rightarrow \frac{2}{183} = \frac{1.2 \times 58}{100 \times M}$$

$$\therefore \qquad M = \frac{183 \times 1.2 \times 58}{2 \times 100}$$

$$M = 63.684 \approx 64\text{ g/mol}$$

7. *(b)* Given, $\Delta G^\circ = 2494.2\text{J}$

$$Q = \frac{[B][C]}{[A]^2} = \frac{2 \times \frac{1}{2}}{\left(\frac{1}{2}\right)^2} = 4$$

$\therefore$ We know,

$$\Delta G = \Delta G^\circ + RT\ln Q$$

$$= 2494.2 + 8.314 \times 300\ \ln 4$$

$$= 28747.27\text{J}$$

$$= \text{positive value}$$

Also, we have

$$\Delta G = RT\ln\frac{Q}{K}$$

if ΔG is positive, $Q > K$.

Therefore, reaction shifts in reverse direction.

8. *(b)* Given,

$$Q = 2F$$

Atomic mass of $\text{Cu} = 63.5\,\text{u}$

Valency of the metal $Z = 2$

We have,

$$\text{CuSO}_4 \longrightarrow \text{Cu}^{2+} + \text{SO}_4^{2-}$$

$$\underset{1\text{mol}}{\text{Cu}^{2+}} + \underset{\substack{2\text{ mol}\\2\text{F}}}{2e^-} \longrightarrow \underset{1\text{mol} = 63.5\,\text{g}}{\text{Cu}}$$

Alternatively,

$$W = ZQ$$

$$= \frac{E}{F} \cdot 2F$$

$$= 2E$$

$$= \frac{2 \times 63.5}{2} = 63.5$$

9. *(a)* The main conditions for the occurrence of a reaction is proper orientation and effective collision of the reactants.

Since the chances of simultaneous collision with proper orientation between more than 3 species is very rare, so reaction with order greater than 3 are rare.

10. *(a)* Given, initial strength of acetic acid $= 0.06$N

Final strength $= 0.042$ N

Volume given $= 50$ mL

$\therefore$ Initial m moles of CH_3COOH

$$= 0.06 \times 50 = 3$$

Final m moles of CH_3COOH

$$= 0.042 \times 50 = 2.1$$

$\therefore$ m moles of CH_3COOH adsorbed

$$= 3 - 2.1$$

$$= 0.9\text{ m mol}$$

Hence, mass of CH_3COOH absorbed per gram of charcoal

$$= \frac{0.9 \times 60}{3} \ (\because \text{molar mass of CH}_3\text{COOH} = 60\text{ gmol}^{-1})$$

$$= \frac{54}{3} = 18\text{ mg.}$$

11. *(c)* Number of electrons in $N^{3-} = 7 + 3 = 10$

Number of electrons in $O^{2-} = 8 + 2 = 10$

Number of electrons in $F^{-} = 9 + 1 = 10$

Since, all the three species have each 10 electrons hence they are isoelectronic species.

It is considered that, in case of isoelectronic species as the negative charge increases, ionic radii increases and therefore the value of ionic radii are

$N^{3-} = 1.71$ (highest among the three)

$O^{2-} = 1.40$

$F^{-} = 1.36$ (lowest among the three)

Time Saving Technique *There is no need to mug up the radius values for different ions. This particular question can be solved through following time saving.*

Trick *The charges on the ions indicate the size as* $N^{3-} > O^{2-} > F^{-}$. *Thus, you have to look for the option in which the above trend is followed. Option (c) is the only one in which this trend is followed. Hence, it is the correct answer.*

12. *(d)* (a) In Hall-Heroult process for extraction of Al, carbon anode is oxidised to CO and CO_2.

(b) When Al_2O_3 is mixed with CaF_2, it lowers the melting point of the mixture and brings conductivity.

(c) Al^{3+} is reduced at cathode to form Al.

(d) Here, Al_2O_3 is an electrolyte, undergoing the redox process. Na_3AlF_6 although is an electrolyte but serves as a solvent, not electrolyte.

13. *(a)* H_2O_2 acts as an oxidising as well as reducing agent, because oxidation number of oxygen in H_2O_2 is –1. So, it can be oxidised to oxidation state 0 or reduced to oxidation state –2.

H_2O_2 decomposes on exposure to light. So, it has to be stored in plastic or wax lined glass bottles in dark for the prevention of exposure. It also has to be kept away from dust.

14. *(b)* As we move down the group, size of metal increases. Be has lower size while SO_4^{2-} has bigger size, that's why $BeSO_4$ breaks easily and lattice energy becomes smaller but due to lower size of Be, water molecules are gathered around and hence hydration energy increases.

On the other hand, rest metals i.e. Ca, Ba, Sr have bigger size and that's why lattice energy is greater than hydration energy.

Time Saving Technique *In the question of finding hydration energy only check the size of atom. Smaller sized atom has more hydration energy.*

Thus, in this question Be *is placed upper most in the group has lesser size and not comparable with the size of sulphates. Hence,* $BeSO_4$ *is the right response.*

15. *(d)* Cl_2, Br_2 and I_2 are homonuclear diatomic molecule in which electronegativity of the combining atoms is same, so they are more stable and less reactive, whereas, I and Cl have different electronegativities and bond between them are polarised and hence, reactive. Therefore, interhalogen compounds are more reactive.

Time Saving Technique *In this type of question of halogen, only go through the polarity of the molecule. As we know, diatomic molecule does not have polarity but molecules with dissimilar sizes have polarity resulting in more reactivity.*

16. *(b)* (a) $TiCl_3$ is used as Ziegler-Natta catalyst for the polymerisation of ethene.

(b) $PdCl_2$ is used in Wacker process, in which alkene changed into aldehyde *via* catalytic cyclic process initiated by $PdCl_2$.

(c) $CuCl_2$ is used in Deacon's process. (for Cl_2)

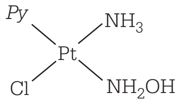
(d) V_2O_5 is used in contact process of manufacturing sulphuric acid.

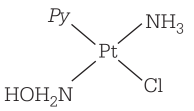
Time Saving Technique *This type of questions can also be solved through elimination technique. There is no need to know all the four matches to select the correct response. Even if you know (b) matches then also you can solve the problem. e.g. suppose you know the usage of* V_2O_5 *in contact process (i.e. D matches with (iii) and* $TiCl_3$ *is connected to Ziegler-Natta catalyst (i.e. A matches with ii). These two combinations are present only in option number (b). Likewise, for this question particularly if you know that* V_2O_5 *is used in contact process then this combination is present in option (b) only out of all the four option given. In this way you can eliminate wrong options to get the correct response.*

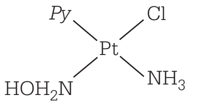
17. *(d)* As we move down the group of noble gases , molecular mass increases by which dipole produced for a moment and hence London forces increases from He to Xe. Therefore more amount of energy is required to break these forces, thus boiling point also increases from He to Xe.

18. *(b)* $[Pt(Cl)(py)(NH_3)(NH_2OH)]^+$ is square planar complex.

The structures are formed by fixing a group and then arranging all the groups.







Hence, this complex shows three geometrical isomers.

19. *(c)* $KMnO_4 \longrightarrow K^+ + MnO_4^-$

$\therefore$ In MnO_4^-, Mn has +7 oxidation state having no electron in *d*-orbitals.

It is considered that higher the oxidation state of metal, greater is the tendency to occur $L \rightarrow M$ charge transfer, because ligand is able to donate the electrons into the vacant *d*- orbital of metal.

Since, charge transfer is Laporte as well as spin allowed, therefore, it shows colour.

Time Saving Technique *There is no need to check all the four options. Just find out the oxidation state of metal ion. If oxidation state is highest and ligand present there is of electron donating nature, gives LMCT, which shows more intense colour.*

20. *(a)* Nitrogen is an inert gas because of the presence of strong bond. That's why although there is 78% N_2 in the atmosphere but nitrogen oxide in not formed under ordinary conditions.

But when temperature is high enough i.e. ≈ 2000 K, it reacts with oxygen to form nitrogen oxide.

$$N_2 + O_2 \xrightarrow{\approx 2000\text{ K}} 2NO$$

Thus, Assertion and Reason are true and Reason is the correct explanation of the Assertion.

21. *(a)* Given,

Weight of organic compound = 250 mg

Weight of AgBr = 141 mg

∴ According to formula of % of bromine by Carius method

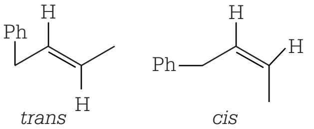
$$\%\text{ of Br} = \frac{\text{Atomic weight of Br}}{\text{Molecular weight of AgBr}} \times \frac{\text{Weight of AgBr}}{\text{Weight of organic bromide}} \times 100$$

$$\therefore \quad \%\text{ of Br} = \frac{80}{188} \times \frac{141}{250} \times 100$$

$$= \frac{1128000}{47000} = 24\ \%$$

22. *(a)* Alkene in which different groups are attached with the double bonded carbon atoms, exhibit geometrical isomerism.

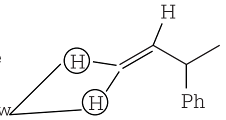
1-phenyl -2-butene =



trans *cis*

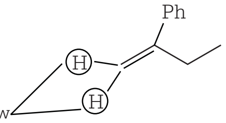
It will show geometrical isomerism.

3-phenyl-1-butene



Same group, does not show geometrical isomerism.

2-phenyl-1-butene



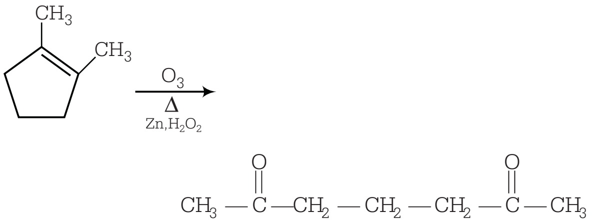
Same group, does not show geometrical isomerism.

1,1-diphenyl-1-propane being an alkane (saturated compound) does not show geometrical isomerism.

Time Saving Technique *We do not need the check all options, but it should remind that double bonded compounds show geometrical isomerism. Thus, (d) is eliminated, (i.e. propane). Now, eliminate the terminal alkene and get the correct response.*

23. *(b)*

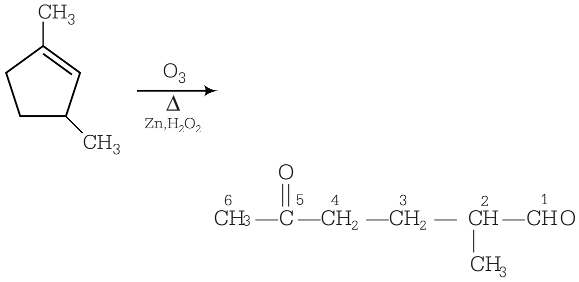
(a)



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$$

Heptan-2,6-dione

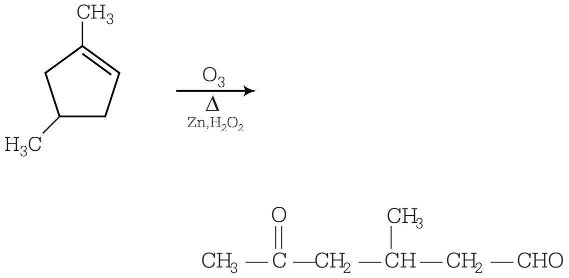
(b)



$$\overset{6}{C}H_3-\overset{\overset{O}{\|}}{\overset{5}{C}}-\overset{4}{C}H_2-\overset{3}{C}H_2-\underset{\underset{CH_3}{|}}{\overset{2}{C}H}-\overset{1}{C}HO$$

5-keto-2-methyl hexanal

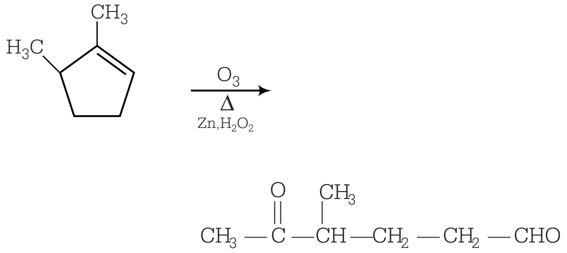
(c)



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{CH_3}{|}}{C}H-CH_2-CHO$$

5-keto-3-methyl hexanal

(d)



$$CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{C}H-CH_2-CH_2-CHO$$

5-keto-4-methyl hexanal

24. *(d)* Alkyl fluorides can be prepared by action of mercurous fluoride or antimony trifluorides (inorganic fluorides) on corresponding alkyl halide. This reaction is known as Swarts reaction.

$$CH_3Br + AgF \longrightarrow \underset{\substack{\text{Methyl}\\ \text{fluoride}}}{CH_3F} + AgBr$$

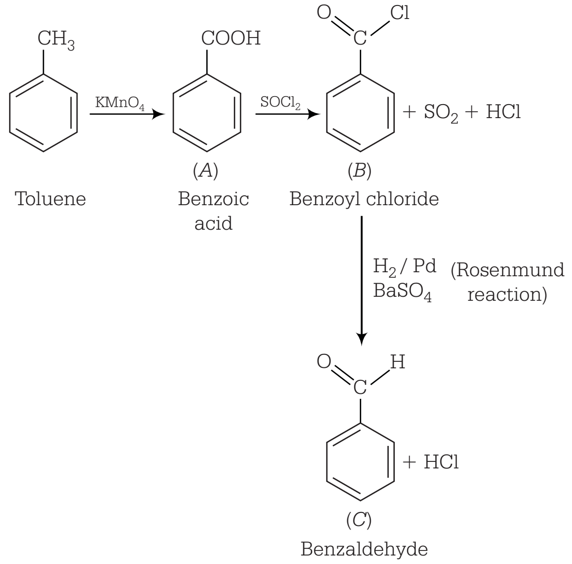
But, when action of NaI/acetone takes place on alkyl chloride or bromide, alkyl iodide forms. This reaction is called 'Finkelstein reaction'.

$$C_2H_5Cl \xrightarrow[\text{acetone}]{\text{NaI}} C_2H_5I + NaCl$$

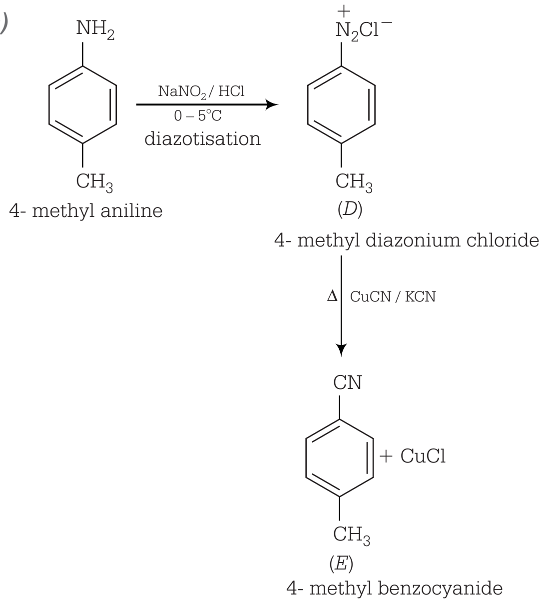
Free radical fluorination is highly explosive reaction. so not preferred for the preparation of fluoride.

25. *(d)* Toluene undergoes oxidation with $KMnO_4$, forms benzoic acid. In this conversion, alkyl part of toluene converts into carboxylic group. Further, benzoic acid reacts with thionyl chloride ($SOCl_2$) to give benzoyl chloride which upon reduction with H_2/Pd or $BaSO_4$ forms benzaldehyde (Rosenmund Reduction).

The conversion look like,



26. *(c)*



27. *(b)* (a) Bakelite is used for making gears, protective coating and electrical fittings.

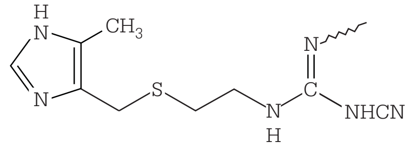
(b) Glyptal is used in the manufacture of paints and lacquers.

(c) PP is used in the manufacture of textile, packaging materials etc.

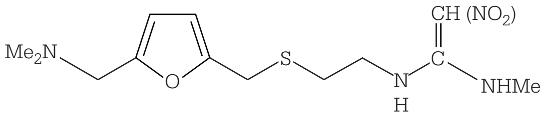
(d) Polyvinyl chloride (PVC) is used in the manufacture of rain coats, hand bags, leather clothes etc.

28. *(a)* Vitamin B and C are water soluble while vitamin A,D,E and K are fat soluble or water insoluble.

29. *(c)* Aluminium hydroxide Al $(OH)_3$, cimetidine and ranitidine are antacids while phenelzine is not.

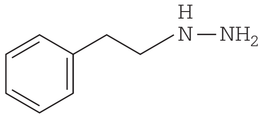


Cimetidine



Ranitidine

Phenelzine is a tranquilizer, not an antacid.



30. *(a)* $Zn_2[Fe(CN)_6]$, $K_3[Co(NO_2)_6]$ and $[(NH_4)_3As(Mo_3O_{10})_4]$ show colour due to *d-d* transition while $BaCrO_4$ is coloured due to charge transfer phenomenon.

Further, according to spectrochemical series the strong ligand possessing complex has higher energy and hence lower wavelength. Therefore, complexes containing NO_2, NH_4^+, O^{2-} etc ligands show yellow colour while CN^- forces the complex to impart white colour.

Spectrochemical Series

$$I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < N_3^- < F^- < OH^- < C_2O_4^{2-} \approx H_2O < NCS^- < CH_3CN < py < NH_3 < en < bipy < Phen < NO_2^- < PPh_3 < CN^- \approx CO$$

SOLVED PAPER 2016 **{OFFLINE}**

JEE MAIN

Joint Entrance Examination

INSTRUCTIONS

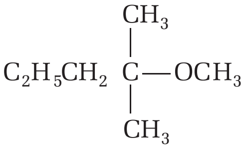
1. This test consists of 30 questions.
2. Each question is allotted 4 marks for correct response.
3. Candidates will be awarded marks as stated above in instruction no. 2 for correct response of each question. 1 mark will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
4. There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted according as per instructions.

Chemistry

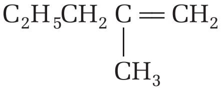
1. A stream of electrons from a heated filament was passed between two charged plates kept at a potential difference V esu. If e and m are charge and mass of an electron, respectively, then the value of h/λ (where, λ is wavelength associated with electron wave) is given by

(a) $2\,meV$ (b) $\sqrt{meV}$
(c) $\sqrt{2\,meV}$ (d) meV

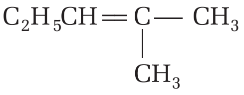
2. 2-chloro-2-methylpentane on reaction with sodium methoxide in methanol yields

I. 

$C_2H_5CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-OCH_3$

II. 

$C_2H_5CH_2-\underset{\displaystyle CH_3}{C}=CH_2$

III. 

$C_2H_5CH=\underset{\displaystyle CH_3}{C}-CH_3$

(a) Both I and III (b) Only III
(c) Both I and II (d) All of these

3. Which of the following compounds is metallic and ferromagnetic?

(a) CrO_2 (b) VO_2
(c) MnO_2 (d) TiO_2

4. Which of the following statements about low density polythene is false?

(a) It is a poor conductor of electricity
(b) Its synthesis required dioxygen or a peroxide initiator as a catalyst
(c) It is used in the manufacture of buckets, dustbins etc.
(d) Its synthesis requires high pressure

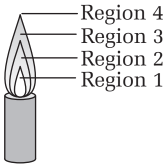
5. For a linear plot of $\log(x/m)$ *versus* $\log p$ in a Freundlich adsorption isotherm, which of the following statements is correct? (k and n are constants)

(a) $1/n$ appears as the intercept
(b) Only $1/n$ appears as the slope
(c) $\log\left(\frac{1}{n}\right)$ appears as the intercept
(d) Both k and $1/n$ appear in the slope term

6. The heats of combustion of carbon and carbon monoxide are -393.5 and -283.5 kJ mol^{-1}, respectively. The heat of formation (in kJ) of carbon monoxide per mole is

(a) 676.5
(b) -676.5
(c) -110.5
(d) 110.5

7. The hottest region of Bunsen flame shown in the figure given below is



(a) region 2 (b) region 3 (c) region 4 (d) region 1

8. Which of the following is an anionic detergent?

(a) Sodium lauryl sulphate
(b) Cetyltrimethyl ammonium bromide
(c) Glyceryl oleate
(d) Sodium stearate

9. 18 g of glucose $(C_6H_{12}O_6)$ is added to 178.2 g water. The vapour pressure of water (in torr) for this aqueous solution is

(a) 76.0 (b) 752.4 (c) 759.0 (d) 7.6

10. The distillation technique most suited for separating glycerol from spent lye in the soap industry is

(a) fractional distillation
(b) steam distillation
(c) distillation under reduced pressure
(d) simple distillation

11. The species in which the N-atom is in a state of *sp* hybridisation is

(a) NO_2^- (b) NO_3^- (c) NO_2 (d) NO_2^+

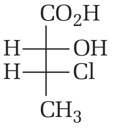
12. Decomposition of H_2O_2 follows a first order reaction. In 50 min, the concentration of H_2O_2 decreases from 0.5 to 0.125 M in one such decomposition. When the concentration of H_2O_2 reaches 0.05 M, the rate of formation of O_2 will be

(a) 6.93×10^{-4} mol min^{-1} (b) 2.66 L min^{-1} at STP
(c) 1.34×10^{-2} mol min^{-1} (d) 6.93×10^{-2} mol min^{-1}

13. The pair having the same magnetic moment is [at. no. Cr = 24, Mn = 25, Fe = 26 and Co = 27]

(a) $[Cr(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{2+}$
(b) $[Mn(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{2+}$
(c) $[CoCl_4]^{2-}$ and $[Fe(H_2O)_6]^{2+}$
(d) $[Cr(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$

14. The absolute configuration of



is

(a) (2S, 3R) (b) (2S, 3S)
(c) (2R, 3R) (d) (2R, 3S)

15. The equilibrium constant at 298 K for a reaction, $A + B \rightleftharpoons C + D$ is 100. If the initial concentrations of all the four species were 1 M each, then equilibrium concentration of D (in mol L^{-1}) will be

(a) 0.818 (b) 1.818 (c) 1.182 (d) 0.182

16. Which one of the following ores is best concentrated by froth floatation method?

(a) Siderite (b) Galena
(c) Malachite (d) Magnetite

17. At 300 K and 1 atm, 15 mL of a gaseous hydrocarbon requires 375 mL air containing 20% O_2 by volume for complete combustion. After combustion, the gases occupy 330 mL. Assuming that the water formed is in liquid form and the volumes were measured at the same temperature and pressure, the formula of the hydrocarbon is

(a) C_3H_8 (b) C_4H_8
(c) C_4H_{10} (d) C_3H_6

18. The pair in which phosphorus atoms have a formal oxidation state of +3 is

(a) pyrophosphorous and hypophosphoric acids
(b) orthophosphorous and hypophosphoric acids
(c) pyrophosphorous and pyrophosphoric acids
(d) orthophosphorous and pyrophosphorous acids

19. Which one of the following complexes shows optical isomerism?

(a) *cis* $[Co(en)_2Cl_2]Cl$ (b) *trans* $[Co(en)_2Cl_2]Cl$
(c) $[Co(NH_3)_4Cl_2]Cl$ (d) $[Co(NH_3)_3Cl_3]$

20. The reaction of zinc with dilute and concentrated nitric acid, respectively, produce

(a) NO_2 and NO (b) NO and N_2O
(c) NO_2 and N_2O (d) N_2O and NO_2

21. Which one of the following statements about water is false?

(a) Water can act both as an acid and as a base
(b) There is extensive intramolecular hydrogen bonding in the condensed phase
(c) Ice formed by heavy water sinks in normal water
(d) Water is oxidised to oxygen during photosynthesis

22. The concentration of fluoride, lead, nitrate and iron in a water sample from an underground lake was found to be 1000 ppb, 40 ppb, 100 ppm and 0.2 ppm, respectively. This water is unsuitable for drinking due to high concentration of

(a) lead (b) nitrate
(c) iron (d) fluoride

23. The main oxides formed on combustion of Li, Na and K in excess of air respectively are

(a) LiO_2, Na_2O_2 and K_2O
(b) Li_2O_2, Na_2O_2 and KO_2
(c) Li_2O, Na_2O_2 and KO_2
(d) Li_2O , Na_2O and KO_2

24. Thiol group is present in

(a) cystine (b) cysteine
(c) methionine (d) cytosine

25. Galvanisation is applying a coating of

(a) Cr (b) Cu
(c) Zn (d) Pb

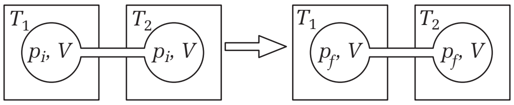
26. Which of the following atoms has the highest first ionisation energy?

(a) Na (b) K
(c) Sc (d) Rb

27. In the Hofmann-bromamide degradation reaction, the number of moles of NaOH and Br_2 used per mole of amine produced are

(a) four moles of NaOH and two moles of Br_2
(b) two moles of NaOH and two moles of Br_2
(c) four moles of NaOH and one mole of Br_2
(d) one mole of NaOH and one mole of Br_2

28. Two closed bulbs of equal volume (V) containing an ideal gas initially at pressure p_i and temperature T_1 are connected through a narrow tube of negligible volume as shown in the figure below. The temperature of one of the bulbs is then raised to T_2. The final pressure p_f is

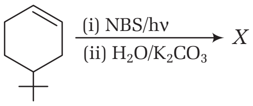


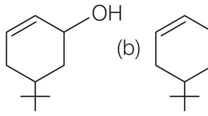
(a) $2p_i\left(\frac{T_1}{T_1+T_2}\right)$ (b) $2p_i\left(\frac{T_2}{T_1+T_2}\right)$
(c) $2p_i\left(\frac{T_1T_2}{T_1+T_2}\right)$ (d) $p_i\left(\frac{T_1T_2}{T_1+T_2}\right)$

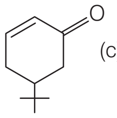
29. The reaction of propene with HOCl $(Cl_2 + H_2O)$ proceeds through the intermediate

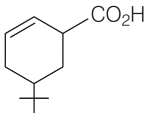
(a) $CH_3-\overset{+}{C}H-CH_2-Cl$ (b) $CH_3-CH(OH)-\overset{+}{C}H_2$
(c) $CH_3-CHCl-\overset{+}{C}H_2$ (d) $CH_3-\overset{+}{C}H-CH_2-OH$

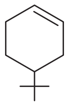
30. The product of the reaction given below is



(a)


(b)


(c)


(d)


ANSWER WITH EXPLANATION

1. *(c)* ***Plan*** As you can see in options, energy term is mentioned hence, we have to find out relation between $\frac{h}{\lambda}$ and energy.

For this, we shall use de-Broglie wavelength and kinetic energy term in eV.

de-Broglie wavelength for an electron $(\lambda) = \frac{h}{p}$

$$\Rightarrow \quad p = \frac{h}{\lambda} \quad \ldots(i)$$

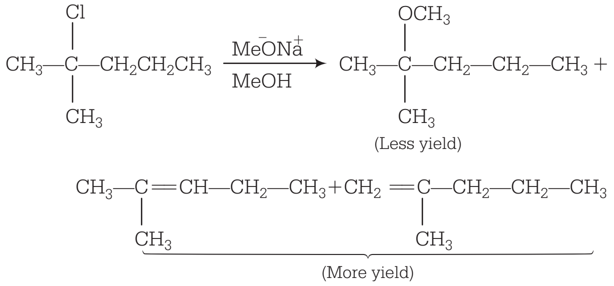
Kinetic energy of an electron = eV

As we know that, $KE = \frac{p^2}{2m}$

$$\therefore \quad eV = \frac{p^2}{2m} \quad \text{or} \quad p = \sqrt{2meV} \quad \ldots(ii)$$

From equations (i) and (ii), we get $\frac{h}{\lambda} = \sqrt{2meV}$

2. *(d)* ***Key concept*** Strong nucleophile ($\bar{O}$Me) in polar solvent (MeOH) gives elimination products over substitution products but all products are possible in different yields.



$$CH_3-\underset{CH_3}{\overset{Cl}{C}}-CH_2CH_2CH_3 \xrightarrow[MeOH]{Me\bar{O}\overset{+}{Na}} \underset{\text{(Less yield)}}{CH_3-\underset{CH_3}{\overset{OCH_3}{C}}-CH_2-CH_2-CH_3} +$$

$$\underbrace{CH_3-\underset{CH_3}{C}=CH-CH_2-CH_3+CH_2=\underset{CH_3}{C}-CH_2-CH_2-CH_3}_{\text{(More yield)}}$$

3. *(a)* Only three elements iron (Fe), cobalt (Co) and nickel (Ni) show ferromagnetism at room temperature. CrO_2 is also a metallic and ferromagnetic compound which is used to make magnetic tapes for cassette recorders.

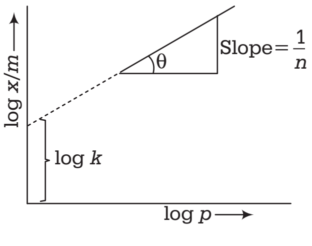
4. *(c)* High density polythene is used in the manufacture of buckets, dustbins etc.

5. *(b)* According to Freundlich adsorption isotherm, $\frac{x}{m} = kp^{1/n}$

On taking logarithm of both sides, we get

$$\log\frac{x}{m} = \log k + \log p^{1/n} \text{ or } \log\frac{x}{m} = \log k + \frac{1}{n}\log p$$

$$y = c + mx$$



$y = \log\frac{x}{m}$, c = intercept = $\log k$, m = slope = $\frac{1}{n}$ and $x = \log p$

6. *(c)* $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H = -393.5 \text{ kJ mol}^{-1}$ …(i)

$CO + \frac{1}{2}O_2 \longrightarrow CO_2(g)$; $\Delta H = -283.5 \text{ kJ mol}^{-1}$ …(ii)

On subtracting Eq. (ii) from Eq. (i), we get

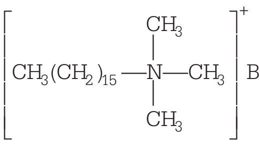
$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$;

$$\Delta H = (-393.5 + 283.5) \text{ kJ mol}^{-1} = -110 \text{ kJ mol}^{-1}$$
(approx.)

7. *(a)* Region 1 (Pre-heating zone)
Region 2 (Primary combustion zone, hottest zone)
Region 3 (Internal zone)
Region 4 (Secondary reaction zone)

8. *(a)* Sodium lauryl sulphate $[(CH_3(CH_2)_{10}CH_2OSO_3^-Na^+)]$ = Anionic detergent

Cetyltrimethyl ammonium bromide



$$\left[CH_3(CH_2)_{15}-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{N}}-CH_3\right]^+ Br^- = \text{Cationic detergent}$$

Glyceryl oleate $[(C_{17}H_{32}COO)_3C_3H_5]$ = Non-ionic detergent
Sodium stearate $[C_{17}H_{35}COO^-Na^+]$ = Anionic soap

9. *(b)* ***Key concept*** Vapour pressure of water $(p^\circ) = 760$ torr

$$\text{Number of moles of glucose} = \frac{\text{Mass (g)}}{\text{Molecular mass (g mol}^{-1})}$$

$$= \frac{18\text{ g}}{180\text{ gmol}^{-1}} = 0.1\text{ mol}$$

Molar mass of water = 18 g/mol
Mass of water (given) = 178.2g
Number of moles of water

$$= \frac{\text{Mass of water}}{\text{Molar mass of water}} = \frac{178.2\text{g}}{18\text{g/mol}} = 9.9\text{ mol}$$

Total number of moles = (0.1 + 9.9) moles = 10 moles

Now, mole fraction of glucose in solution = Change in pressure with respect to initial pressure

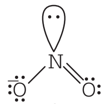
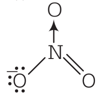
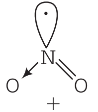
i.e. $$\frac{\Delta p}{p^\circ} = \frac{0.1}{10}$$

or $\Delta p = 0.01p^\circ = 0.01 \times 760 = 7.6$ torr

$\therefore$ Vapour pressure of solution = (760 − 7.6) torr = 752.4 torr

10. *(c)* Glycerol with high boiling point (290°C) can be separated from spent lye by distillation under reduced pressure. This process is used to purify liquids having very high boiling points. By this process, liquid is made to boil at lower temperature than its boiling point by lowering the pressure on its surface.

11. *(d)*

Species	Hybridisation
	sp^2
	sp^2
	sp^2
$O=\overset{+}{N}=O$	sp

12. *(a)* For first order reaction, $k = \frac{2.303}{t}\log\frac{a}{a-x}$

Given, $t = 50$ min, $a = 0.5$ M, $a - x = 0.125$ M

$$\therefore \quad k = \frac{2.303}{50}\log\frac{0.5}{0.125} = 0.0277\text{ min}^{-1}$$

Now, as per reaction

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

$$-\frac{1}{2}\frac{d[H_2O_2]}{dt} = \frac{1}{2}\frac{d[H_2O]}{dt} = \frac{d[O_2]}{dt}$$

Rate of reaction, $-\frac{d[H_2O_2]}{dt} = k[H_2O_2]$

$$\therefore \quad \frac{d[O_2]}{dt} = -\frac{1}{2}\frac{d[H_2O_2]}{dt} = \frac{1}{2}k[H_2O_2] \quad \text{...(i)}$$

When the concentration of H_2O_2 reaches 0.05 M,

$$\frac{d[O_2]}{dt} = \frac{1}{2} \times 0.0277 \times 0.05 \quad \text{[from Eq. (i)]}$$

or $$\frac{d[O_2]}{dt} = 6.93 \times 10^{-4}\text{ mol min}^{-1}$$

Alternative Method

In fifty minutes, the concentration of H_2O_2 decreases from 0.5 to 0.125 M or in one half-life, concentration of H_2O_2 decreases from 0.5 to 0.25 M. In two half-lives, concentration of H_2O_2 decreases from 0.5 to 0.125 M or $2t_{1/2} = 50$ min

$$t_{1/2} = 25\text{ min}$$

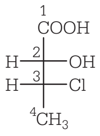
$$\therefore \quad k = \left(\frac{0.693}{25}\right)\text{min}^{-1}$$

or $$\frac{d[O_2]}{dt} = -\frac{1}{2}\frac{d[H_2O_2]}{dt} = \frac{k[H_2O_2]}{2} = 6.93 \times 10^{-4}\text{ mol min}^{-1}$$

13. *(a)*

Complex ion	Electronic configuration of metal ion	Number of unpaired electrons (*n*)
$[Cr(H_2O)_6]^{2+}$	Cr^{2+}; [Ar] $3d^4$	↿ ↿ ↿ ↿ ☐ ; 4
$[Fe(H_2O)_6]^{2+}$	Fe^{2+}; [Ar] $3d^6$	⥮ ↿ ↿ ↿ ↿ ; 4
$[Mn(H_2O)_6]^{2+}$	Mn^{2+}; [Ar] $3d^5$	↿ ↿ ↿ ↿ ↿ ; 5
$[CoCl_4]^{2-}$	Co^{2+}; [Ar] $3d^7$	⥮ ⥮ ↿ ↿ ↿ ; 3

14. *(a)*



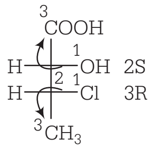
For C-2, order of priority of substituents is

$$OH > CH(Cl)(CH_3) > COOH$$

For C-3, order of priority of substituents is

$$Cl > CH(OH)COOH > CH_3$$

Hence, according to CIP rules,



15. *(b)*

$$\begin{array}{lcccc} & A\ + & B \rightleftharpoons & C\ + & D \\ \text{Initially at } t=0 & 1 & 1 & 1 & 1 \\ \text{At equilibrium} & 1-x & 1-x & 1+x & 1+x \end{array}$$

$$K_{eq} = \frac{[C][D]}{[A][B]} = \frac{(1+x)(1+x)}{(1-x)(1-x)} = \frac{(1+x)^2}{(1-x)^2}$$

$$\text{or} \quad 100 = \left(\frac{1+x}{1-x}\right)^2$$

$$\text{or} \quad 10 = \frac{1+x}{1-x}$$

$$\text{or} \quad 10 - 10x = 1 + x$$

$$10 - 1 = x + 10x$$

$$9 = 11x$$

$$x = \frac{9}{11} = 0.818$$

$$\therefore \quad [D] = 1 + x = 1 + 0.818 = 1.818$$

16. *(b)* Sulphide ores are concentrated by froth floatation method e.g. Galena (PbS)

17. *(None)* $C_xH_y(g) + \underset{75\text{ mL}}{\left(x + \frac{y}{4}\right)O_2(g)} \longrightarrow \underset{30\text{ mL}}{xCO_2(g)} + \frac{y}{2}H_2O(l)$

O_2 used = 20% of 375 = 75 mL

Inert part of air = 80% of 375 = 300 mL

Total volume of gases = CO_2 + Inert part of air

= 30 + 300 = 330 mL

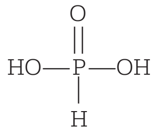
$$\frac{x}{1} = \frac{30}{15} \Rightarrow x = 2$$

$$\frac{x + \frac{y}{4}}{1} = \frac{75}{15}$$

$$\Rightarrow \quad x + \frac{y}{4} = 5$$

$$\Rightarrow \quad x = 2,\ y = 12 \Rightarrow C_2H_{12}$$

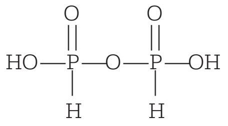
18. *(d)* Orthophosphorous acid, $H_3\ PO_3$:



$$HO-\overset{\overset{\displaystyle O}{||}}{\underset{\underset{\displaystyle H}{|}}{P}}-OH$$

$$H_3\overset{x}{P}O_3 = 3 + x + 3(-2) = 0 \text{ or } x = +3$$

Pyrophosphorous acid, $H_4P_2O_5$:



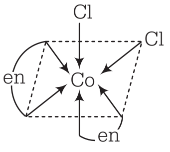
$$HO-\overset{\overset{\displaystyle O}{||}}{\underset{\underset{\displaystyle H}{|}}{P}}-O-\overset{\overset{\displaystyle O}{||}}{\underset{\underset{\displaystyle H}{|}}{P}}-OH$$

$$H_4\overset{x}{P_2}O_5 = 4 + 2x + 5(-2) = 0$$

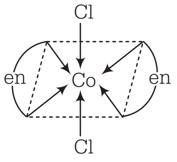
$$4 + 2x - 10 = 0$$

$$x = +3$$

19. *(a)*

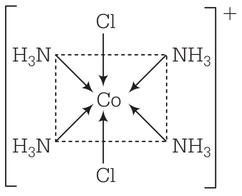


cis-$[Co(en)_2Cl_2]Cl$
(optically active)

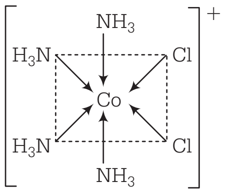


trans-$[Co(en)_2Cl_2]Cl$
(optically inactive due to plane of symmetry)

$[Co(NH_3)_4Cl_2]Cl$ can exist in both *cis* and *trans* forms that are given below:

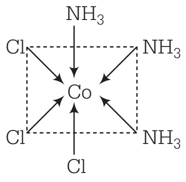


trans-$[Co(NH_3)_4Cl_2]Cl$
(optically inactive)

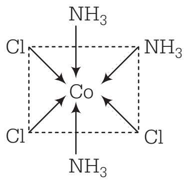


cis-$[Co(NH_3)_4Cl_2]Cl$
(optically inactive)

$[Co(NH_3)_3Cl_3]$ exists in *fac* and *mer*-isomeric forms and both are optically inactive.



fac-isomer
(optically inactive)



mer-isomer
(optically inactive)

20. *(d)* $Zn + \underset{(\text{Conc.})}{4HNO_3} \longrightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2$

$$4Zn + \underset{(\text{Dil.})}{10HNO_3} \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$$

21. *(b)* There is extensive intermolecular H-bonding in the condensed phase.

22. *(b)* This water is unsuitable for drinking due to high concentration of nitrate. In drinking water, maximum permissible concentration of

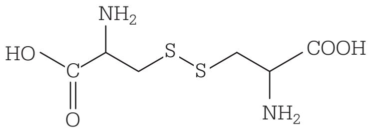
Lead ≃ 50 ppb
Nitrate ≃ 50 ppb
Iron ≃ 0.2 ppm
Fluoride ≃ 1 ppm

23. *(c)* $2Li + \underset{(\text{Excess})}{\frac{1}{2}O_2(g)} \longrightarrow Li_2O$

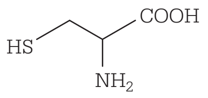
$$2Na + \underset{(\text{Excess})}{O_2(g)} \longrightarrow Na_2O_2; \quad K + \underset{(\text{Excess})}{O_2(g)} \longrightarrow KO_2$$

24. *(b)*

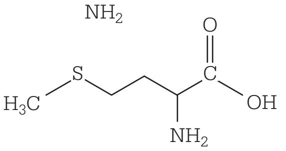
Cystine



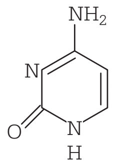
Cysteine



Methionine



Cytosine



Thiol group (SH) is present in cysteine.

25. *(c)* Zinc metal is the most stable metal to cover iron surfaces. The process of coating the iron surface by zinc is called galvanisation.

26. *(c)* Order of first ionisation energy is Sc > Na > K > Rb.

Due to poor shielding effect, removal of one electron from $4s$ orbital is difficult as compared to $3s$-orbital.

27. *(c)* Hofmann-bromamide degradation reaction is given as:

$$RCONH_2 + 4NaOH + Br_2 \longrightarrow \underset{(1^\circ \text{ amine})}{RNH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$

Hence, four moles of NaOH and one mole of Br_2 are used.

28. *(b)* Initially,

Number of moles of gases in each container $= \dfrac{p_iV}{RT_1}$

Total number of moles of gases in both containers $= 2\dfrac{p_iV}{RT_1}$

After mixing, number of moles in left chamber $= \dfrac{p_fV}{RT_1}$

Number of moles in right chamber

$$= \frac{p_fV}{RT_2}$$

Total number of moles

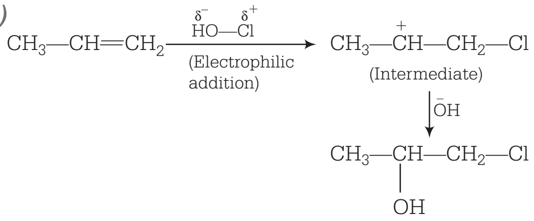
$$= \frac{p_fV}{RT_1} + \frac{p_fV}{RT_2} = \frac{p_fV}{R}\left(\frac{1}{T_1} + \frac{1}{T_2}\right)$$

As total number of moles remains constant.

Hence, $$\frac{2p_iV}{RT_1} = \frac{p_fV}{RT_1} + \frac{p_fV}{RT_2}$$

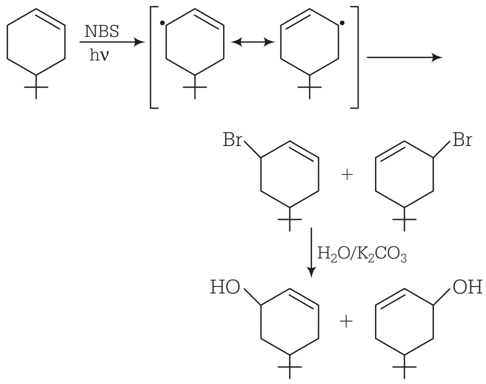
$$\Rightarrow \quad p_f = 2p_i\left(\frac{T_2}{T_1 + T_2}\right)$$

29. *(a)*



$$CH_3-CH=CH_2 \xrightarrow[\text{(Electrophilic addition)}]{\overset{\delta^-}{HO}-\overset{\delta^+}{Cl}} \underset{\text{(Intermediate)}}{CH_3-\overset{+}{C}H-CH_2-Cl} \xrightarrow{\overset{-}{O}H} CH_3-\underset{\displaystyle OH}{\underset{|}{C}H}-CH_2-Cl$$

30. *(a)*



SOLVED PAPER 2017

JEE MAIN

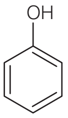
Joint Entrance Examination

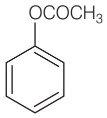
INSTRUCTIONS

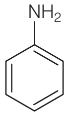
1. This test consists of 30 questions.
2. Each question is allotted 4 marks for correct response.
3. Candidates will be awarded marks as stated above in instruction no. 2 for correct response of each question. 1 mark will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
4. There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted according as per instructions.

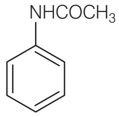
Chemistry

1. Which of the following compounds will give significant amount of *meta*-product during mononitration reaction?

(a) 

(b) 

(c) 

(d) 

2. ΔU is equal to

(a) isochoric work (b) isobaric work
(c) adiabatic work (d) isothermal work

3. The increasing order of reactivity of the following halides for the S_N1 reaction is

I. $CH_3CH(Cl)CH_2CH_3$
II. $CH_3CH_2CH_2Cl$
III. p-$H_3CO—C_6H_4—CH_2Cl$

(a) (III) < (II) < (I)
(b) (II) < (I) < (III)
(c) (I) < (III) < (II)
(d) (II) < (III) < (I)

4. The radius of the second Bohr orbit for hydrogen atom is (Planck's constant $(h) = 6.6262 \times 10^{-34}$ Js; mass of electron $= 9.1091 \times 10^{-31}$ kg ; charge of electron $(e) = 1.60210 \times 10^{-19}$ C; permitivity of vacuum $(\in_0) = 8.854185 \times 10^{-12} \text{kg}^{-1}\text{m}^{-3}\text{A}^2$)

(a) 1.65 Å (b) 4.76 Å
(c) 0.529 Å (d) 2.12 Å

5. pK_a of a weak acid (HA) and pK_b of a weak base (BOH) are 3.2 and 3.4, respectively. The pH of their salt (AB) solution is

(a) 7.2 (b) 6.9 (c) 7.0 (d) 1.0

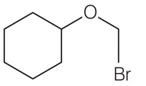
6. The formation of which of the following polymers involves hydrolysis reaction?

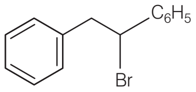
(a) Nylon-6 (b) Bakelite
(c) Nylon-6, 6 (d) Terylene

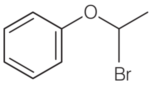
7. The most abundant elements by mass in the body of a healthy human adult are Oxygen (61.4%); Carbon (22.9%), Hydrogen (10.0 %); and Nitrogen (2.6%). The weight which a 75 kg person would gain if all ^{1}H atoms are replaced by ^{2}H atoms is

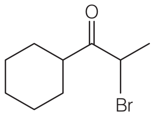
(a) 15 kg (b) 37.5 kg
(c) 7.5 kg (d) 10 kg

8. Which of the following, upon treatment with *tert*-BuONa followed by addition of bromine water, fails to decolourise the colour of bromine ?

(a)


(b)


(c)


(d)


9. In the following reactions, ZnO is respectively acting as a/an

(i) $ZnO + Na_2O \longrightarrow Na_2ZnO_2$

(ii) $ZnO + CO_2 \longrightarrow ZnCO_3$

(a) base and acid (b) base and base
(c) acid and acid (d) acid and base

10. Both lithium and magnesium display several similar properties due to the diagonal relationship; however, the one which is incorrect is

(a) Both form basic carbonates
(b) Both form soluble bicarbonates
(c) Both form nitrides
(d) nitrates of both Li and Mg yield NO_2 and O_2 on heating

11. 3-methyl-pent-2-ene on reaction with HBr in presence of peroxide forms an addition product. The number of possible stereoisomers for the product is

(a) six (b) zero (c) two (d) four

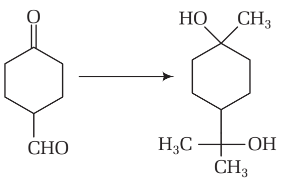
12. A metal crystallises in a face centred cubic structure. If the edge length of its unit cell is 'a', the closest approach between two atoms in metallic crystal will be

(a) $2a$ (b) $2\sqrt{2}\,a$ (c) $\sqrt{2}\,a$ (d) $\frac{a}{\sqrt{2}}$

13. Two reactions R_1 and R_2 have identical pre-exponential factors. Activation energy of R_1 exceeds that of R_2 by 10 kJ mol^{-1}. If k_1 and k_2 are rate constants for reactions R_1 and R_2, respectively at 300 K, then $\ln\left(\frac{k_2}{k_1}\right)$ is equal to $(R = 8.314 \text{ J mol}^{-1}\text{K}^{-1})$

(a) 8 (b) 12 (c) 6 (d) 4

14. The correct sequence of reagents for the following conversion will be



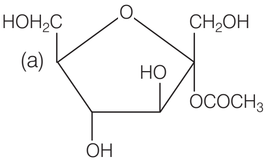
(a) $[Ag(NH_3)_2]^+ OH^-$, H^+ / CH_3OH, CH_3MgBr
(b) CH_3MgBr, H^+ / CH_3OH, $[Ag(NH_3)_2]^+ OH^-$
(c) CH_3MgBr, $[Ag(NH_3)_2]^+ OH^-$, H^+ / CH_3OH
(d) $[Ag(NH_3)_2]^+ OH^-$, CH_3MgBr, H^+ / CH_3OH

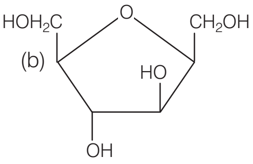
15. The Tyndall effect is observed only when following conditions are satisfied

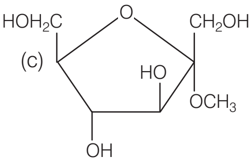
1. The diameter of the dispersed particles is much smaller than the wavelength of the light used.
2. The diameter of the dispersed particle is not much smaller than the wavelength of the light used.
3. The refractive indices of the dispersed phase and dispersion medium are almost similar in magnitude.
4. The refractive indices of the dispersed phase and dispersion medium differ greatly in magnitude.

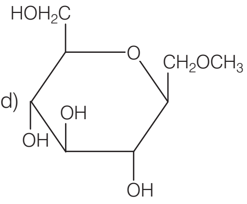
(a) 1 and 4 (b) 2 and 4
(c) 1 and 3 (d) 2 and 3

16. Which of the following compounds will behave as a reducing sugar in an aqueous KOH solution?

(a)


(b)


(c)


(d)


17. Given, $C_{(graphite)} + O_2(g) \longrightarrow CO_2(g)$;

$$\Delta_r H° = -393.5 \text{ kJ mol}^{-1}$$

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$;

$$\Delta_r H° = -285.8 \text{ kJ mol}^{-1}$$

$CO_2(g) + 2\,H_2O(l) \longrightarrow CH_4(g) + 2O_2(g)$;

$$\Delta_r H° = +890.3 \text{ kJ mol}^{-1}$$

Based on the above thermochemical equations, the value of $\Delta_r H°$ at 298 K for the reaction,

$$C_{(graphite)} + 2\,H_2(g) \longrightarrow CH_4(g) \text{ will be}$$

(a) + 78.8 kJ mol^{-1} (b) + 144.0 kJ mol^{-1}
(c) − 74.8 kJ mol^{-1} (d) − 144.0 kJ mol^{-1}

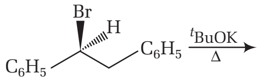
18. Which of the following reactions is an example of a redox reaction?

(a) $XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$
(b) $XeF_2 + PF_5 \longrightarrow [XeF]^+PF_6^-$
(c) $XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$
(d) $XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$

19. The products obtained when chlorine gas reacts with cold and dilute aqueous NaOH are

(a) ClO^- and ClO_3^- (b) ClO_2^- and ClO_3^-
(c) Cl^- and ClO^- (d) Cl^- and ClO_2^-

20. The major product obtained in the following reaction is



(a) (±) $C_6H_5CH(O^tBu)CH_2C_6H_5$

(b) $C_6H_5CH = CHC_6H_5$

(c) (+) $C_6H_5CH(O^tBu)CH_2C_6H_5$

(d) (−)$C_6H_5CH(O^tBu)CH_2C_6H_5$

21. Sodium salt of an organic acid '*X*' produces effervescence with conc. H_2SO_4. '*X*' reacts with the acidified aqueous $CaCl_2$ solution to give a white precipitate which decolourises acidic solution of $KMnO_4$. '*X*' is

(a) C_6H_5COONa (b) $HCOONa$

(c) CH_3COONa (d) $Na_2C_2O_4$

22. Which of the following species is not paramagnetic?

(a) NO (b) CO

(c) O_2 (d) B_2

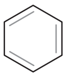
23. The freezing point of benzene decreases by 0.45°C when 0.2 g of acetic acid is added to 20 g of benzene. If acetic acid associates to form a dimer in benzene, percentage association of acetic acid in benzene will be (K_f for benzene = 5.12 K kg mol^{-1})

(a) 64.6 % (b) 80.4 %

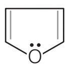
(c) 74.6 % (d) 94.6 %

24. Which of the following molecules is least resonance stabilised?

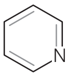
(a)



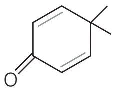
(b)



(c)



(d)



25. On treatment of 100 mL of 0.1 M solution of $CoCl_3.6H_2O$ with excess of $AgNO_3$; 1.2×10^{22} ions are precipitated. The complex is

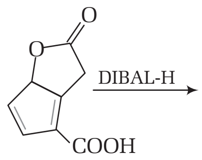
(a) $[Co(H_2O)_4Cl_2]\,Cl.2H_2O$

(b) $[Co(H_2O)_3Cl_3].3H_2O$

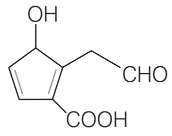
(c) $[Co(H_2O)_6]Cl_3$

(d) $[Co(H_2O)_5Cl]\,Cl_2.H_2O$

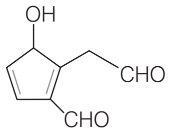
26. The major product obtained in the following reaction is



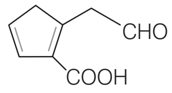
(a)



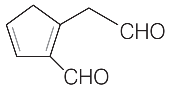
(b)



(c)



(d)



27. A water sample has ppm level concentration of following anions

$F^- = 10;\ SO_4^{2-} = 100;\ NO_3^- = 50$

the anion/anions that make/makes the water sample unsuitable for drinking is/are

(a) Only NO_3^-

(b) Both SO_4^{2-} and NO_3^-

(c) Only F^-

(d) Only SO_4^{2-}

28. 1 g of a carbonate (M_2CO_3) on treatment with excess HCl produces 0.01186 mole of CO_2. The molar mass of M_2CO_3 in g mol^{-1} is

(a) 1186 (b) 84.3

(c) 118.6 (d) 11.86

29. Given, $E^\circ_{Cl_2/Cl^-} = 1.36$ V, $E^\circ_{Cr^{3+}/Cr} = -0.74$ V

$E^\circ_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33$ V, $E^\circ_{MnO_4^-/Mn^{2+}} = 1.51$ V

Among the following, the strongest reducing agent is

(a) Cr (b) Mn^{2+}

(c) Cr^{3+} (d) Cl^-

30. The group having isoelectronic species is

(a) O^{2-}, F^-, Na^+, Mg^{2+}

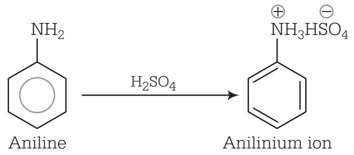
(b) O^-, F^-, Na, Mg^+

(c) O^{2-}, F^-, Na, Mg^{2+}

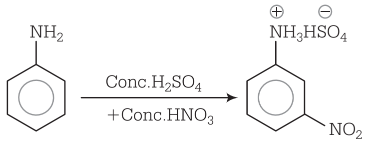
(d) O^-, F^-, Na^+, Mg^{2+}

Answer with Explanation

1. ***(c)*** Aniline in presence of nitrating mixture (conc. HNO_3 + conc. H_2SO_4) gives significance amount ($\approx$47%) of meta-product because in presence of H_2SO_4 its protonation takes place and anilinium ion is formed.



Here, anilinium ion is strongly deactivating group and *meta*-directing in nature. So, it gives *meta*-nitration product.



2. ***(c)*** According to first law of thermodynamics,

$$\Delta U = q + W = q - p\Delta V$$

In isochoric process ($\Delta V = 0$),

$$\Delta U = q$$

In isobaric process ($\Delta p = 0$),

$$\Delta U = q$$

In adiabatic process ($q = 0$)

$$\Delta U = W$$

In isothermal process ($\Delta T = 0$) and $\Delta U = 0$

$\therefore$ ΔU is equal to adiabatic work.

3. ***(b)*** ***(i) The rate of S_N1 reaction depends only upon the concentration of the alkyl halide.***

(ii) S_N1 reaction proceeds through the formation of carbocation.

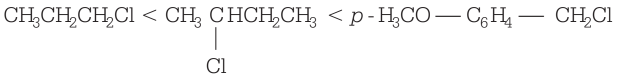
The reactivity is decided by ease of dissociation of alkyl halide.

$$R—X \rightleftharpoons R^{\oplus} + X^{\ominus}$$

Higher the stability of R^+ (carbocation), higher would be the reactivity towards S_N1 reaction.

p-$H_3CO—C_6H_4—CH_2^{\oplus}$ is the most stable carbocation due to resonance and then $CH_3\underset{\oplus}{C}HCH_2CH_3$ (2° carbocation) while $CH_3CH_2\overset{\oplus}{C}H_2$ (1°) is least stable.

Thus, the correct increasing order of the reactivity of the given halides towards the S_N1 reaction is



$$\underset{\text{(II)}}{CH_3CH_2CH_2Cl} < \underset{\text{(I)}}{CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCH_2CH_3} < \underset{\text{(III)}}{p\text{-}H_3CO—C_6H_4—CH_2Cl}$$

(II) (I) (III)

4. ***(d)*** Bohr radius $(r_n) = \epsilon_0\, n^2h^2$

$$r_n = \frac{n^2h^2}{4\pi^2me^2kZ}$$

$$k = \frac{1}{4\pi\epsilon_0}$$

$$\therefore \quad r_n = \frac{n^2h^2\epsilon_0}{\pi me^2Z}$$

$$= n^2\frac{a_0}{Z}$$

where, m = mass of electron

e = charge of electron

h = Planck's constant

k = Coulomb constant

$$r_n = \frac{n^2 \times 0.53}{Z}\,\text{Å}$$

Radius of n^{th} Bohr orbit for H-atom

$= 0.53\, n^2$ Å [Z = 1 for H-atom]

$\therefore$ Radius of 2^{nd} Bohr orbit for H-atom

$= 0.53 \times (2)^2 = 2.12$ Å

5. ***(b)*** For a salt of weak acid and weak base,

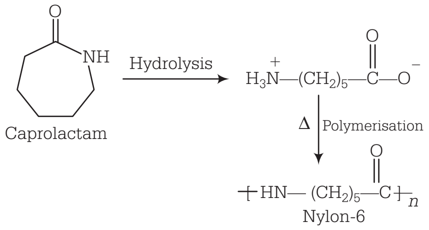
$$\text{pH} = 7 + \frac{1}{2}\,\text{p}K_a - \frac{1}{2}\,\text{p}K_b$$

Given, $\text{p}K_a(HA) = 3.2$, $\text{p}K_a(BOH) = 3.4$

$$\therefore \quad \text{pH} = 7 + \frac{1}{2}(3.2) - \frac{1}{2}(3.4)$$

$$= 7 + 1.6 - 1.7 = 6.9$$

6. ***(a)*** Nylon-6 or perlon is prepared by polymerisation of amino caproic acid at high temperature. Caprolactam is first hydrolysed with water to form amino acid which on heating undergoes polymerisation to give nylon-6.



7. ***(c)*** Given, abundance of elements by mass oxygen = 61.4%, carbon = 22.9%, hydrogen = 10% and nitrogen = 2.6%

Total weight of person = 75 kg

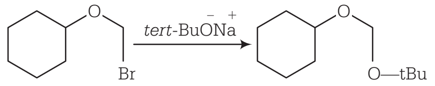
$$\text{Mass due to } {}^1\text{H} = \frac{75 \times 10}{100} = 7.5 \text{ kg}$$

^{1}H atoms are replaced by ^{2}H atoms,

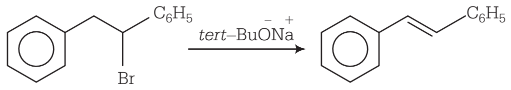
Mass due to ${}^2\text{H} = (7.5 \times 2)$ kg

$\therefore$ Mass gain by person = 7.5 kg

8. *(a)* To show decolourisation, compound must be unsaturated.



(Saturated)
(cannot decolourise Br_2 water)



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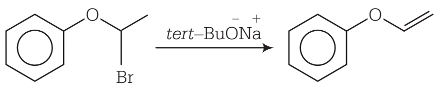
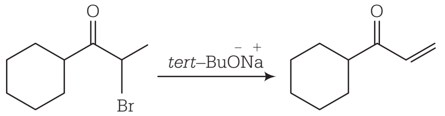
(decolourise Br_2 water)



(Unsaturated)
(decolourise Br_2 water)



(Unsaturated)
(decolourise Br_2 water)

9. *(d)* Zinc oxide (ZnO) when react with Na_2O it act as acid while with CO_2 it act as base. Therefore, it is an amphoteric oxide.

$$\underset{\text{Acid}}{ZnO} + \underset{\text{Base}}{Na_2O} \longrightarrow \underset{\text{Salt}}{Na_2ZnO_2}$$

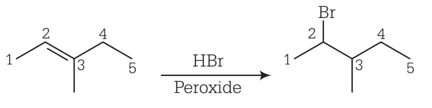
$$\underset{\text{Base}}{ZnO} + \underset{\text{Acid}}{CO_2} \longrightarrow \underset{\text{Salt}}{ZnCO_3}$$

10. *(a)* **Mg** can form basic carbonate while **Li** can not.

$$5\,Mg^{2+} + 6\,CO_3^{2-} + 7H_2O \longrightarrow 4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O + 2\,HCO_3^-$$

11. *(d)* The number of stereoisomers in molecules which are not divisible into two equal halves and have n number of asymmetric C-atoms $= 2^n$.

3-methyl-pent-2-ene on reaction with HBr in presence of peroxide forms an addition product i.e. 2-bromo-3-methyl pentane. It has two chiral centres. Therefore, 4 stereoisomers are possible



3-methylpent-2-ene

Anti-Markownikoff's addition
Four stereoisomers are possible
(As molecule has two chiral centres and asymmetric).

12. *(d)* For fcc arrangement, $4r = \sqrt{2}a$

where, r = radius and a = edge length

$\therefore$ Closest distance $= 2r = \dfrac{\sqrt{2}\,a}{2} = \dfrac{a}{\sqrt{2}}$

13. *(d)* According to Arrhenius equation

$$k = Ae^{-E_a/RT}$$

where, A = collision number or pre-exponential factor.

R = gas constant

T = absolute temperature

E_a = energy of activation

For reaction R_1, $k_1 = Ae^{-E_{a_1}/RT}$ ...(i)

For reaction R_2, $k_2 = Ae^{-E_{a_2}/RT}$ ...(ii)

On dividing Eq. (ii) by Eq. (i), we get

$$\frac{k_2}{k_1} = e^{-\frac{(E_{a_2} - E_{a_1})}{RT}} \quad \text{...(iii)}$$

[$\because$ Pre-exponential factor 'A' is same for both reactions]

Taking ln on both the sides of Eq. (iii), we get

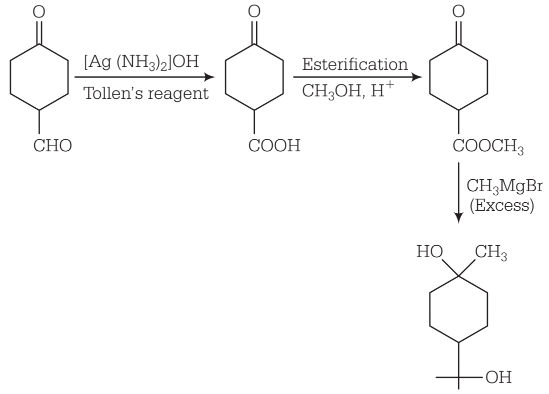
$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_{a_1} - E_{a_2}}{RT}$$

Given, $E_{a_1} = E_{a_2} + 10\text{ kJ mol}^{-1}$

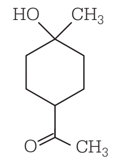
$= E_{a_2} + 10{,}000\text{ J mol}^{-1}$

$$\therefore \quad \ln\frac{k_2}{k_1} = \frac{10{,}000\text{ J mol}^{-1}}{8.314\text{ J mol}^{-1}\text{K}^{-1} \times 300\text{ K}} = 4$$

14. *(a)*



Before final product is formed, intermediate is

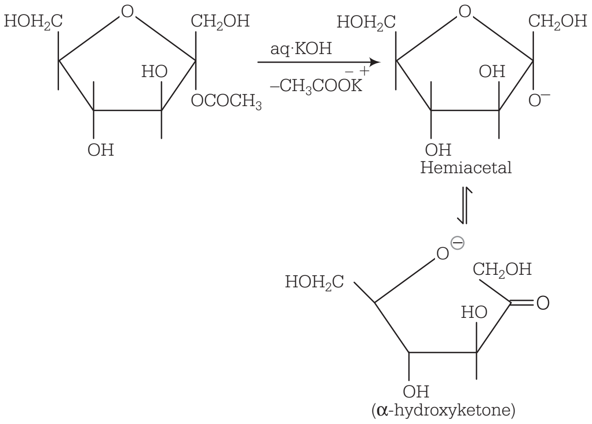


15. *(b)* Colloidal solutions show Tyndall effect due to scattering of light by colloidal particles in all directions in space. It is observed only under the following conditions.

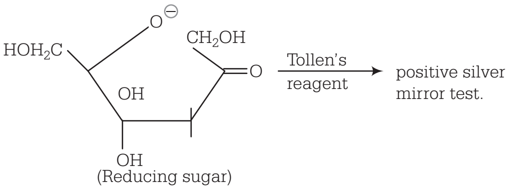
(i) The diameter of the colloids should not be much smaller than the wavelength of light used.

(ii) The refractive indices of the dispersed phase and dispersion medium should differ greatly in magnitude.

16. *(a)* Sugars that have an aldehyde, a ketone, a hemiacetal or a hemiketal group is able to reduce an oxidising agent. These sugars are classified as reducing sugars.



Hemiacetal can be easily reduced by oxidising agent such as Tollen's reagent.



17. *(c)* Based on given $\Delta_r H^\circ$

$$\Delta_f H^\circ = H^\circ_{CO_2} = -393.5 \text{ kJ mol}^{-1} \quad \ldots(i)$$

$$\Delta_f H^\circ = H^\circ_{H_2O} = -285.8 \text{ kJ mol}^{-1} \quad \ldots(ii)$$

$$\Delta_f H^\circ = H^\circ_{O_2} = 0.00 \text{ (elements)} \quad \ldots(iii)$$

Required thermal reaction is for $\Delta_f H^\circ$ of CH_4

Thus, from III

$$890.3 = [\Delta_f H^\circ(CH_4) + 2\Delta_f H^\circ(O_2)]$$

$$-[\Delta_f H^\circ(CO_2) + 2\Delta_f H^\circ(H_2O)]$$

$$= \Delta_f H^\circ(CH_4) + 0] - [-393.5 - 2 \times 285.5]$$

$$\therefore \quad \Delta_f H^\circ(CH_4) = -74.8 \text{ kJ/mol}$$

18. *(a)* The reaction in which oxidation and reduction occur simultaneously are termed as redox reaction.

$$(\overset{+4}{X})eF_4 + \overset{+1}{O_2}(F_2) \longrightarrow \overset{+6}{X}eF_6 + \overset{0}{O_2}$$

Since, Xe undergoes oxidation while O undergoes reduction.

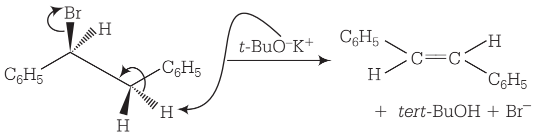
So, it is an example of redox reaction.

19. *(c)* Cl_2, Br_2 and I_2 form a mixture of halide and hypohalites when react with cold dilute alkalies while a mixture of halides and haloate when react with concentrated cold alkalies.

$$\underset{\text{Cold and dilute}}{Cl_2 + 2NaOH} \longrightarrow NaCl + NaClO + H_2O$$

$\therefore$ Cl^- and ClO^- are obtained as products when chlorine gas reacts with cold and dilute aqueous NaOH.

20. *(b)* An alkyl halide in presence of a bulkier base removes a proton from a carbon adjacent to the carbon bonded to the halogen. This reaction is called E2 (β-elimination reaction).



21. *(d)* The reaction takes place as follows

$$\underset{(X)}{Na_2C_2O_4} + \underset{\text{(conc.)}}{H_2SO_4} \longrightarrow Na_2SO_4 + H_2O \underset{\text{Effervescence}}{+ CO\uparrow + CO_2\uparrow}$$

$$\underset{(X)}{Na_2C_2O_4} + CaCl_2 \longrightarrow \underset{\text{White ppt.}}{CaC_2O_4} + 2NaCl$$

$$5CaC_2O_4 + \underset{\text{Purple}}{2KMnO_4} + 8H_2SO_4 \longrightarrow K_2SO_4 + 5CaSO_4 + \underset{\text{Colourless}}{2MnSO_4} + 10CO_2 + 8H_2O$$

Hence, X is $Na_2C_2O_4$.

22. *(b)* To identify the magnetic nature we need to check the molecular orbital configuration. If all orbitals are fully occupied, species is diamagnetic while when one or more molecular orbitals is/are singly occupied, species is paramagnetic.

(a) NO (7 + 8 = 15) – $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2,$

$$\pi 2p_x^2 = \pi 2p_y^2, \pi 2p_z^2, \pi^* 2p_x^1 = \pi^* 2p_y^0$$

One unpaired electron is present.

Hence, it is paramagnetic.

(b) CO (6 + 8 = 14) – $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2,$

$$\pi 2p_x^2 = \pi 2p_y^2, \sigma 2p_z^2$$

No unpaired electron is present.

Hence, it is diamagnetic.

(c) O_2 (8 + 8 = 16) – $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$

$$\pi 2p_x^2 = \pi 2p_x^2, \pi^* 2p_x^1 = \pi^* 2p_y^1$$

Two unpaired electrons are present.
Hence, it is paramagnetic.

(d) B_2(5 + 5) – $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_x^1 = \pi 2p_y^1$

Two unpaired electrons are present.

Hence, it is paramagnetic.

23. *(d)* Let the degree of association of acetic acid (CH_3COOH) in benzene is α, then

	$2CH_3COOH \rightleftharpoons$	$(CH_3COOH)_2$
Initial moles	1	0
Moles at equilibrium	$1-\alpha$	$\frac{\alpha}{2}$

$$\therefore \text{ Total moles} = 1 - \alpha + \frac{\alpha}{2} = 1 - \frac{\alpha}{2} \quad \text{or} \quad i = 1 - \frac{\alpha}{2}$$

Now, depression in freezing point (ΔT_f) is given as

$$\Delta T_f = i K_f m \quad \ldots(i)$$

where, K_f = molal depression constant or cryoscopic constant.

m = molality

$$\text{Molality} = \frac{\text{number of moles of solute}}{\text{weight of solvent (in kg)}} = \frac{0.2}{60} \times \frac{1000}{20}$$

Putting the values in Eq. (i)

$$\therefore \quad 0.45 = \left[1 - \frac{\alpha}{2}\right](5.12)\left[\frac{0.2}{60} \times \frac{1000}{20}\right]$$

$$1 - \frac{\alpha}{2} = \frac{0.45 \times 60 \times 20}{5.12 \times 0.2 \times 1000}$$

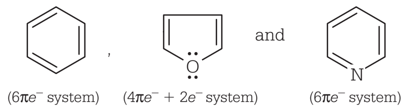
$$\Rightarrow \quad 1 - \frac{\alpha}{2} = 0.527$$

$$\Rightarrow \quad \frac{\alpha}{2} = 1 - 0.527$$

$$\therefore \quad \alpha = 0.946$$

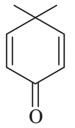
Thus, percentage of association = 94.6%

24. *(d)* Aromatic compounds are stable due to resonance while non-aromatics are not. According to Huckel's rule (or $4n + 2$ rule), "For a planar, cyclic compound to be aromatic, its π cloud must contain $(4n + 2)\pi$ electrons, where, n is any whole number." Thus,



($6\pi e^-$ system) ($4\pi e^- + 2e^-$ system) ($6\pi e^-$ system)

are aromatic and stabilised by resonance.
They follow Huckel's rule.



is non-aromatic, hence, least stabilised by resonance.

25. *(d)* Molarity $(M) = \dfrac{\text{Number of moles of solute}}{\text{Volume of solution (in L)}}$

$\therefore$ Number of moles of complex

$$= \frac{\text{Molarity} \times \text{volume (in mL)}}{1000}$$

$$= \frac{0.1 \times 100}{1000} = 0.01 \text{ mole}$$

Number of moles of ions precipitate

$$= \frac{1.2 \times 10^{22}}{6.02 \times 10^{23}} = 0.02 \text{ moles}$$

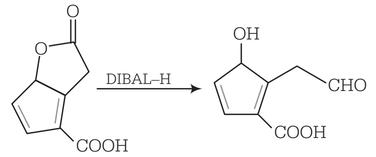
$\therefore$ Number of Cl^- present in ionisation sphere

$$= \frac{\text{Number of moles of ions precipitated}}{\text{Number of moles of complex}} = \frac{0.02}{0.01} = 2$$

$\therefore$ 2 Cl^- are present outside the square brackets, i.e. in ionisation sphere. Thus, the formula of complex is

$$[Co(H_2O)_5Cl]Cl_2 \cdot H_2O.$$

26. *(a)* DIBAL-H (Di-isobutyl aluminium hydride) is a reducing agent with formula. This is generally used for the preparation of aldehydes. Using DIBAL —H, Lactones are reduced directly to aldehydes.



27. *(c)* **NO_3^-** The maximum limit of nitrate (NO_3^-) in drinking water is 50 ppm and its source is fertilisers. If the maximum limit is increased in water it will cause methemoglobinemia (blue baby syndrome.)

SO_4^{2-} The maximum limit of sulphate (SO_4^{2-}) according to WHO is 500 pm and its sources are acid rain, industries. Excess SO_4^{2-} has laxative effect.

F^- The maximum limit of fluoride (F^-) is about 1.5 ppm. Its higher concentration converts enamel to more harder fluorapatite. Concentration (>2ppm) causes brown mottling of teeth and high concentration (>10 ppm) are harmful for bones and teeth.

$\therefore$ SO_4^{2-} (100 ppm) and NO_3^- (50 ppm) in water is suitable for drinking but the concentration of F^- (10 ppm) makes water unsuitable for drinking.

28. *(b)* $\underset{1\text{ g}}{M_2CO_3} + 2HCl \longrightarrow 2MCl + H_2O + \underset{0.01186\text{ mole}}{CO_2}$

Number of moles of M_2CO_3 reacted = Number of moles of CO_2 evolved

$$\frac{1}{M} = 0.01186 \qquad [M = \text{molar mass of } M_2CO_3]$$

$$M = \frac{1}{0.01186} = 84.3 \text{ g mol}^{-1}$$

29. *(a)* The substances which have lower reduction potentials are stronger reducing agents. Therefore, Cr ($E^\circ_{Cr^{3+}/Cr} = -0.74$ V) is the strongest reducing agent among all the other given options.

30. *(a)* Isoelectronic species are those which contains same number of electrons.

Species	**Atomic number**	**Number of electrons**
O^{2-}	8	10
F^-	9	10
Na^+	11	10
Mg^{2+}	12	10
O^-	8	9
Na	11	11
Mg^+	12	11

$\therefore$ Option (a) is correct which contains isoelectronic species O^{2-}, F^-, Na^+, Mg^{2+}.

JEE MAIN

SOLVED PAPER 2018

1. The ratio of mass per cent of C and H of an organic compound $(C_xH_yO_z)$ is 6 : 1. If one molecule of the above compound $(C_xH_yO_z)$ contains half as much oxygen as required to burn one molecule of compound C_xH_y completely to CO_2 and H_2O. The empirical formula of compound $C_xH_yO_z$ is

(a) $C_3H_6O_3$ (b) C_2H_4O (c) $C_3H_4O_2$ (d) $C_2H_4O_3$

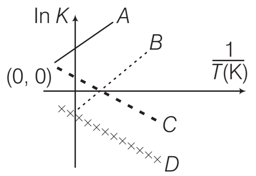
2. Which type of 'defect' has the presence of cations in the interstitial sites?

(a) Schottky defect (b) Vacancy defect
(c) Frenkel defect (d) Metal deficiency defect

3. According to molecular orbital theory, which of the following will not be a viable molecule?

(a) He_2^{2+} (b) He_2^+ (c) H_2^- (d) H_2^{2-}

4. Which of the following lines correctly show the temperature dependence of equilibrium constant, K, for an exothermic reaction?



(a) A and B (b) B and C
(c) C and D (d) A and D

5. The combustion of benzene (l) gives $CO_2(g)$ and $H_2O(l)$. Given that heat of combustion of benzene at constant volume is –3263.9 kJ mol^{-1} at 25° C; heat of combustion (in kJ mol^{-1}) of benzene at constant pressure will be $(R = 8.314\ JK^{-1}mol^{-1})$

(a) 4152.6 (b) –452.46 (c) 3260 (d) –3267.6

6. For 1 molal aqueous solution of the following compounds, which one will show the highest freezing point?

(a) $[Co(H_2O)_6]Cl_3$ (b) $[Co(H_2O)_5Cl]Cl_2 \cdot H_2O$
(c) $[Co(H_2O)_4Cl_2]Cl \cdot 2H_2O$ (d) $[Co(H_2O)_3Cl_3] \cdot 3H_2O$

7. An aqueous solution contains 0.10 M H_2S and 0.20 M HCl. If the equilibrium constants for the formation of HS^- from H_2S is 1.0×10^{-7} and that of S^{2-} from HS^- ions is 1.2×10^{-13} then the concentration of S^{2-} ions in aqueous solution is :

(a) 5×10^{-8} (b) 3×10^{-20}
(c) 6×10^{-21} (d) 5×10^{-19}

8. An aqueous solution contains an unknown concentration of Ba^{2+}. When 50 mL of a 1 M solution of Na_2SO_4 is added, $BaSO_4$ just begins to precipitate. The final volume is 500 mL. The solubility product of $BaSO_4$ is 1×10^{-10}. What is the original concentration of Ba^{2+}?

(a) 5×10^{-9} M (b) 2×10^{-9} M
(c) 1.1×10^{-9} M (d) 1.0×10^{-10} M

9. At 518°C, the rate of decomposition of a sample of gaseous acetaldehyde, initially at a pressure of 363 Torr, was 1.00 Torr s^{-1} when 5% had reacted and 0.5 Torr s^{-1} when 33% had reacted. The order of the reaction is :

(a) 2 (b) 3 (c) 1 (d) 0

10. How long (approximate) should water be electrolysed by passing through 100 amperes current so that the oxygen released can completely burn 27.66 g of diborane?
(Atomic weight of $B = 10.8\ \mu$)

(a) 6.4 hours (b) 0.8 hours
(c) 3.2 hours (d) 1.6 hours

11. The recommended concentration of fluoride ion in drinking water is up to 1 ppm as fluoride ion is required to make teeth enamel harder by converting $[3Ca_3(PO_4)_2 \cdot Ca(OH)_2]$ to :

(a) $[CaF_2]$ (b) $[3(CaF_2) \cdot Ca(OH)_2]$
(c) $[3Ca_3(PO_4)_2 \cdot CaF_2]$ (d) $[3\{Ca_3(PO_4)_2\} \cdot CaF_2]$

12. Which of the following compounds contain(s) no covalent bond(s)?

$$KCl, PH_3, O_2, B_2H_6, H_2SO_4$$

(a) KCl, B_2H_6, PH_3 (b) KCl, H_2SO_4
(c) KCl (d) KCl, B_2H_6

13. Which of the following are Lewis acids?

(a) PH_3 and BCl_3 (b) $AlCl_3$ and $SiCl_4$
(c) PH_3 and $SiCl_4$ (d) BCl_3 and $AlCl_3$

14. Total number of lone pair of electron in I_3^- ion is

(a) 3 (b) 6 (c) 9(d) 12

15. Which of the following salts is the most basic in aqueous solution?

(a) $Al(CN)_3$ (b) CH_3COOK (c) $FeCl_3$ (d $Pb(CH_3COO)_2$

16. Hydrogen peroxide oxidises $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_6]^{3-}$ in acidic medium but reduces $[Fe(CN)_6]^{3-}$ to $[Fe(CN)_6]^{4-}$ in alkaline medium. The other products formed are, respectively.

(a) $(H_2O + O_2)$ and H_2O (b) $(H_2O + O_2)$ and $(H_2O + OH^-)$
(c) H_2O and $(H_2O + O_2)$ (d) H_2O and $(H_2O + OH^-)$

17. The oxidation states of Cr, in $[Cr(H_2O)_6]Cl_3$, $[Cr(C_6H_6)_2]$, and $K_2[Cr(CN)_2(O)_2(O_2)(NH_3)]$ respectively are

(a) +3, +4 and +6 (b) +3, +2 and +4
(c) +3, 0 and +6 (d) +3, 0 and +4

18. The compound that does not produce nitrogen gas by the thermal decomposition is

(a) $Ba(N_3)_2$ (b) $(NH_4)_2Cr_2O_7$
(c) NH_4NO_2 (d) $(NH_4)_2SO_4$

19. When metal '*M*' is treated with NaOH, a white gelatinous precipitate '*X*' is obtained, which is soluble in excess of NaOH. Compound '*X*' when heated strongly gives an oxide which is used in chromatography as an adsorbent. The metal '*M*' is

(a) Zn (b) Ca (c) Al (d) Fe

20. Consider the following reaction and statements :

$$[Co(NH_3)_4Br_2]^+ + Br^- \longrightarrow [Co(NH_3)_3Br_3] + NH_3$$

I. Two isomers are produces if the reactant complex ion is a *cis*-isomer.
II. Two isomers are produced if the reactant complex ion is a *trans*-isomer.
III. Only one isomer is produced if the reactant complex ion is a *trans*-isomer.
IV. Only one isomer is produced if the reactant complex ion is a *cis*-isomer.

The correct statements are

(a) (I) and (II) (b) (I) and (III)
(c) (III) and (IV) (d) (II) and (IV)

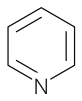
21. Glucose on prolonged heating with HI gives

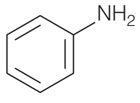
(a) *n*-hexane (b) 1-hexene
(c) Hexanoic acid (d) 6-iodohexanal

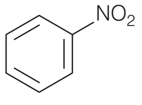
22. The *trans*-alkenes are formed by the reduction of alkynes with

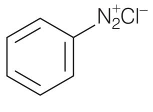
(a) H_2-Pd/C, $BaSO_4$ (b) $NaBH_4$
(c) Na/liq. NH_3 (d) Sn-HCl

23. Which of the following compounds will be suitable for Kjeldahl's method for nitrogen estimation?

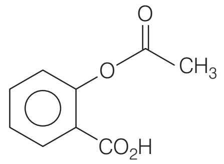
(a) 

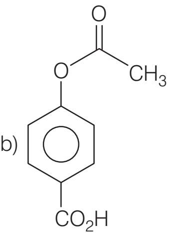
(b) 

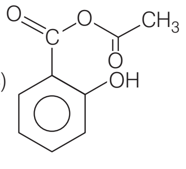
(c) 

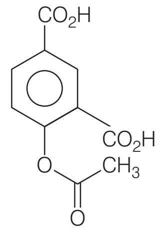
(d) 

24. Phenol on treatment with CO_2 in the presence of NaOH followed by acidification produces compound *X* as the major product. *X* on treatment with $(CH_3CO)_2O$ in the presence of catalytic amount of H_2SO_4 produces:

(a) 

(b) 

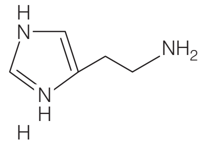
(c) 

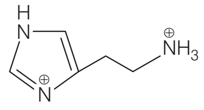
(d) 

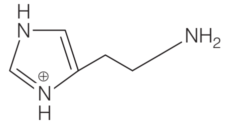
25. An alkali is titrated against an acid with methyl orange as indicator, which of the following is a correct combination?

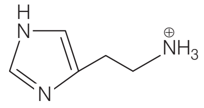
	Base	Acid	End point
(a)	Weak	Strong	Colourless to pink
(b)	Strong	Strong	Pinkish red to yellow
(c)	Weak	Strong	Yellow to pinkish red
(d)	Strong	Strong	Pink to colourless

26. The predominant form of histamine present in human blood is (pK_a, Histidine = 6.0)

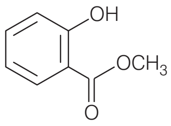
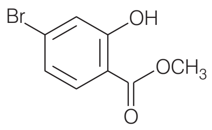
(a) 

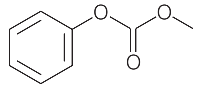
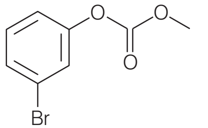
(b) 

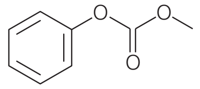
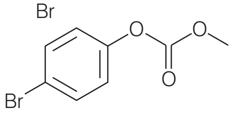
(c) 

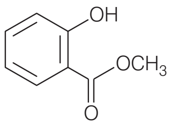
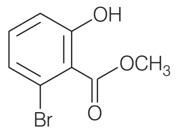
(d) 

27. Phenol reacts with methyl chloroformate in the presence of NaOH to form product *A*. *A* reacts with Br_2 to form product *B*. *A* and *B* are respectively

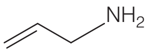
(a)  and 

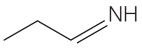
(b)  and 

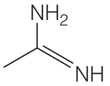
(c)  and 

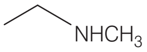
(d)  and 

28. The increasing order of basicity of the following compounds is

I. 

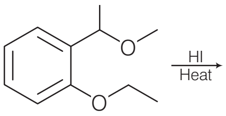
II. 

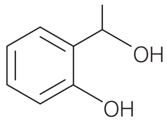
III. 

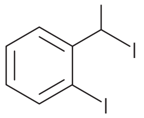
IV. 

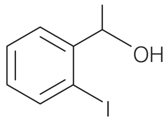
(a) (I) < (II) < (III) < (IV)
(b) (II) < (I) < (III) < (IV)
(c) (II) < (I) < (IV) < (III)
(d) (IV) < (II) < (I) < (III)

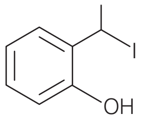
29. The major product formed in the following reaction is



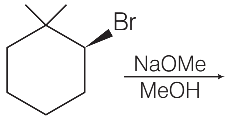
(a) 

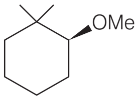
(b) 

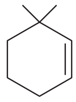
(c) 

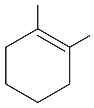
(d) 

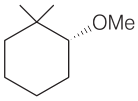
30. The major product of the following reaction is



(a) 

(b) 

(c) 

(d) 

Answers

1.	*(d)*	2.	*(c)*	3.	*(d)*	4.	*(a)*	5.	*(d)*	6.	*(d)*	7.	*(b)*	8.	*(c)*	9.	*(a)*	10.	*(c)*
11.	*(c)*	12.	*(c)*	13.	*(d)*	14.	*(c)*	15.	*(b)*	16.	*(c)*	17.	*(c)*	18.	*(d)*	19.	*(c)*	20.	*(b)*
21.	*(a)*	22.	*(c)*	23.	*(b)*	24.	*(a)*	25.	*(c)*	26.	*(d)*	27.	*(c)*	28.	*(c)*	29.	*(d)*	30.	*(b)*

Answer *with* Explanations

1. ***(d)*** We can calculate the simplest whole number ratio of C and H from the data given, as

Element	Relative mass	Molar mass	Relative mole	Simplest whole number ratio
C	6	12	$\frac{6}{12} = 0.5$	$\frac{0.5}{0.5} = 1$
H	1	1	$\frac{1}{1} = 1$	$\frac{1}{0.5} = 2$

Alternatively this ratio can also be calculated directly in the terms of x and y as

$\frac{12x}{y} = \frac{6}{1}$ (given and molar mass of C $= 12$, H $= 1$)

Now, after calculating this ratio look for condition 2 given in the question i.e. quantity of oxygen is half of the quantity required to burn one molecule of compound C_xH_y completely to CO_2 and H_2O. We can calculate number of oxygen atoms from this as consider the equation.

$$C_xH_y + \left[x + \frac{y}{4}\right]O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O$$

Number of oxygen atoms required $= 2 \times \left[x + \frac{y}{4}\right] = \left[2x + \frac{y}{2}\right]$

Now given, $$z = \frac{1}{2}\left[2x + \frac{y}{2}\right] = \left[x + \frac{y}{4}\right]$$

Here we consider x and y as simplest ratios for C and H so now putting the values of x and y in the above equation.

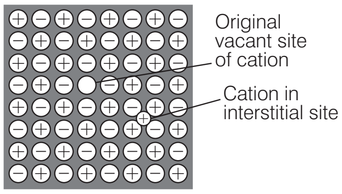
$$z = \left[x + \frac{y}{4}\right] = \left[1 + \frac{2}{4}\right] = 1.5$$

Thus, the simplest ratio figures for x, y and z are $x = 1$, $y = 2$ and $z = 1.5$

Now, put these values in the formula given i.e. $C_xH_yO_z = C_1H_2O_{1.5}$

So, empirical formula will be $[C_1H_2O_{1.5}] \times 2 = C_2H_4O_3$

2. ***(c)*** It is the "Frenkel defect" in which cations leave their original site and occupy interstitial site as shown below.



3. ***(d)*** ***Key Idea*** *According to M.O.T, the viability of any molecule can be judged through the calculation of bond order.*

Electronic	Configuration	Bond order
He_2^+	$\sigma_{1s^2}\sigma^*_{1s^1}$	$\frac{2-1}{2} = 0.5$
H_2^-	$\sigma_{1s^2}\sigma^*_{1s^1}$	$\frac{2-1}{2} = 0.5$
H_2^{2-}	$\sigma_{1s^2}\sigma^*_{1s^2}$	$\frac{2-2}{2} = 0$
He_2^{2+}	σ_{1s^2}	$\frac{2-0}{2} = 1$

The molecule having zero bond order will not be viable hence, H_2^{2-} (option d) is the correct answer.

4. *(a)* From thermodynamics,

$$\ln k = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad \ldots\text{(i)}$$

Mathematically, the equation of straight line is

$$y = c + mx \quad \ldots\text{(ii)}$$

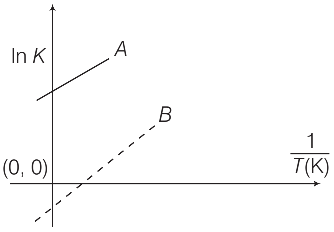
After comparing Eq. (ii) with (i) we get,

slope $= \frac{-\Delta H^\circ}{R}$ and intercept $= \frac{\Delta S^\circ}{R}$

Now, we know for exothermic reaction ΔH is negative (−)ve. But here,

$$\text{Slope} = \frac{-\Delta H^\circ}{R} \text{ is positive}$$

So, lines A and B in the graph represent temperature dependence of equilibrium constant K for an exothermic reaction as shown below



5. *(d)* ***Key idea***

Calculate the heat of combustion with the help of following formula

$$\Delta H_p = \Delta U + \Delta n_g RT$$

where, ΔH_p *= Heat of combustion at constant pressure*

ΔU *= Heat at constant volume (It is also called* ΔE*)*

Δn_g *= Change in number of moles (In gaseous state).*

R *= Gas constant;* T *= Temperature.*

From the equation,

$$C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)$$

Change in the number of gaseous moles i.e.

$$\Delta n_g = 6 - \frac{15}{2} = -\frac{3}{2} \text{ or } -1.5$$

Now we have Δn_g and other values given in the question are

$\Delta U = -3263.9$ kJ/mol

$T = 25°\text{C} = 273 + 25 = 298$ K

$R = 8.314\ \text{JK}^{-1}\text{mol}^{-1}$

So, $\Delta H_p = (-3263.9) + (-1.5) \times 8.314 \times 10^{-3} \times 298$

$= -3267.6\ \text{kJ mol}^{-1}$

6. *(d)* ***Key idea*** *"Addition of solute particles to a pure solvent results to depression in its freezing point."*

All the compounds given in question are ionic in nature so, consider their van't Hoff factor (i) to reach at final conclusion.

The solution with maximum freezing point must have minimum number of solute particles. This generalisation can be done with the help of van't Hoff factor (i) i.e.

Number of solute particles ∝ van't Hoff factor (i)

Thus, we can say directly

Solution with maximum freezing point will be the one in which solute with minimum van't Hoff factor is present

Now, for $Co(H_2O)_6]Cl_3 \rightleftharpoons [Co(H_2O)_6]^{3+} + 3Cl^-$

van't Hoff factor (i) is 4. Similarly for,

$[Co(H_2O)_5Cl]Cl_2 \cdot H_2O \rightleftharpoons [Co(H_2O)_5Cl]^{2+} + 2Cl^-$ 'i' is 3

$[Co(H_2O)_4Cl_2]Cl \cdot 2H_2O \rightleftharpoons [Co(H_2O)_4Cl_2]^+ + Cl^-$ 'i' is 2

and for $[Co(H_2O)_3Cl_3] \cdot 3H_2O$, '$i$' is 1 as it does not show ionisation. Hence, $[Co(H_2O)_3Cl_3] \cdot 3H_2O$ have minimum number of particles in the solution.

So, freezing point of its solution will be maximum.

7. *(b)* Given $[H_2S] = 0.10$ M

$[HCl] = 0.20$ M So, $[H^+] = 0.20$ M

$H_2S \rightleftharpoons H^+ + HS^-,\ K_1 = 1.0 \times 10^{-7}$

$HS^- \rightleftharpoons H^+ + S^{2-},\ K_2 = 1.2 \times 10^{-13}$

It means for,

$H_2S \rightleftharpoons 2H^+ + S^{2-}$

$K = K_1 \times K_2 = 1.0 \times 10^{-7} \times 1.2 \times 10^{-13} = 1.2 \times 10^{-20}$

Now $[S^{2-}] = \frac{K \times [H_2S]}{[H^+]^2}$ [according to the final equation]

$= \frac{1.2 \times 10^{-20} \times 0.1\ \text{M}}{(0.2\text{M})^2} = \frac{1.2 \times 10^{-20} \times 1 \times 10^{-1}\ \text{M}}{4 \times 10^{-2}\text{M}}$

$= 3 \times 10^{-20}$ M

8. *(c)* Its given that the final volume is 500 mL and this final volume was arrived when 50 mL of 1 M Na_2SO_4 was added to unknown Ba^{2+} solution.

So, we can interpret the volume of unknown Ba^{2+} solution as 450 mL i.e.

$$\underset{\substack{Ba^{2+}\\ \text{solution}}}{450\text{mL}} + \underset{\substack{Na_2SO_4\\ \text{solution}}}{50\text{mL}} \longrightarrow \underset{\substack{BaSO_4\\ \text{solution}}}{500\text{mL}}$$

From this we can calculate the concentration of SO_4^{2-} ion in the solution *via*

$M_1V_1 = M_2V_2$

$1 \times 50 = M_2 \times 500$

(as 1M Na_2SO_4 is taken into consideration)

$M_2 = \frac{1}{10} = 0.1$ M

Now for just precipitation,

Ionic product = Solubility product (K_{sp})

i.e. $[Ba^{2+}][SO_4^{2-}] = K_{sp}$ of $BaSO_4$

Given K_{sp} of $BaSO_4 = 1 \times 10^{-10}$

So, $[Ba^{2+}][0.1] = 1 \times 10^{-10}$

or $[Ba^{2+}] = 1 \times 10^{-9}$ M

Remember This is the concentration of Ba^{2+} ions in final solution. Hence, for calculating the $[Ba^{2+}]$ in original solution we have to use

$M_1V_1 = M_2V_2$

as $M_1 \times 450 = 10^{-9} \times 500$

so, $M_1 = 1.1 \times 10^{-9}$M

9. *(a)* For the reaction,

$$CH_3CHO(g) \xrightarrow{\text{Decomposes}} CH_4 + CO$$

Let order of reaction with respect to CH_3CHO is m.

Its given, $r_1 = 1$ torr/sec. when CH_3CHO is 5% reacted i.e. 95% unreacted. Similarly, $r_2 = 0.5$ torr/sec when CH_3CHO is 33% reacted i.e., 67% unreacted.

Use the formula, $r \propto (a - x)^m$

where $(a - x)$ = amount unreacted

so, $\dfrac{r_1}{r_2} = \dfrac{(a - x_1)^m}{(a - x_2)^m}$ or $\dfrac{r_1}{r_2} = \left[\dfrac{a - x_1}{a - x_2}\right]^m$

Now putting the given values

$$\frac{1}{0.5} = \left(\frac{0.95}{0.67}\right)^m \Rightarrow 2 = (1.41)^m \quad \text{or } m = 2$$

10. ***(c)*** Given that, $i = 100$ amp. also, 27.66 g of diborane (B_2H_6)

Molecular mass of $B_2H_6 = 10.8 \times 2 + 6 = 27.6$

Number of moles of B_2H_6 in 27.66 g $= \dfrac{\text{Given mass}}{\text{Molar mass}} = \dfrac{27.66}{27.6} \approx 1$

Now consider the equation

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$$

From the equation we can interpret that 3 moles of oxygen is required to burn 1 mole (i.e. 27.6 g) B_2H_6 completely.

Also consider the electrolysis reaction of water i.e.

$$H_2O \rightleftharpoons 2H^+ + O^{--}$$

$$2H^+ \xrightarrow[\text{Cathode}]{+2e^-} 2H \longrightarrow H_2 \uparrow$$

$$O^{--} \xrightarrow[-2e^-]{\text{Anode}} O \xrightarrow[\text{atoms}]{\text{2 such}} O_2 \uparrow$$

From the above equation it can be easily interpreted that in electrolysis of water for the production of 1 mole of oxygen from 1 mole of H_2O at anode 4 moles electrons are required.

Likewise for the production of 3 moles of O_2 $12 (3 \times 4)$ moles of electrons will be needed.

So, the total amount of charge required to produce 3 moles of oxygen will be $12 \times F$ or 12×96500

We know $Q = it$

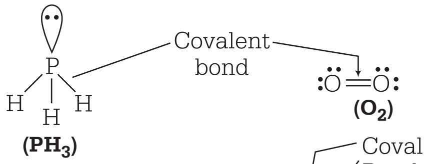
So, $12 \times 96500 = 100 \times t$ in seconds

or $\dfrac{12 \times 96500}{100 \times 3600} = t$ in hours $= 3.2$ hours

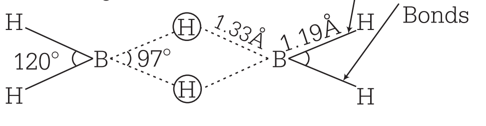
11. ***(c)*** Fluoride ions help in making teeth enamel harder by converting $[3Ca_3(PO_4)_2 \cdot Ca(OH)_2]$ i.e. Hydroxy apatite to $[3Ca_3(PO_4)_2 \cdot CaF_2]$ i.e., Fluorapatite (Harder teeth enamel) *via* following reaction:

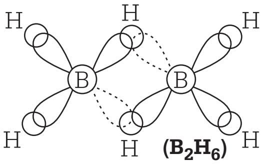
$$[3Ca_3(PO_4)_2 \cdot Ca(OH)_2] + \underset{\substack{\text{From}\\ \text{drinking}\\ \text{water}}}{2F^-} \longrightarrow [3Ca_3(PO_4)_2 \cdot CaF_2] + 2OH^-$$

12. ***(c)*** KCl is the only ionic compound. The structure of PH_3, O_2, B_2H_6 and H_2SO_4 are given below

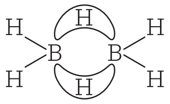


(PH₃) **(O₂)**

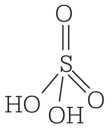




(B_2H_6)



Banana bond



Sulphuric acid

(H_2SO_4)

All bond between S and O atom are covalent bonds.

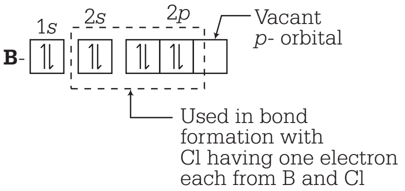
13. ***(d)*** ***Key Idea*** *Lewis acids are defined as,*

"Electron deficient compounds which have the ability to accept atleast one lone pair."

The compound given are

PH_3 -Octet complete although P has vacant $3d$-orbital but does not have the tendency to accept lone pair in it. Hence, it cannot be considered as Lewis acid.

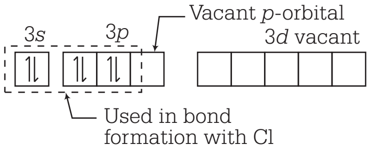
BCl_3 -Incomplete octet with following orbital picture.



Hence, vacant p-orbital of B can accept one lone pair thus it can be considered as Lewis acid.

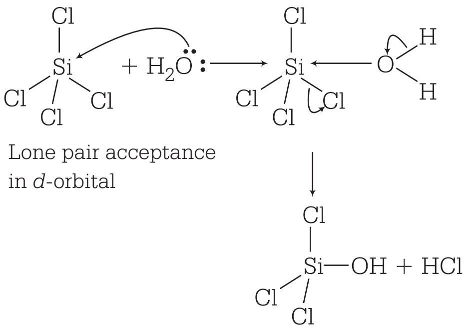
$AlCl_3$ -Similar condition is visible in $AlCl_3$ as well i.e.

Al (Valence orbital only) =



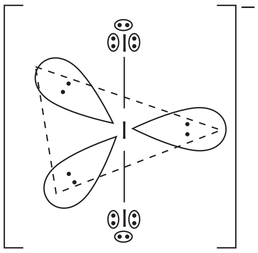
Hence this compound can also be considered as Lewis acid.

$SiCl_4$ - Although this compound does not have incomplete octet but it shows the tendency to accept lone pair of electrons in its vacant d-orbital. This tendency of $SiCl_4$ is visible in following reaction.



Thus option (b) and (d) both appear as correct but most suitable answer is (d) as the condition of a proper Lewis acid is more well defined in BCl_3 and $AlCl_3$.

14. *(c)* The structure of I_3^- ion is



Hence, 9 is the correct answer.

15. *(b)* Among the given salts

$FeCl_3$ is acidic in nature i.e., have acidic solution as it is the salt of weak base and strong acid.

$Al(CN)_3$ and **$Pb(CH_3COO)_2$** are the salts of weak acid and weak base.

CH_3COOK is the salt of strong base and weak acid.

Hence, the solution of CH_3COOK will be most basic because of the following reaction.

$$CH_3COOK + H_2O \rightleftharpoons \underset{\text{(Weak acid)}}{CH_3COOH} + \underset{\text{(Strong base)}}{KOH}$$

16. *(c)* Both reactions in their complete format are written below

(i) In acidic medium,

$$[Fe^{2+}(CN)_6]^{4-} + H_2\overset{-1}{O_2} + 2H^+ \longrightarrow [Fe^{3+}(CN)_6]^{3-} + 2H_2\overset{-2}{O}$$

(ii) In alkaline medium,

$$[Fe^{3+}(CN)_6]^{3-} + H_2\overset{-1}{O_2} + 2OH^- \longrightarrow [Fe^{2+}(CN)_6]^{4-} + O_2 + 2H_2O$$

Hence, H_2O (for reaction (i)) and $O_2 + H_2O$ (for reaction (ii)) are produced as by product.

17. *(c)* Let the oxidation state of Cr in all cases is 'x'

(i) Oxidation state of Cr in $[Cr(H_2O)_6]Cl_3$

$$x + (0 \times 6) + (-1 \times 3) = 0$$

or $x + 0 - 3 = 0$

or $x = +3$

(ii) Oxidation state of Cr in $[Cr(C_6H_6)_2]$

$$x + (2 \times 0) = 0$$

or $x = 0$

(iii) Oxidation state of Cr in

$$K_2[Cr(CN)_2(O)_2(O_2)(NH_3)]$$

$$1 \times 2 + x + (-1 \times 2) + (-2 \times 2) + (-2) + 0 = 0$$

or $2 + x - 2 - 4 - 2 = 0$ or $x - 6 = 0$

hence $x = +6$

Thus, +3, 0 and +6 is the answer.

18. *(d)* The thermal decomposition of given compounds is shown below

$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + 4H_2O + Cr_2O_3$$

$$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$$

$$(NH_4)_2SO_4 \xrightarrow{\Delta} 2NH_3 + H_2SO_4$$

$$Ba(N_3)_2 \longrightarrow Ba + 3N_2$$

Thus, only $(NH_4)_2SO_4$ does not gives N_2 on heating (It give NH_3). While rest of the given compounds gives N_2 on their thermal decomposition.

19. *(c)* Among the given metals Al forms white gelatinous ppt. with NaOH.

Hence, the probable metal can be Al. This ppt. is dissolved in excess of NaOH due to the formation of sodium metal Aluminate. Both the reactions are shown below.

$$Al^{3+} \xrightarrow{\text{NaOH}} \underset{\substack{\text{White gelatinous}\\ \text{ppt. }(X)\text{ of}\\ \text{aluminium}\\ \text{hydroxide}}}{Al(OH)_3} \xrightarrow{\text{Excess of NaOH}} \underset{\substack{\text{Sodium}\\ \text{metaaluminate)}\\ \text{soluble}}}{NaAlO_2}$$

Aluminium hydroxide on strong heating gives alumina (Al_2O_3) which is used as an adsorbent in chromatography. This reaction can be seen as :

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$$

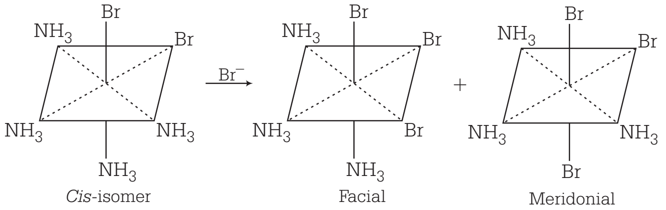
Thus, metal M is Al.

Ca, being below sodium in electrochemical reactivity series, cannot displaces Na from its aqueous solution.

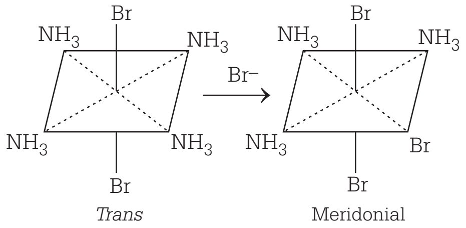
Zn reacts with NaOH to form sodium zincate which is a soluble compound.

Fe reacts with sodium hydroxide to form tetrahydroferrate (II) sodium which is again a soluble complex.

20. *(b)* If the reactant is *cis* isomer than following reaction takes place.

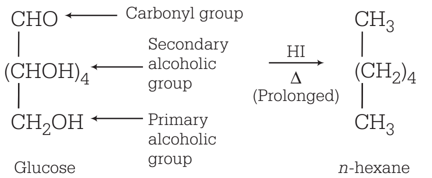


i.e. two isomers are produced. If the reactant is *trans* isomer than following reaction takes place.



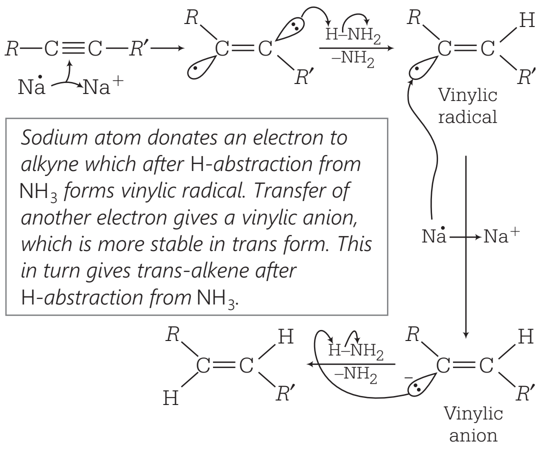
i.e. only 1 isomer is produced. Thus, statement (I) and (III) are correct resulting to option (b) as the correct answer.

21. *(a)* HI is a strong reducing agent. It reduces both primary and secondary alcoholic groups of glucose along with the carbonyl group to produce *n*-hexane as



22. *(c)* Sodium metal in liquid ammonia reduces alkynes with anti stereochemistry to give *trans* alkenes. The reduction is selectively *anti* since the vinyl radical formed during reduction is more stable in *trans* configuration.

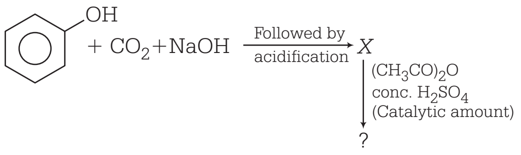
Mechanism



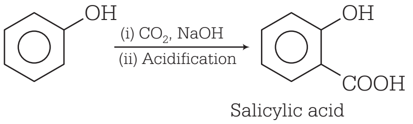
Sodium atom donates an electron to alkyne which after H*-abstraction from* NH_3 *forms vinylic radical. Transfer of another electron gives a vinylic anion, which is more stable in trans form. This in turn gives trans-alkene after* H*-abstraction from* NH_3.

23. *(b)* Estimation of nitrogen through Kjeldahl's method is not suitable for organic compounds containing nitrogen in ring or nitrogen in nitro or azo groups. It is because of the fact that nitrogen of these compounds does not show conversion to Ammonium sulphate $((NH_4)_2SO_4)$ during the process. Hence, among the given compounds only aniline can be used suitably for estimation of nitrogen by Kjeldahl's method.

24. *(a)*

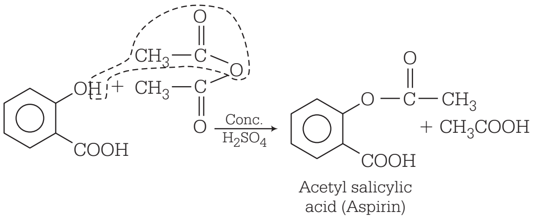


The very first reaction in the above road map looks like Kolbe's reaction which results to salicylic acid as



Salicylic acid
(X)

The salicylic acid with acetic anhydride $[(CH_3CO)_2O]$ in the presence of catalytic amount of conc. H_2SO_4 undergoes acylation to produce aspirin as



Acetyl salicylic acid (Aspirin)

Aspirin is a non-narcotic analgesic (Pain killer).

25. *(c)* Methyl orange show Pinkish colour towards more acidic medium and yellow orange colour towards basic or less acidic media. Its working pH range is

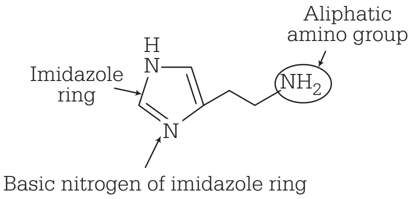
Pinkish Red ← 3.9 –4.5 → Yellow orange

Weak base have the pH range greater than 7. When methyl orange is added to this weak base solution it shows yellow orange colour.

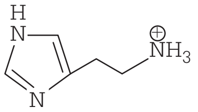
Now when this solution is titrated against strong acid the pH move towards more acidic range and reaches to end point near 3.9 where yellow orange colour of methyl orange changes to Pinkish red resulting to similar change in colour of solution as well.

26. *(d)* Our blood is slightly basic in nature with pH range from 7.35-7.4.

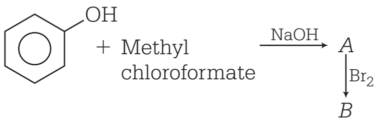
The structure of histamine is given below :



It is produced by decarboxylation of histidine having following structure. It is clearly visible from the above structure that histamine has two basic centres namely aliphatic amino group and basic nitrogen of imidazole ring. The aliphatic amino group has pK_a around 9.4. In blood with pH around 7.4 the aliphatic amino group of histamine become protonated to give a single charged cation as shown below

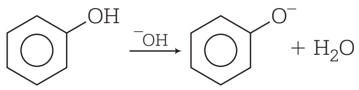


27. *(c)* Given

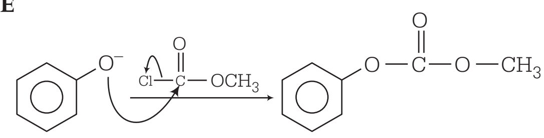


In the above road map, first reaction appears as acid base reaction followed by S_NAE (Nucleophilic substitution through Addition and Elimination). Both the steps are shown below

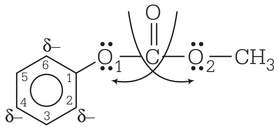
(i) ***Acid base reaction***

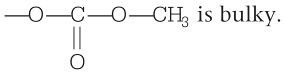


(ii) **S_N AE**

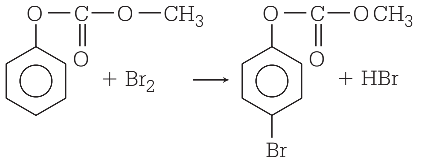


In the product of S_NAE the attached group is *ortho* and *para*-directing due to following cross conjugation

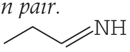


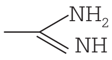
Cross conjugation due to which lone pair of oxygen 1 will be easily available to ring resulting to higher electron density at 2, 4, 6 position with respect to group. However from the stability point of view *ortho* positions are not preferred by substituents as group  $-O-\underset{\underset{O}{\|}}{C}-O-CH_3$ is bulky.

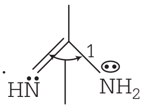
Hence, on further bromination of S_NAE product *para* bromo derivative will be the preferred product i.e.



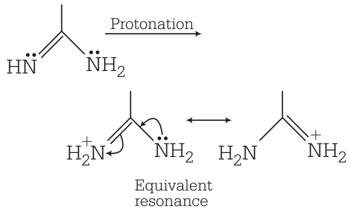
28. ***(c) Key Idea*** *Among the given compounds the basic nature depends upon their tendency to donate electron pair.*

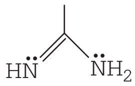
Among the given compounds in  , Nitrogen is sp^2-hybridised. This marginally increases the electronegativity of nitrogen which in turn decreases the electron donation tendency of nitrogen. Thus making compound least basic.

Among the rest  is totally different from others as in this compound lone pair of one nitrogen are in conjugation with π bond i.e. As a result of this conjugation the cation formed after protonation becomes resonance stabilised

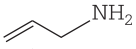


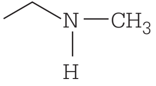
In conjugation



This equivalent resonance in cation makes  most basic among all.

Categorisation is very simple between rest two as

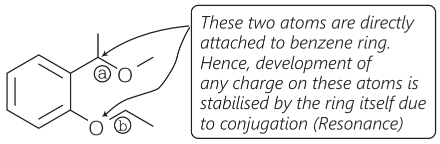
 (primary amine) is less basic than

 (secondary amine)

Hence, the correct order is

(II) < (I) < (IV) < (III) i.e. option ***(c)*** is correct.

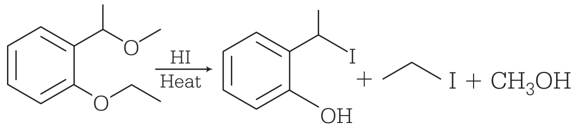
29. ***(d) Key idea*** *The reaction given is a nucleophilic substitution reaction in which cleavage at C—O bond is visible. The product formation can be visualised with the help of following analysis.*



These two atoms are directly attached to benzene ring. Hence, development of any charge on these atoms is stabilised by the ring itself due to conjugation (Resonance)

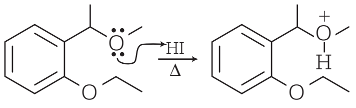
*If any one properly visualise the fact written with figure above, than a conclusion can be made that C—O bonds marked **(a)** and (b) in the figure will undergo heterolysis during the reaction.*

The reaction can be represented as



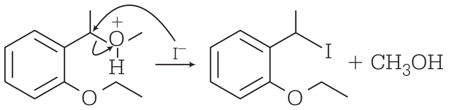
Mechanism

Step I The reaction begins with the attack of H^+ of HI on oxygen to form oxonium ion as

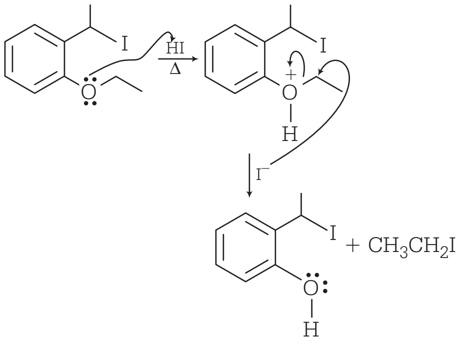


Oxonium ion

Step II This oxonium ion undergoes lysis and addition of $I^-$to form two products as

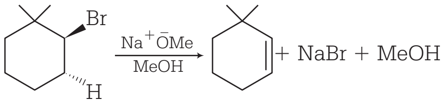


Step III Similar pathway is followed at the other oxygen atom, which can be visualised as



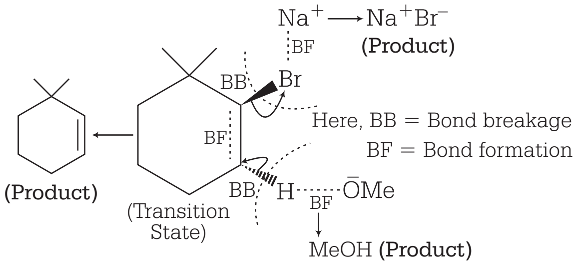
Note *Mechanism of a reaction is always a logical sequencing of events which may occur simultaneously as well.*

30. ***(b)*** Complete reaction can be represented as



Thus, the given reaction is dehydrohalogenation which is a β-elimination proceeding through E_2 mechanism.

Mechanism The reaction proceeds through the formation of following transition state with simultaneous removal of Br and H atoms.



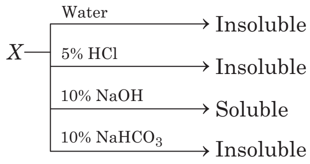
ONLINE QUESTION PAPERS

JEE Main 2019 (April & January Attempt)

APRIL ATTEMPT

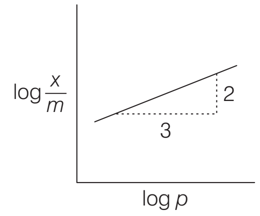
8 April, Shift-I

1 An organic compound X showing the following solubility profile is



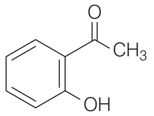
(a) o-toluidine (b) oleic acid
(c) m-cresol (d) benzamide

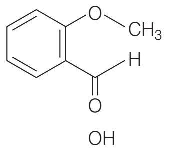
2 Adsorption of a gas follows Freundlich adsorption isotherm. x is the mass of the gas adsorbed on mass m of the adsorbent. The plot of $\log \frac{x}{m}$ *versus* $\log p$ is shown in the given graph. $\frac{x}{m}$ is proportional to

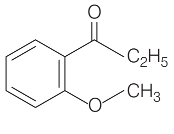


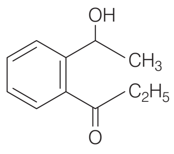
(a) $p^{2/3}$ (b) $p^{3/2}$ (c) p^3 (d) p^2

3 An organic compound neither reacts with neutral ferric chloride solution nor with Fehling solution. It however, reacts with Grignard reagent and gives positive iodoform test. The compound is

(a)


(b)


(c)


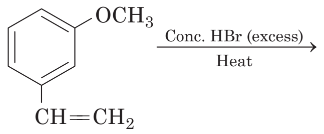
(d)


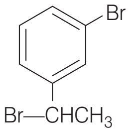
4 The size of the iso-electronic species Cl^-, Ar and Ca^{2+} is affected by
(a) azimuthal quantum number of valence shell
(b) electron-electron interaction in the outer orbitals
(c) principal quantum number of valence shell
(d) nuclear charge

5 In order to oxidise a mixture of one mole of each of FeC_2O_4, $Fe_2(C_2O_4)_3$, $FeSO_4$ and $Fe_2(SO_4)_3$ in acidic medium, the number of moles of $KMnO_4$ required is
(a) 2 (b) 1 (c) 3 (d) 1.5

6 In the following compounds, the decreasing order of basic strength will be
(a) $C_2H_5NH_2 > NH_3 > (C_2H_5)_2NH$
(b) $(C_2H_5)_2NH > NH_3 > C_2H_5NH_2$
(c) $(C_2H_5)_2NH > C_2H_5NH_2 > NH_3$
(d) $NH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$

7 The major product of the following reaction is



(a)


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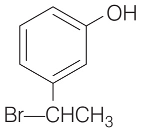

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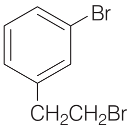

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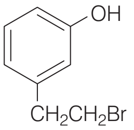
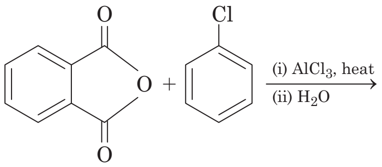


8 The correct order of the spin only magnetic moment of metal ions in the following low spin complexes, $[V(CN)_6]^{4-}$, $[Fe(CN)_6]^{4-}$, $[Ru(NH_3)_6]^{3+}$, and $[Cr(NH_3)_6]^{2+}$, is
(a) $Cr^{2+} > Ru^{3+} > Fe^{2+} > V^{2+}$
(b) $V^{2+} > Cr^{2+} > Ru^{3+} > Fe^{2+}$
(c) $V^{2+} > Ru^{3+} > Cr^{2+} > Fe^{2+}$
(d) $Cr^{2+} > V^{2+} > Ru^{3+} > Fe^{2+}$

9 The major product of the following reaction is



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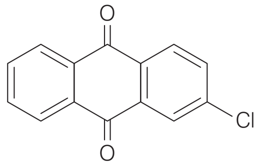

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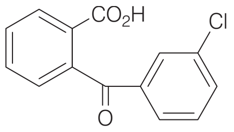

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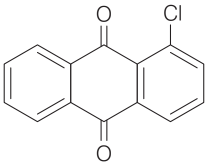

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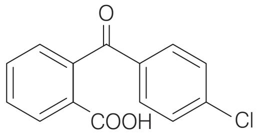
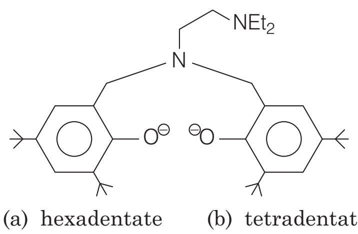


10 For silver, C_p (J K^{-1}mol^{-1}) = 23 + 0.01 T. If the temperature (T) of 3 moles of silver is raised from 300 K to 1000 K at 1 atm pressure, the value of ΔH will be close to
(a) 62 kJ (b) 16 kJ (c) 21 kJ (d) 13 kJ

11 Which is wrong with respect to our responsibility as a human being to protect our environment?
(a) Restricting the use of vehicles
(b) Avoiding the use of floodlighted facilities
(c) Setting up compost tin in gardens
(d) Using plastic bags

12 The following ligand is



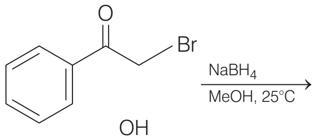
(a) hexadentate (b) tetradentate
(c) bidentate (d) tridentate

13 If solubility product of $Zr_3(PO_4)_4$ is denoted by K_{sp} and its molar solubility is denoted by S, then which of the following relation between S and K_{sp} is correct?

(a) $S = \left(\frac{K_{sp}}{144}\right)^{1/6}$ (b) $S = \left(\frac{K_{sp}}{6912}\right)^{1/7}$

(c) $S = \left(\frac{K_{sp}}{929}\right)^{1/9}$ (d) $S = \left(\frac{K_{sp}}{216}\right)^{1/7}$

14 The major product of the following reaction is



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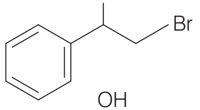

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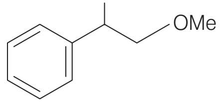

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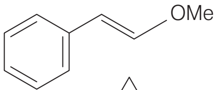

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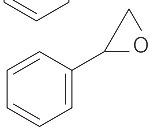


15 Diborane (B_2H_6) reacts independently with O_2 and H_2O to produce, respectively.

(a) B_2O_3 and H_3BO_3
(b) B_2O_3 and $[BH_4]^-$
(c) H_3BO_3 and B_2O_3
(d) HBO_2 and H_3BO_3

16 Which one of the following equations does not correctly represent the first law of thermo- dynamics for the given processes involving an ideal gas ? (Assume non-expansion work is zero)

(a) Cyclic process : $q = -W$
(b) Adiabatic process : $\Delta U = -W$
(c) Isochoric process : $\Delta U = q$
(d) Isothermal process : $q = -W$

17 With respect to an ore, Ellingham diagram helps to predict the feasibility of its

(a) electrolysis
(b) zone refining
(c) vapour phase refining
(d) thermal reduction

18 100 mL of a water sample contains 0.81 g of calcium bicarbonate and 0.73 g of magnesium bicarbonate. The hardness of this water sample expressed in terms of equivalents of $CaCO_3$ is (molar mass of calcium bicarbonate is 162 g mol^{-1} and magnesium bicarbonate is 146 g mol^{-1})

(a) 5,000 ppm (b) 1,000 ppm
(c) 100 ppm (d) 10,000 ppm

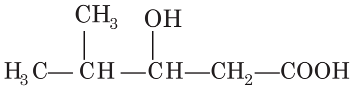
19 Given, that $E^{\ominus}_{O_2/H_2O} = +1.23V$;

$E^{\ominus}_{S_2O_8^{2-}/SO_4^{2-}} = 2.05V$;
$E^{\ominus}_{Br_2/Br^{\ominus}} = +1.09V$,
$E^{\ominus}_{Au^{3+}/Au} = +1.4V$

The strongest oxidising agent is

(a) Au^{3+} (b) O_2 (c) $S_2O_8^{2-}$ (d) Br_2

20 The IUPAC name of the following compound is



$$H_3C—\overset{\overset{\large CH_3}{|}}{C}H—\overset{\overset{\large OH}{|}}{C}H—CH_2—COOH$$

(a) 4,4-dimethyl-3-hydroxybutanoic acid
(b) 2-methyl-3-hydroxypentan-5-oic acid
(c) 3- hydroxy -4- methylpentanoic acid
(d) 4-methyl-3-hydroxypentanoic acid

21 Element 'B' forms ccp structure and 'A' occupies half of the octahedral voids, while oxygen atoms occupy all the tetrahedral voids. The structure of bimetallic oxide is

(a) A_2BO_4 (b) AB_2O_4
(c) A_2B_2O (d) A_4B_2O

22 For the reaction, $2A + B \rightarrow C$, the values of initial rate at different reactant concentrations are given in the table below.

The rate law for the reaction is

$[A]$(mol L^{-1})	$[B]$(mol L^{-1})	**Initial rate** (mol $L^{-1}s^{-1}$)
0.05	0.05	0.045
0.10	0.05	0.090
0.20	0.10	0.72

(a) rate = $k[A][B]^2$ (b) rate = $k[A]^2[B]^2$
(c) rate = $k[A][B]$ (d) rate = $k[A]^2[B]$

23 The lanthanide ion that would show colour is

(a) Gd^{3+} (b) Sm^{3+} (c) La^{3+} (d) Lu^{3+}

24 Maltose on treatment with dil. HCl gives

(a) D-glucose and D-fructose
(b) D-fructose
(c) D-galactose
(d) D-glucose

25 The vapour pressures of pure liquids A and B are 400 and 600 mmHg, respectively at 298 K. On mixing the two liquids, the sum of their initial volumes is equal to the volume of the final mixture. The mole fraction of liquid B is 0.5 in the mixture. The vapour pressure of the final solution, the mole fractions of components A and B in vapour phase, respectively are

(a) 450 mmHg, 0.4, 0.6
(b) 500 mmHg, 0.5, 0.5
(c) 450 mmHg, 0.5,0.5
(d) 500 mmHg, 0.4,0.6

26 Which of the following amines can be prepared by Gabriel phthalimide reaction?

(a) n-butylamine
(b) triethylamine
(c) t-butylamine
(d) *neo* -pentylamine

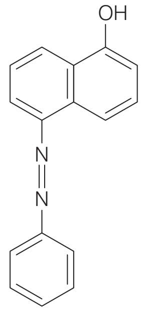
27 The quantum number of four electrons are given below:

I. $n = 4, l = 2, m_l = -2, m_s = -\frac{1}{2}$
II. $n = 3, l = 2, m_l = 1, m_s = +\frac{1}{2}$
III. $n = 4, l = 1, m_l = 0, m_s = +\frac{1}{2}$
IV. $n = 3, l = 1, m_l = 1, m_s = -\frac{1}{2}$

The correct order of their increasing energies will be

(a) IV < III < II < I
(b) I < II < III < IV
(c) IV < II < III < I
(d) I < III < II < IV

28 Coupling of benzene diazonium chloride with 1-naphthol in alkaline medium will give

(a)


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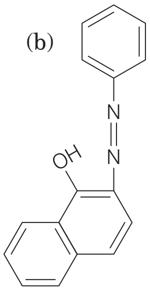
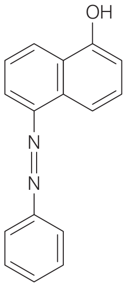


(a)


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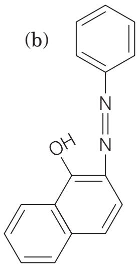

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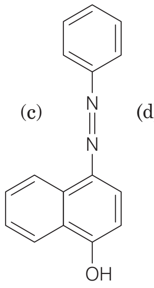

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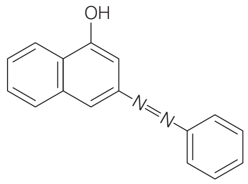


29 **Assertion** (A) Ozone is destroyed by CFCs in the upper stratosphere.

Reason (R) Ozone holes increase the amount of UV radiation reaching the earth.

(a) Assertion and Reason are incorrect.
(b) Assertion and Reason are both correct and the Reason is the correct explanation for the Assertion.
(c) Assertion and Reason are correct, but the Reason is not the explanation for the Assertion.
(d) Assertion is false, but the Reason is correct.

30 The correct order of hydration enthalpies of alkali metal ions is

(a) $Li^+ > Na^+ > K^+ > Cs^+ > Rb^+$
(b) $Na^+ > Li^+ > K^+ > Rb^+ > Cs^+$
(c) $Na^+ > Li^+ > K^+ > Cs^+ > Rb^+$
(d) $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

ANSWERS

1. *(c)*	2. *(a)*	3. *(d)*	4. *(d)*	5. *(a)*	6. *(c)*	7. *(b)*	8. *(b)*	9. *(d)*	10. *(a)*
11. *(d)*	12. *(b)*	13. *(b)*	14. *(d)*	15. *(a)*	16. *(b)*	17. *(d)*	18. *(d)*	19. *(c)*	20. *(c)*
21. *(b)*	22. *(a)*	23. *(b)*	24. *(d)*	25. *(d)*	26. *(a)*	27. *(c)*	28. *(c)*	29. *(c)*	30. *(d)*

For Detailed Solutions
Visit : http://tinyurl.com/y577ow9l
Or Scan :

8 April, Shift-II

1 Calculate the standard cell potential (in V) of the cell in which following reaction takes place

$Fe^{2+}(aq) + Ag^+(aq) \rightarrow Fe^{3+}(aq) + Ag(s)$

Given that,

$E^\circ_{Ag^+/Ag} = x V, E^\circ_{Fe^{2+}/Fe} = y V$
$E^\circ_{Fe^{3+}/Fe} = z V$

(a) $x + 2y - 3z$ (b) $x - y$
(c) $x + y - z$ (d) $x - z$

2 The compound that inhibits the growth of tumors is

(a) *trans*-$[Pt(Cl)_2(NH_3)_2]$
(b) *cis*-$[Pd(Cl)_2(NH_3)_2]$
(c) *cis*-$[Pt(Cl)_2(NH_3)_2]$
(d) *trans*-$[Pd(Cl)_2(NH_3)_2]$

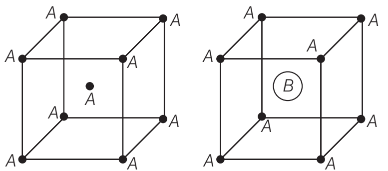
3 The statement that is incorrect about the interstitial compounds is

(a) they are very hard
(b) they have metallic conductivity
(c) they have high melting points
(d) they are chemically reactive

4 The ion that has sp^3d^2 hybridisation for the central atom, is

(a) $[ICl_2]^-$ (b) $[BrF_2]^-$
(c) $[ICl_4]^-$ (d) $[IF_6]^-$

5 Consider the bcc unit cells of the solids 1 and 2 with the position of atoms as shown below. The radius of atom B is twice that of atom A. The unit cell edge length is 50% more is solid 2 than in 1. What is the approximate packing efficiency in solid 2?



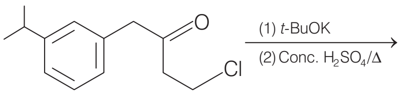
Solid 1 Solid 2

(a) 65% (b) 90%
(c) 75% (d) 45%

6 Which of the following compounds will show the maximum 'enol' content?

(a) CH_3COCH_3
(b) $CH_3COCH_2COCH_3$
(c) $CH_3COCH_2COOC_2H_5$
(d) $CH_3COCH_2CONH_2$

7 The major product of the following reaction is



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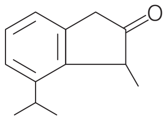

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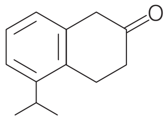

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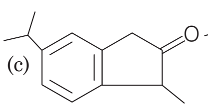

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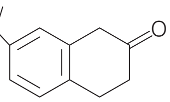
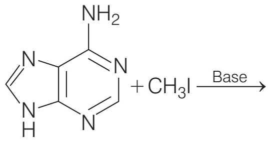


8 The major product in the following reaction is



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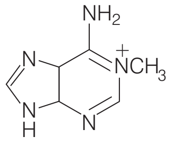

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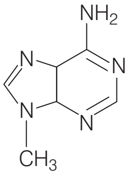

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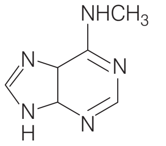

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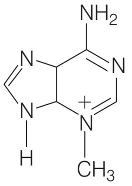


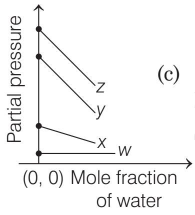
9 5 moles of an ideal gas at 100 K are allowed to undergo reversible compression till its temperature becomes 200 K. If $C_V = 28\ JK^{-1}\ mol^{-1}$, calculate ΔU and ΔpV for this process. ($R = 8.0\ JK^{-1} mol^{-1}$)

(a) $\Delta U = 2.8\ kJ; \Delta(pV) = 0.8\ kJ$
(b) $\Delta U = 14\ J; \Delta(pV) = 0.8\ J$
(c) $\Delta U = 14\ kJ; \Delta(pV) = 4\ kJ$
(d) $\Delta U = 14\ kJ; \Delta(pV) = 18\ kJ$

10 Which one of the following alkenes when treated with HCl yields majorly an anti Markownikov product?

(a) $Cl—CH = CH_2$
(b) $H_2N—CH = CH_2$
(c) $CH_3O—CH = CH_2$
(d) $F_3C—CH = CH_2$

11 For the solution of the gases w, x, y and z in water at 298 K, the Henry's law constants (K_H) are 0.5, 2, 35 and 40 K bar, respectively. The correct plot for the given data is

(a)


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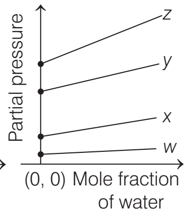

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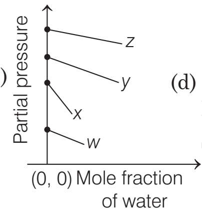

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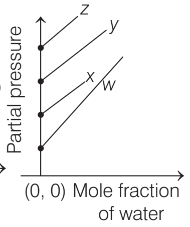


12 The covalent alkaline earth metal halide (X = Cl, Br, I) is

(a) SrX_2 (b) CaX_2
(c) MgX_2 (d) BeX_2

13 0.27 g of a long chain fatty acid was dissolved in 100 cm^3 of hexane. 10 mL of this solution was added dropwise to the surface of water in a round watch glass.

Hexane evaporates and a monolayer is formed. The distance from edge to centre of the watch glass is 10 cm. What is the height of the monolayer? [Density of fatty acid = 0.9 g cm^{-3}; $\pi = 3$]

(a) 10^{-6} m (b) 10^{-4} m
(c) 10^{-8} m (d) 10^{-2} m

14 The percentage composition of carbon by mole in methane is

(a) 75% (b) 20% (c) 25% (d) 80%

15 The maximum prescribed concentration of copper in drinking water is

(a) 5 ppm (b) 0.5 ppm
(c) 0.05 ppm (d) 3 ppm

16 For the following reactions, equilibrium constants are given :

$S(s) + O_2(g) \rightleftharpoons SO_2(g); K_1 = 10^{52}$
$2S(s) + 3O_2(g) \rightleftharpoons 2SO_3(g); K_2 = 10^{129}$

The equilibrium constant for the reaction,

$2SO(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ is

(a) 10^{25} (b) 10^{77} (c) 10^{154} (d) 10^{181}

17 The strength of 11.2 volume solution of H_2O_2 is [Given that molar mass of H = 1 g mol^{-1} and O = 16 g mol^{-1}]

(a) 1.7% (b) 34%
(c) 13.6% (d) 3.4%

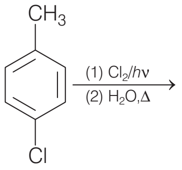
18 If p is the momentum of the fastest electron ejected from a metal surface after the irradiation of light having wavelength λ, then for 1.5 p momentum of the photoelectron, the wavelength of the light should be (Assume kinetic energy of ejected photoelectron to be very high in comparison to work function)

(a) $\frac{4}{9}\lambda$ (b) $\frac{3}{4}\lambda$
(c) $\frac{2}{3}\lambda$ (d) $\frac{1}{2}\lambda$

19 The correct statement about ICl_5 and ICl_4^- is

(a) ICl_5 is square pyramidal and ICl_4^- is tetrahedral
(b) ICl_5 is square pyramidal and ICl_4^- is square planar
(c) Both are isostructural
(d) ICl_5 is trigonal bipyramidal and ICl_4^- is tetrahedral

20 The major product of the following reaction is



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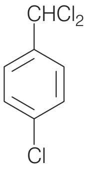

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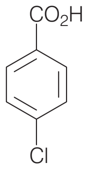

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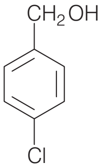

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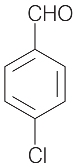
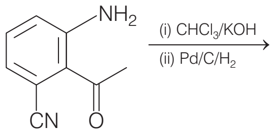
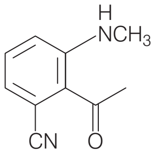


21 The calculated spin only magnetic moments (BM) of the anionic and cationic species of $[Fe(H_2O)_6]_2$ and $[Fe(CN)_6]$, respectively, are

(a) 0 and 4.9 (b) 2.84 and 5.92
(c) 0 and 5.92 (d) 4.9 and 0

22 The major product obtained in the following reaction is



(a)


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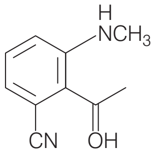

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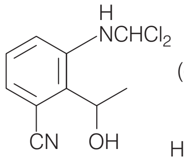

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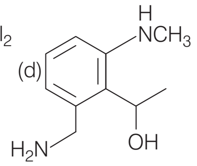
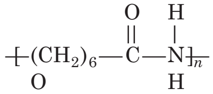
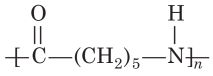
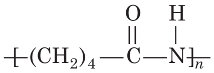
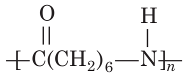


23 The structure of nylon-6 is

(a)

$\left[(CH_2)_6-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}} \right]_n$

(b)

$\left[\overset{O}{\overset{\|}{C}}-(CH_2)_5-\overset{H}{\overset{|}{N}} \right]_n$

(c)

$\left[(CH_2)_4-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}} \right]_n$

(d)

$\left[\overset{O}{\overset{\|}{C}}(CH_2)_6-\overset{H}{\overset{|}{N}} \right]_n$

24 Fructose and glucose can be distinguished by

(a) Fehling's test (b) Barfoed's test
(c) Benedict's test (d) Seliwanoff's test

25 Polysubstitutiion is a major drawback in

(a) Friedel-Craft's alkylation
(b) Reimer-Tiemann reaction
(c) Friedel-Craft's acylation
(d) Acetylation of aniline

26 For a reaction scheme, $A \xrightarrow{k_1} B \xrightarrow{k_2} C$, if rate of formation of B is set to be zero then the concentration of B is given by

(a) $k_1k_2[A]$ (b) $\left(\frac{k_1}{k_2}\right)[A]$
(c) $(k_1 - k_2)[A]$ (d) $(k_1 + k_2)[A]$

27 The IUPAC symbol for the element with atomic number 119 would be

(a) unh (b) uue (c) uun (d) une

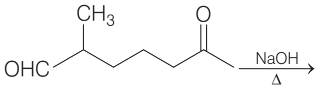
28 The Mond process is used for the

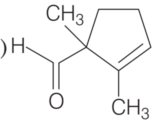
(a) purification of Ni
(b) extraction of Mo
(c) purification of Zr and Ti
(d) extraction of Zn

29 Among the following molecules/ions, C_2^{2-}, N_2^{2-}, O_2^{2-}, O_2
Which one is diamagnetic and has the shortest bond length?

(a) C_2^{2-} (b) O_2 (c) O_2^{2-} (d) N_2^{2-}

30 The major product obtained in the following reaction is



(a)


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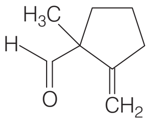

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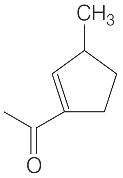
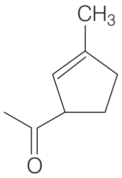


(d)


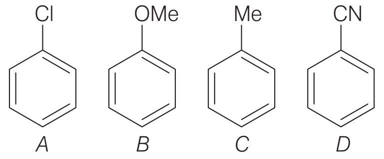
ANSWERS

1. (a)	2. (c)	3. (d)	4. (c)	5. (b)	6. (b)	7. (d)	8. (*)	9. (c)	10. (d)
11. (a)	12. (d)	13. (a)	14. (b)	15. (d)	16. (a)	17. (d)	18. (a)	19. (b)	20. (d)
21. (a)	22. (d)	23. (b)	24. (d)	25. (a)	26. (b)	27. (b)	28. (a)	29. (a)	30. (c)

For Detailed Solutions
Visit : http://tinyurl.com/y2jatzvs
Or Scan :

9 April, Shift-I

1 The increasing order of reactivity of the following compounds towards aromatic electrophilic substitution reaction is



(a) $A < B < C < D$ (b) $B < C < A < D$
(c) $D < A < C < B$ (d) $D < B < A < C$

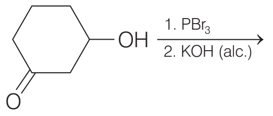
2 The standard Gibbs energy for the given cell reaction in kJ mol^{-1} at 298 K is

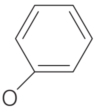
$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s),$$
$$E° = 2V \text{ at } 298 \text{ K}$$

(Faraday's constant, $F = 96000$ C mol^{-1})

(a) 384 (b) 192
(c) –384 (d) –192

3 The major product of the following reaction is



(a)


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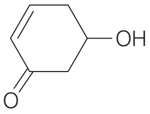

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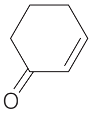

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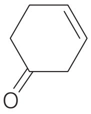


4 Which of the following statement is not true about sucrose?

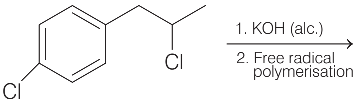
(a) It is also named as invert sugar.
(b) The glycosidic linkage is present between C_1 of α-glucose and C_1 of β-fructose
(c) It is a non-reducing sugar
(d) On hydrolysis, it produces glucose and fructose

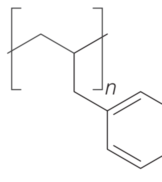
5 For a reaction,

$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$, identify dihydrogen ($H_2$) as a limiting reagent in the following reaction mixtures.

(a) 56 g of N_2 + 10 g of H_2
(b) 35 g of N_2 + 8 g of H_2
(c) 14 g of N_2 + 4 g of H_2
(d) 28 g of N_2 + 6 g of H_2

6 The major product of the following reaction is



(a)


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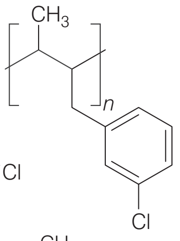

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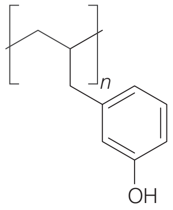
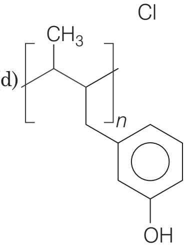


(d)


7 Among the following the set of parameters that represents path functions, is

(A) $q + W$ (B) q
(C) W (D) $H - TS$

(a) (A) and (D) (b) (A), (B) and (C)
(c) (B), (C) and (D) (d) (B) and (C)

8 The degenerate orbitals of $[Cr(H_2O)_6]^{3+}$ are

(a) d_{z^2} and d_{xz} (b) d_{xz} and d_{yz}
(c) $d_{x^2-y^2}$ and d_{xy} (d) d_{yz} and d_{z^2}

9 The aerosol is a kind of colloid in which

(a) gas is dispersed in liquid
(b) gas is dispersed in solid
(c) liquid is dispersed in water
(d) solid is dispersed in gas

10 C_{60} an allotrope of carbon contains

(a) 16 hexagons and 16 pentagons
(b) 20 hexagons and 12 pentagons
(c) 12 hexagons and 20 pentagons
(d) 18 hexagons and 14 pentagons

11 The major product of the following reaction is

$$CH_3CH{=}CHCO_2CH_3 \xrightarrow{LiAlH_4}$$

(a) $CH_3CH{=}CHCH_2OH$
(b) $CH_3CH_2CH_2CH_2OH$
(c) $CH_3CH_2CH_2CO_2CH_3$
(d) $CH_3CH_2CH_2CHO$

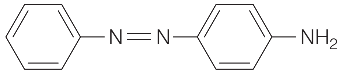
12 The ore that contains the metal in the form of fluoride is

(a) magnetite (b) sphalerite
(c) malachite (d) cryolite

13 The number of water molecule(s) not coordinated to copper ion directly in $CuSO_4 \cdot 5H_2O$, is

(a) 2 (b) 3 (c) 1 (d) 4

14 Aniline dissolved in dil. HCl is reacted with sodium nitrite at 0° C. This solution was added dropwise to a solution containing equimolar mixture of aniline and phenol in dil. HCl. The structure of the major product is

(a)


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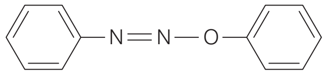
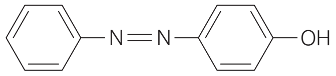


(c)


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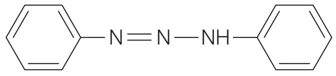


15 The osmotic pressure of a dilute solution of an ionic compound XY in water is four times that of a solution of 0.01 M $BaCl_2$ in water. Assuming complete dissociation of the given ionic compounds in water, the concentration of XY (in mol L^{-1}) in solution is

(a) 4×10^{-2} (b) 16×10^{-4}
(c) 4×10^{-4} (d) 6×10^{-2}

16 For any given series of spectral lines of atomic hydrogen, let $\Delta\bar{\nu} = \bar{\nu}_{max} - \bar{\nu}_{min}$ be the difference in maximum and minimum frequencies in cm^{-1}. The ratio $\Delta\bar{\nu}_{Lyman} / \Delta\bar{\nu}_{Balmer}$ is

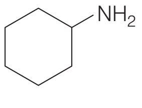
(a) 27 : 5 (b) 5 : 4
(c) 9 : 4 (d) 4 : 1

17 The element having greatest difference between its first and second ionisation energy, is

(a) Ca (b) Sc (c) Ba (d) K

18 The organic compound that gives following qualitative analysis is

Test	Inference
(i) Dil. HCl	Insoluble
(ii) NaOH solution	Soluble
(iii) Br_2/water	Decolourisation

(a)


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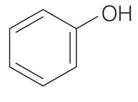

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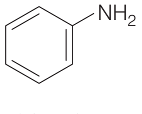

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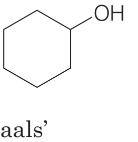


19 Consider the van der Waals' constants, a and b, for the following gases.

Gas	Ar	Ne	Kr	Xe
a/(atm dm^6 mol^{-2})	1.3	0.2	5.1	4.1
b/(10^{-2} dm^3 mol^{-1})	3.2	1.7	1.0	5.0

Which gas is expected to have the highest critical temperature ?

(a) Kr (b) Xe

(c) Ar (d) Ne

20 The major product of the following reaction is

$CH_3C \equiv CH \xrightarrow[\text{(ii) DI}]{\text{(i) DCl (1 equiv.)}}$

(a) $CH_3CD(Cl)CHD(I)$

(b) $CH_3CD_2CH(Cl)(I)$

(c) $CH_3CD(I)CHD(Cl)$

(d) $CH_3C(I)(Cl)CHD_2$

21 Magnesium powder burns in air to give

(a) MgO and Mg_3N_2

(b) $Mg(NO_3)_2$ and Mg_3N_2

(c) MgO only

(d) MgO and $Mg(NO_3)_2$

22 Liquid M and liquid N form an ideal solution. The vapour pressures of pure liquids M and N are 450 and 700 mmHg, respectively, at the same temperature. Then correct statement is

x_M = mole fraction of M in solution;

x_N = mole fraction of N in solution;

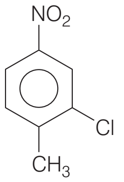
y_M = mole fraction of M in vapour phase;

y_N = mole fraction of N in vapour phase

(a) $\frac{x_M}{x_N} > \frac{y_M}{y_N}$ (b) $\frac{x_M}{x_N} = \frac{y_M}{y_N}$

(c) $\frac{x_M}{x_N} < \frac{y_M}{y_N}$ (d) $(x_M - y_M) < (x_N - y_N)$

23 The correct IUPAC name of the following compound is



(a) 2-methyl-5-nitro-1-chlorobenzene

(b) 3-chloro-1-methyl-1-nitrobenzene

(c) 2-chloro-1-methyl 1-4-nitrobenzene

(d) 5-chloro-4-methyl 1-1-nitrobenzene

24 Excessive release of CO_2 into the atmosphere results in

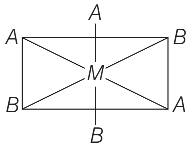
(a) formation of smog

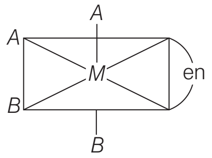
(b) depletion of ozone

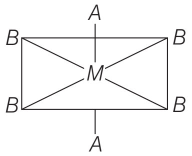
(c) polar vortex

(d) global warming

25 The one that will show optical activity is (en = ethane-1, 2-diamine)

(a)


(c)


(b)


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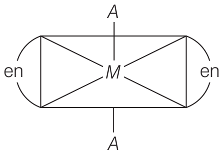
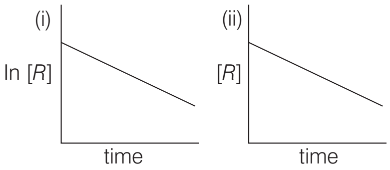


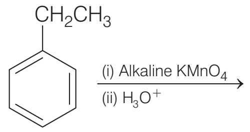
26 The given plots represent the variation of the concentration of a reaction R with time for two different reactions (i) and (ii). The respective orders of the reactions are

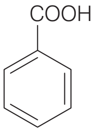


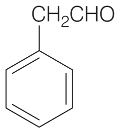
(a) 1, 1 (b) 0, 2

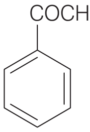
(c) 0, 1 (d) 1, 0

27 The major product of the following reaction is



(a)


(b)


(c)


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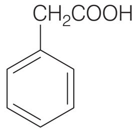

28 Among the following, the molecule expected to be stabilised by anion formation is C_2, O_2, NO, F_2.

(a) C_2 (b) F_2

(c) NO (d) O_2

29 The correct order of the oxidation states of nitrogen in NO, NO_2, NO_2 and N_2O_3 is

(a) $NO_2 < NO < N_2O_3 < N_2O$

(b) $N_2O < NO < N_2O_3 < NO_2$

(c) $O_2 < N_2O_3 < NO < N_2O$

(d) $N_2O < N_2O_3 < NO < NO_2$

30 Match the catalysts Column I with products Column II.

	Column I (Catalyst)		**Column II** (Product)
(A)	V_2O_5	(i)	Polyethlyene
(B)	$TiCl_4 / Al(Me)_3$	(ii)	Ethanal
(C)	$PbCl_2$	(iii)	H_2SO_4
(D)	Iron oxide	(iv)	NH_3

(a) (A)-(ii), (B)-(iii), (C)-(i), (D)-(iv)

(b) (A)-(iv), (B)-(iii), (C)-(ii), (D)-(i)

(c) (A)-(iii), (B)-(i), (C)-(ii), (D)-(iv)

(d) (A)-(iii), (B)-(iv), (C)-(i), (D)-(ii)

ANSWERS

1. (c)	2. (c)	3. (c)	4. (b)	5. (a)	6. (b)	7. (d)	8. (b)	9. (d)	10. (b)
11. (a)	12. (d)	13. (c)	14. (a)	15. (d)	16. (c)	17. (d)	18. (b)	19. (a)	20. (d)
21. (a)	22. (a)	23. (c)	24. (d)	25. (c)	26. (d)	27. (a)	28. (a)	29. (b)	30. (c)

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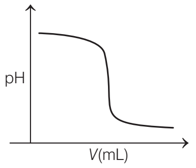
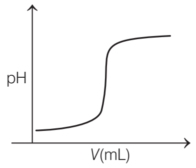
9 April, Shift-II

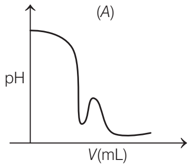
1 In an acid-base titration, 0.1 M HCl solution was added to the NaOH solution of unknown strength. Which of the following correctly shows the change of pH of the titration mixture in this experiment?



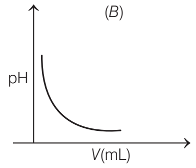
(A)



(B)



(C)



(D)

(a) (D) (b) (A) (c) (B) (d) (C)

2 Among the following species, the diamagnetic molecule is

(a) CO (b) B_2
(c) NO (d) O_2

3 The amorphous form of silica is

(a) tridymite (b) kieselguhr
(c) cristobalite (d) quartz

4 HF has highest boiling point among hydrogen halides, because it has

(a) lowest ionic character
(b) strongest van der Waals' interactions
(c) strongest hydrogen bonding
(d) lowest dissociation enthalpy

5 The structures of beryllium chloride in the solid state and vapour phase, respectively are

(a) dimeric and dimeric
(b) chain and chain
(c) dimeric and chain
(d) chain and dimeric

6 The correct statements among I to III are

I. Valence bond theory cannot explain the color exhibited by transition metal complexes.
II. Valence bond theory can predict quantitatively the magnetic properties of transition metal complexes.
III. Valence bond theory cannot distinguish ligands as weak and strong field ones.

(a) II and III only (b) I, II and III
(c) I and II only (d) I and III only

7 **Assertion** For the extraction of iron, haematite ore is used.

Reason Heamatite is a carbonate ore of iron.

(a) Only the reason is correct.
(b) Both the assertion and reason are correct explanation for the assertion.
(c) Both the assertion and reason are correct and the reason is the correct explanation for the assertion.
(d) Only the assertion is correct.

8 In the following reaction,
Carbonyl compound +

$$\text{MeOH} \overset{\text{HCl}}{\rightleftharpoons} \text{acetal}$$

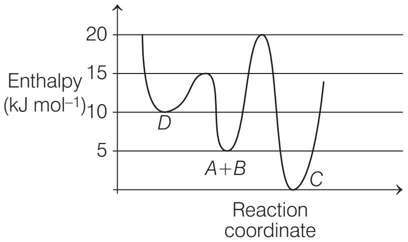
Rate of the reaction is the highest for:

(a) Acetone as substrate and methanol in excess
(b) Propanal as substrate and methanol in stoichiometric amount
(c) Acetone as substrate and methanol in stoichiometric amount
(d) Propanal as substrate and methanol in excess

9 Consider the given plot of enthalpy of the following reaction between A and B.

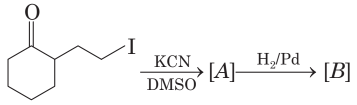
$$A + B \longrightarrow C + D$$

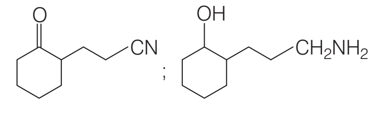
Identify the incorrect statement.

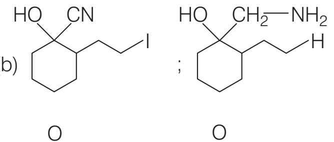


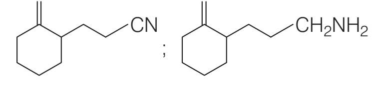
(a) D is kinetically stable product.
(b) Formation of A and B from C has highest enthalpy of activation.
(c) C is the thermodynamically stable product.
(d) Activation enthalpy to form C is 5 kJ mol^{-1} less than that to form D.

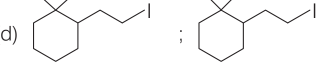
10 The major products A and B for the following reactions are, respectively



(a) 

(b) 

(c) 

(d) 

11 Which one of the following about an electron occupying the 1s-orbital in a hydrogen atom is incorrect? (The Bohr radius is represented by a_0)

(a) The electron can be found at a distance $2a_0$ from the nucleus.
(b) The magnitude of the potential energy is double that of its kinetic energy on an average.
(c) The probability density of finding the electron is maximum at the nucleus.
(d) The total energy of the electron is maximum when it is at a distance a_0 from the nucleus.

12 Hinsberg's reagent is

(a) $SOCl_2$ (b) C_6H_5COCl
(c) $C_6H_5SO_2Cl$ (d) $(COCl)_2$

13 The one that is not a carbonate ore is

(a) siderite (b) calamine
(c) malachite (d) bauxite

14 Molal depression constant for a solvent is 4.0 K kg mol^{-1}. The depression in the freezing point of the solvent for 0.03 mol kg^{-1} solution of K_2SO_4 is (Assume complete dissociation of the electrolyte)

(a) 0.18 K (b) 0.36 K
(c) 0.12 K (d) 0.24 K

15 What would be the molality of 20% (mass/mass) aqueous solution of KI? (Molar mass of KI = 166 g mol^{-1})

(a) 1.48 (b) 1.51
(c) 1.35 (d) 1.08

16 The correct statements among I to III regarding group 13 element oxides are:

I. Boron trioxide is acidic.
II. Oxides of aluminium and gallium are amphoteric.
III. Oxides of indium and thallium are basic.

(a) I, II and III (b) I and III only
(c) I and II only (d) II and III only

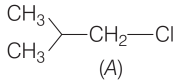
17 During compression of a spring the work done is 10 kJ and 2 kJ escaped to the surroundings as heat. The change in internal energy, ΔU (in kJ) is

(a) 8 (b) –12
(c) 12 (d) –8

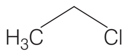
18 The layer of atmosphere between 10 km to 50 km above the sea level is called as

(a) stratosphere
(b) mesosphere
(c) thermosphere
(d) troposphere

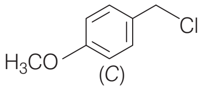
19 Increasing order of reactivity of the following compounds for S_N1 substitution is



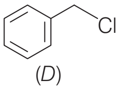
(*A*)



(*B*)



(*C*)



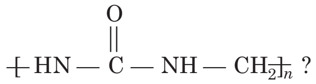
(*D*)

(a) (*A*) < (*B*) < (*D*) < (*C*)
(b) (*B*) < (*C*) < (*D*) < (*A*)
(c) (*B*) < (*A*) < (*D*) < (*C*)
(d) (*B*) < (*C*) < (*A*) < (*D*)

20 Noradrenaline is a/an

(a) antidepressant (c) antihistamine
(c) neurotransmitter
(d) antacid

21 Which of the following compounds is a constituent of the polymer



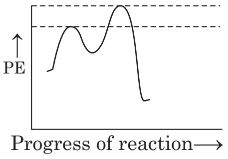
$$-\!\!\left[HN - \overset{\overset{\displaystyle O}{\|}}{C} - NH - CH_2 \right]_n ?$$

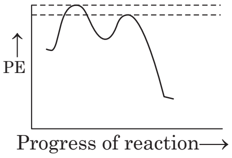
(a) *N*-methyl urea
(b) Methylamine
(c) Ammonia
(d) Formaldehyde

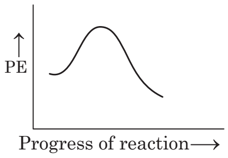
22 A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using 0.1 Faraday electricity. How many mole of Ni will be deposited at the cathode?

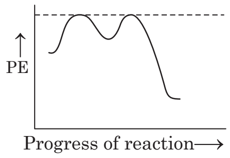
(a) 0.20 (b) 0.10 (c) 0.15 (d) 0.05

23 Which of the following potential energy (PE) diagrams represents the S_N1 reaction?

(a)


(b)


(c)


(d)


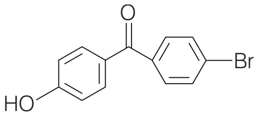
24 The maximum number of possible oxidation states of actinoides are shown by

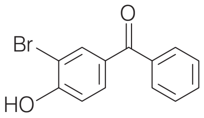
(a) berkelium, (Bk) and californium (Cf)
(b) nobelium (No) and lawrencium (Lr)
(c) actinium (Ac) and thorium (Th)
(d) neptunium (Np) and plutonium (Pu)

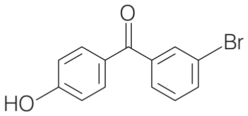
25 The peptide that gives positive ceric ammonium nitrate and carbylamine tests is

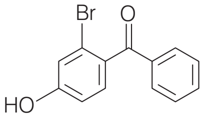
(a) Lys-Asp (b) Ser-Lys
(c) Gln-Asp (d) Asp-Gln

26 *p*-hydroxybenzophenone upon reaction with bromine in carbon tetrachloride gives

(a)


(b)


(c)


(d)


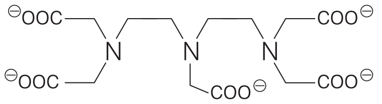
27 At a given temperature *T*, gases Ne, Ar, Xe and Kr are found to deviate from ideal gas behaviour. Their equation of state is given as,

$$p = \frac{RT}{V - b} \text{ at } T.$$

Here, *b* is the van der Waals' constant. Which gas will exhibit steepest increase in the plot of *Z* (compression factor) *vs p*?

(a) Xe (b) Ar (c) Kr (d) Ne

28 The maximum possible denticities of a ligand given below towards a common transition and inner-transition metal ion, respectively, are

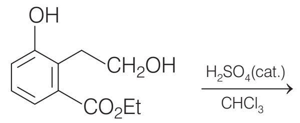


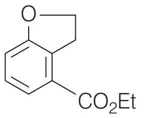
(a) 8 and 8 (b) 8 and 6
(c) 6 and 6 (d) 6 and 8

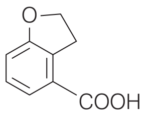
29 10 mL of 1 mM surfactant solution forms a monolayer covering 0.24 cm^2 on a polar substrate. If the polar head is approximated as a cube, what is its edge length?

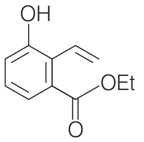
(a) 2.0 pm (b) 0.1 nm
(c) 1.0 pm (d) 2.0 nm

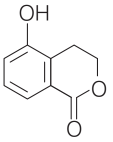
30 The major product of the following reaction is



(a)


(b)


(c)


(d)


ANSWERS

1. (*b*)	2. (*a*)	3. (*b*)	4. (*c*)	5. (*d*)	6. (*d*)	7. (*d*)	8. (*d*)	9. (*d*)	10. (*c*)
11. (*d*)	12. (*c*)	13. (*d*)	14. (*b*)	15. (*b*)	16. (*a*)	17. (*a*)	18. (*a*)	19. (*c*)	20. (*c*)
21. (*d*)	22. (*d*)	23. (*b*)	24. (*d*)	25. (*b*)	26. (*b*)	27. (*a*)	28. (*d*)	29. (*a*)	30. (*d*)

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10 April, Shift-I

1 Match the refining methods Column I with metals Column II.

Column I (Refining Methods)	Column II (Metals)
I. Liquation	(A) Zr
II. Zone refining	(B) Ni
III. Mond process	(C) Sn
IV. van Arkel method	(D) Ga

(a) I- (C) ; II-(D); III-(B) ; IV-(A)
(b) I- (B) ; II-(C); III-(D) ; IV-(A)
(c) I- (C) ; II-(A); III-(B) ; IV-(D)
(d) I- (B) ; II-(D); III-(A) ; IV-(C)

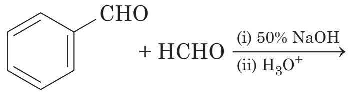
2 Consider the statements S_1 and S_2 :

S_1 : Conductivity always increases with decrease in the concentration of electrolyte.

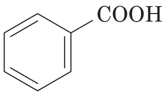
S_2 : Molar conductivity always increases with decrease in the concentration of electrolyte.

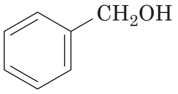
The correct option among the following is
(a) S1 is correct and S2 is wrong
(b) S1 is wrong and S2 is correct
(c) Both S1 and S2 are wrong
(d) Both S1 and S2 are correct

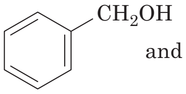
3 Major products of the following reaction are

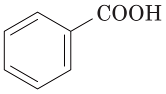


(a) CH_3OH and HCO_2H

(b) CH_3OH and 

(c) HCOOH and 

(d) 

and 

5 A gas undergoes physical adsorption on a surface and follows the given Freundlich adsorption isotherm equation $\frac{x}{m} = Kp^{0.5}$

Adsorption of the gas increases with
(a) increase in p and increase in T
(b) increase in p and decrease in T
(c) decrease in p and decrease in T
(d) decrease in p and increase in T

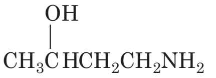
6 Three complexes, $[CoCl(NH_3)_5]^{2+}$ (I), $[Co(NH_3)_5\ H_2O]^{3+}$ (II) and $[Co(NH_3)_6]^{3+}$ (III) absorb light in the visible region. The correct order of the wavelength of light absorbed by them is
(a) II > I > III
(b) I > II > III
(c) III > I > II
(d) III > II > I

7 At 300 K and 1 atmospheric pressure, 10 mL of a hydrocarbon required 55 mL of O_2 for complete combustion and 40 mL of CO_2 is formed. The formula of the hydrocarbon is
(a) C_4H_7Cl
(b) C_4H_6
(c) C_4H_{10}
(d) C_4H_8

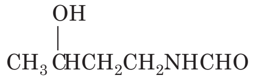
8 The isoelectronic set of ions is
(a) F^-, Li^+, Na^+ and Mg^{2+}
(b) N^{3-}, Li^+, Mg^{2+} and O^{2-}
(c) Li^+, Na^+, O^{2-} and F^-
(d) N^{3-}, O^{2-}, F^- and Na^+

9 The principle of column chromatography is
(a) differential absorption of the substances on the solid phase
(b) differential adsorption of the substances on the solid phase
(c) gravitational force
(d) capillary action

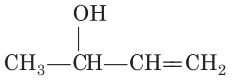
10 The major product of the following reaction is

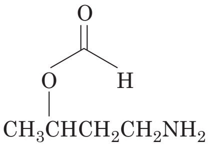

$CH_3\overset{OH}{C}HCH_2CH_2NH_2$

$\xrightarrow[\text{Triethylamine}]{\text{Ethyl formate (1 equiv.)}}$

(a) 
$CH_3\overset{OH}{C}HCH_2CH_2NHCHO$

(b) $CH_3CH{=}CH—CH_2NH_2$

(c) 
$CH_3—\overset{OH}{C}H—CH{=}CH_2$

(d) 

11 Consider the hydrated ions of Ti^{2+}, V^{2+}, Ti^{3+} and Sc^{3+}. The correct order of their spin-only magnetic moment is
(a) $Sc^{3+} < Ti^{3+} < Ti^{2+} < V^{2+}$
(b) $Sc^{3+} < Ti^{3+} < V^{2+} < Ti^{2+}$
(c) $Ti^{3+} < Ti^{2+} < Sc^{3+} < V^{2+}$
(d) $V^{2+} < Ti^{2+} < Ti^{3+} < Sc^{3+}$

12 Consider the following statements.

I. The pH of a mixture containing 400 mL of 0.1 M H_2SO_4 and 400 mL of 0.1 M NaOH will be approximately 1.3.
II. Ionic product of water is temperature dependent.
III. A monobasic acid with $K_a = 10^{-5}$ has a pH = 5. The degree of dissociation of this acid is 50%.
IV. The Le-Chatelier's principle is not applicable to common-ion effect. The correct statements are

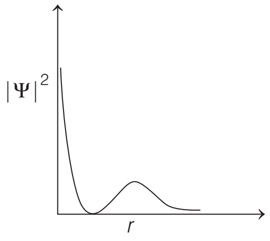
(a) I, II and IV
(b) II and III
(c) I and II
(d) I, II and III

13 The oxoacid of sulphur that does not contain bond between sulphur atoms is
(a) $H_2S_2O_3$
(b) $H_2S_2O_4$
(c) $H_2S_2O_7$
(d) $H_2S_4O_6$

14 At room temperature, a dilute solution of urea is prepared by dissolving 0.60 g of urea in 360 g of water. If the vapour pressure of pure water at this temperature is 35 mm Hg, lowering of vapour pressure will be (Molar mass of urea = 60 g mol^{-1})
(a) 0.027 mmHg
(b) 0.031 mmHg
(c) 0.017 mmHg
(d) 0.028 mmHg

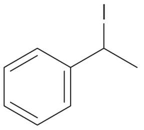
15 The alloy used in the construction of aircrafts is
(a) Mg-Zn
(b) Mg-Mn
(c) Mg-Sn
(d) Mg-Al

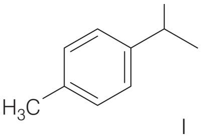
16 The graph between $|\psi|^2$ and r (radial distance) is shown below. This represents

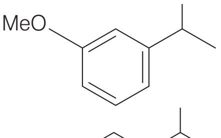


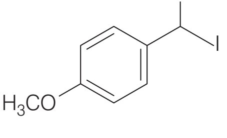
(a) 1*s*-orbital
(b) 2*p*-orbital
(c) 3*s*-orbital
(d) 2*s*-orbital

17 Increasing rate of S_N1 reaction in the following compounds is

(A) 

(C) 

(B) 

(D) 

(a) (A) < (B) < (C) < (D)
(b) (B) < (A) < (C) < (D)
(c) (A) < (B) < (D) < (C)
(d) (B) < (A) < (D) < (C)

18 A process will be spontaneous at all temperature if
(a) $\Delta H > 0$ and $\Delta S < 0$
(b) $\Delta H < 0$ and $\Delta S > 0$
(c) $\Delta H < 0$ and $\Delta S < 0$
(d) $\Delta H > 0$ and $\Delta S > 0$

19 During the change of O_2 to O_2^-, the incoming electron goes to the orbital.
(a) $\pi 2p_x$ (b) $\pi^* 2p_x$
(c) $\pi 2p_y$ (d) $\sigma^* 2p_z$

20 The synonym for water gas when used in the production of methanol is
(a) natural gas (b) laughing gas
(c) *syn* gas (d) fuel gas

21 Amylopectin is composed of
(a) β-D-glucose, C_1-C_4 and C_2-C_6 linkages
(b) α-D-glucose, C_1-C_4 and C_2-C_6 linkages
(c) β-D-glucose, C_1-C_4 and C_1-C_6 linkages
(d) α-D-glucose, C_1-C_4 and C_1 -C_6linkages

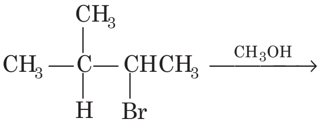
22 Consider the following table.

Gas	*a*/(k Pa dm^6 mol^{-1})	*b*/(dm^{3}mol^{-1})
A	642.32	0.05196
B	155.21	0.04136
C	431.91	0.05196
D	155.21	0.4382

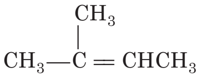
a and *b* are van der Waals' constants. The correct statement about the gases is
(a) gas *C* will occupy lesser volume than gas *A*; gas *B* will be lesser compressible than gas *D*
(b) gas *C* will occupy more volume than gas *A*; gas *B* will be more compressible than gas *D*
(c) gas *C* will occupy more volume than gas *A*; gas *B* will be lesser compressible than gas *D*
(d) gas *C* will occupy more volume than gas *A*; gas *B* will be lesser compressible than gas *D*

23 Which of the following is a condensation polymer?
(a) Nylon-6, 6 (b) Neoprene
(c) Teflon (d) Buna - S

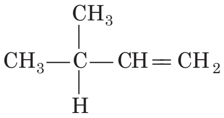
24 The major product of the following reaction is



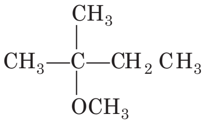
$$CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large H}{|}}{C}}-\underset{\underset{\large Br}{|}}{C}HCH_3 \xrightarrow{CH_3OH}$$

(a) 

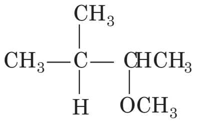
$$CH_3-\overset{\overset{\large CH_3}{|}}{C}=CHCH_3$$

(b) 

$$CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large H}{|}}{C}}-CH=CH_2$$

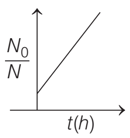
(c) 

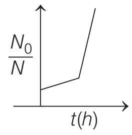
$$CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large OCH_3}{|}}{C}}-CH_2\,CH_3$$

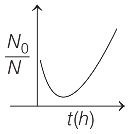
(d) 

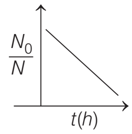
$$CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large H}{|}}{C}}-\underset{\underset{\large OCH_3}{|}}{C}HCH_3$$

25 A bacterial infection in an internal wound grows as $N'(t) = N_0 \exp(t)$, where the time *t* is in hours. A dose of antibiotic, taken orally, needs 1 hour to reach the wound. Once it reaches there, the bacterial population goes down as $\frac{dN}{dt} = -5N^2$. What will be the plot of $\frac{N_0}{N}$ *vs t* after 1 hour ?

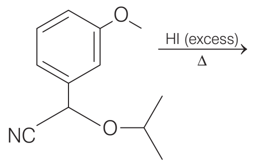
(a) 

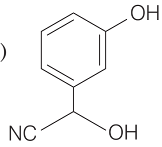
(b) 

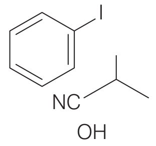
(c) 

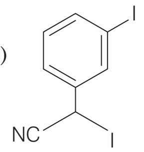
(d) 

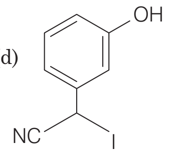
26 The major product of the following reaction is



(a) 

(b) 

(c) 

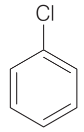
(d) 

27 The species that can have a *trans*-isomer is (en = ethane -1, 2-diamine, ox = oxalate)
(a) $[Pt(en)Cl_2]$ (b) $[Cr(en)_2(ox)]^+$
(c) $[Pt(en)_2Cl_2]^{2+}$ (d) $[Zn(en)Cl_2]$

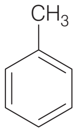
28 Ethylamine ($C_2H_5NH_2$) can be obtained from *N*-ethylphthalimide on treatment with
(a) $NaBH_4$ (b) NH_2NH_2
(c) H_2O (d) CaH_2

29 The correct order of catenation is
(a) C > Sn > Si ≈ Ge (b) Si > Sn > C > Ge
(c) C > Si > Ge ≈ Sn (d) Ge > Sn > Si > C

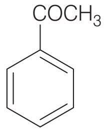
30 The increasing order of the reactivity of the following compounds towards electrophilic aromatic substitution reaction is



(I)



(II)



(III)

(a) III < I < II (b) II < I < III
(c) III < II < I (d) I < III < II

ANSWERS

1. *(a)*	2. *(b)*	3. *(c)*	4. *(b)*	5. *(b)*	6. *(b)*	7. *(b)*	8. *(d)*	9. *(b)*	10. *(a)*
11. *(a)*	12. *(d)*	13. *(c)*	14. *(c)*	15. *(d)*	16. *(d)*	17. *(b)*	18. *(b)*	19. *(b)*	20. *(c)*
21. *(d)*	22. *(b)*	23. *(a)*	24. *(c)*	25. *(a)*	26. *(d)*	27. *(c)*	28. *(b)*	29. *(c)*	30. *(a)*

For Detailed Solutions
Visit : http://tinyurl.com/y4u9y2m5
Or Scan :

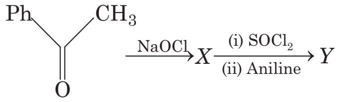
10 April, Shift-II

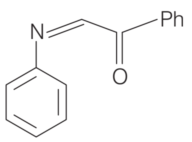
1 The correct statement is
(a) zone refining process is used for the refining of titanium.
(b) zincite is a carbonate ore.
(c) sodium cyanide cannot be used in the metallurgy of silver.
(d) aniline is a froth stabiliser.

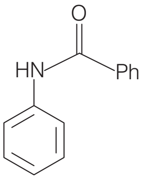
2 For the reaction of H_2 with I_2, the rate constant is 2.5×10^{-4} dm^3 mol^{-1}s^{-1} at 327°C and 1.0 dm^3 mol^{-1} s^{-1} at 527°C. The activation energy for the reaction, in kJ mol^{-1} is ($R = 8.314$ JK^{-1} mol^{-1})
(a) 59 (b) 72
(c) 150 (d) 166

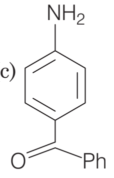
3 In chromatography, which of the following statements is incorrect for R_f?
(a) R_f value depends on the type of chromatography
(b) Higher R_f value means higher adsorption
(c) R_f value is dependent on the mobile phase
(d) The value of R_f can not be more than one

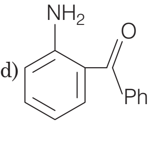
4 The major product Y in the following reaction is



(a) 

(b) 

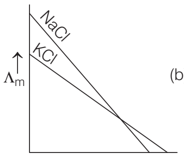
(c) 

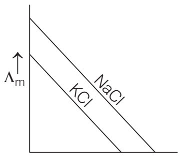
(d) 

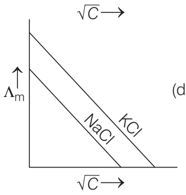
5 The correct option among the following is
(a) colloidal medicines are more effective, because they have small surface area.
(b) brownian motion in colloidal solution is faster if the viscosity of the solution is very high.
(c) addition of alum to water makes it unfit for drinking.
(d) colloidal particles in lyophobic sols can be precipitated by electrophoresis.

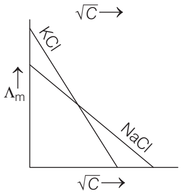
6 The highest possible oxidation states of uranium and plutonium, respectively, are
(a) 7 and 6 (b) 6 and 7
(c) 6 and 4 (d) 4 and 6

7 Which one of the following graphs between molar conductivity (Λ_m) *versus* $\sqrt{C}$ is correct?

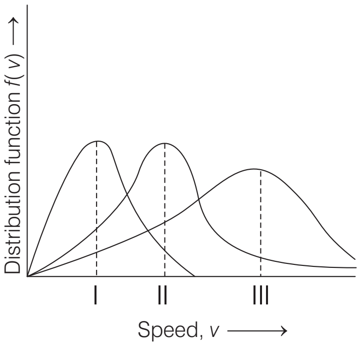
(a) 

(b) 

(c) 

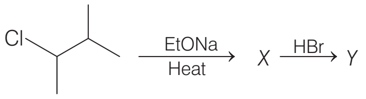
(d) 

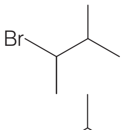
8 Points I, II and III in the following plot respectively correspond to (V_{mp} : most probable velocity)

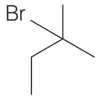


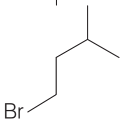
(a) v_{mp} of H_2(300 K); v_{mp} of N_2(300 K); v_{mp} of O_2(400 K)
(b) v_{mp} of O_2(400 K); v_{mp} of N_2(300 K); v_{mp} of H_2(300 K)
(c) v_{mp} of N_2(300 K); v_{mp} of O_2(400 K); v_{mp} of H_2(300 K)
(d) v_{mp} of N_2(300 K); v_{mp} of H_2(300 K); v_{mp} of O_2(400 K)

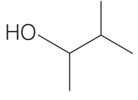
9 The major product Y in the following reaction is



(a) 

(b) 

(c) 

(d) 

10 The correct order of the first ionisation enthalpies is
(a) Mn < Ti < Zn < Ni
(b) Ti < Mn < Zn < Ni
(c) Zn < Ni < Mn < Ti
(d) Ti < Mn < Ni < Zn

11 A hydrated solid X on heating initially gives a monohydrated compound Y.
Y upon heating above 373 K leads to an anhydrous white powder Z. X and Z, respectively, are
(a) baking soda and soda ash
(b) washing soda and soda ash
(c) baking soda and dead burnt plaster
(d) washing soda and dead burnt plaster

12 Air pollution that occurs in sunlight is
(a) acid rain
(b) oxidising smog
(c) fog
(d) reducing smog

13 The incorrect statement is
(a) the gemstone, ruby, has Cr^{3+} ions occupying the octahedral sites of beryl
(b) the color of $[CoCl(NH_3)_5]^{2+}$ is violet as it absorbs the yellow light
(c) the spin only magnetic moments of $Fe(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{2+}$ are nearly similar
(d) the spin only magnetic moment of $[Ni(NH_3)_4(H_2O)_2]^{2+}$ is 2.83 BM

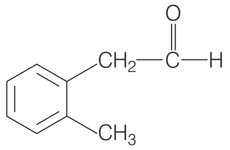
14 For the reaction,
$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$,
$\Delta H = -57.2$ kJ mol^{-1} and
$K_c = 1.7 \times 10^{16}$. Which of the following statement is incorrect?
(a) The equilibrium constant decreases as the temperature increases
(b) The addition of inert gas at constant volume will not affect the equilibrium constant
(c) The equilibrium will shift in forward direction as the pressure increases
(d) The equilibrium constant is large suggestive of reaction going to completion and so no catalyst is required

15 The ratio of the shortest wavelength of two spectral series of hydrogen spectrum is found to be about 9. The spectral series are
(a) Lyman and Paschen
(b) Brackett and Pfund
(c) Paschen and Pfund
(d) Balmer and Brackett

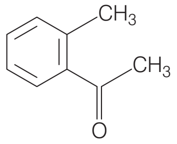
16 Number of stereo-centers present in linear and cyclic structures of glucose are respectively
(a) 4 and 5 (b) 4 and 4
(c) 5 and 4 (d) 5 and 5

17 Compound $A(C_9H_{10}O)$ shows positive iodoform test. Oxidation of A with $KMnO_4/KOH$ gives acid $B(C_8H_6O_4)$. Anhydride of B is used for the preparation of phenolphthalein. Compound A is

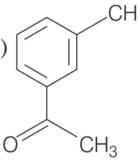
(a)



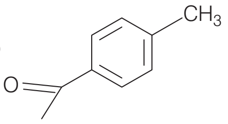
(c)



(b)



(d)



18 1 g of a non-volatile, non-electrolyte solute is dissolved in 100 g of two different solvents A and B, whose ebullisocopic constants are in the ratio of 1 : 5. The ratio of the elevation in their boiling points, $\frac{\Delta T_b(A)}{\Delta T_b(B)}$, is

(a) 5 : 1 (b) 10 : 1
(c) 1 : 5 (d) 1 : 0.2

19 The pH of a 0.02 M NH_4Cl solution will be [Given $K_b(NH_4OH) = 10^{-5}$ and $\log 2 = 0.301$]

(a) 4.65 (b) 2.65
(c) 5.35 (d) 4.35

20 The difference between ΔH and ΔU ($\Delta H - \Delta U$), when the combustion of one mole of heptane (l) is carried out at a temperature T, is equal to

(a) $-4RT$ (b) $3RT$
(c) $4RT$ (d) $-3RT$

21 Which of the following is not a correct method of the preparation of benzylamine from cyanobenzene?

(a) H_2 / Ni
(b) (i) HCl / H_2O (ii) $NaBH_4$
(c) (i) $LiAlH_4$ (ii) H_3O^+
(d) (i) $SnCl_2$ + HCl(gas) (ii) $NaBH_4$

22 The number of pentagons in C_{60} and trigons (triangles) in white phosphorus, respectively, are

(a) 20 and 3 (b) 12 and 4
(c) 20 and 4 (d) 12 and 3

23 The increasing order of nucleophilicity of the following nucleophiles is

(1) $CH_3CO_2^{\ominus}$ (2) H_2O
(3) $CH_3SO_3^{\ominus}$ (4) $\overset{\ominus}{O}H$

(a) (1) < (4) < (3) < (2)
(b) (2) < (3) < (1) < (4)
(c) (4) < (1) < (3) < (2)
(d) (2) < (3) < (4) < (1)

24 Which of these factors does not govern the stability of a conformation in acyclic compounds?

(a) Electrostatic forces of interaction
(b) Torsional strain
(c) Angle strain
(d) Steric interactions

25 The correct match between **Item**-I and **Item**-II is

Item-I	**Item-II**
A. High density polythene	I. Peroxide catalyst
B. Polyacrylonitrile	II. Condensation at high temperature and pressure
C. Novolac	III. Ziegler-Natta catalyst
D. Nylon-6	IV. Acid or base catalyst

Codes

	A	B	C	D
(a)	III	I	IV	II
(b)	IV	II	I	III
(c)	II	IV	I	III
(d)	III	I	II	IV

26 The minimum amount of $O_2(g)$ consumed per gram of reactant is for the reaction (Given atomic mass : Fe = 56, O = 16, Mg = 24, P = 31, C = 12, H = 1)

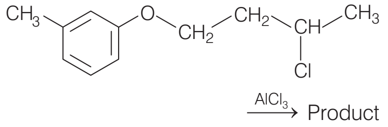
(a) $C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$
(b) $P_4(s) + 5O_2(g) \longrightarrow P_4O_{10}(s)$
(c) $4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$
(d) $2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$

27 The correct statements among (a) to (d) are:

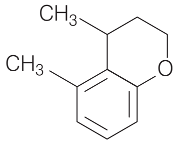
1. Saline hydrides produce H_2 gas when reacted with H_2O.
2. Reaction of $LiAlH_4$ with BF_3 leads to B_2H_6.
3. PH_3 and CH_4 are electron rich and electron precise hydrides, respectively.
4. HF and CH_4 are called as molecular hydrides.

(a) (1), (2), (3) and (4)
(b) (1), (2) and (3) only
(c) (3) and (4) only
(d) (1), (3) and (4) only

28 The major product obtained in the given reaction is



(a)



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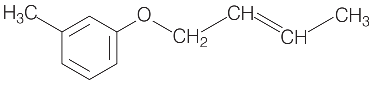
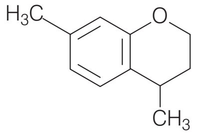
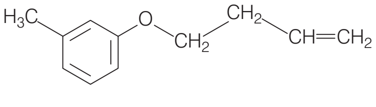


(c)



(d)



29 The noble gas that does not occur in the atmosphere is

(a) Ra (b) Kr (c) He (d) Ne

30 The crystal field stabilisation energy (CFSE) of $[Fe(H_2O)_6]Cl_2$ and $K_2[NiCl_4]$, respectively, are

(a) $-0.4\,\Delta_o$ and $-1.2\,\Delta_t$
(b) $-0.4\,\Delta_o$ and $-0.8\,\Delta_t$
(c) $-2.4\,\Delta_o$ and $-1.2\,\Delta_t$
(d) $-0.6\,\Delta_o$ and $-0.8\,\Delta_t$

ANSWERS

1. *(d)*	2. *(d)*	3. *(b)*	4. *(b)*	5. *(d)*	6. *(b)*	7. *(c)*	8. *(c)*	9. *(b)*	10. *(d)*
11. *(b)*	12. *(b)*	13. *(a)*	14. *(d)*	15. *(a)*	16. *(a)*	17. *(c)*	18. *(c)*	19. *(c)*	20. *(a)*
21. *(b)*	22. *(b)*	23. *(b)*	24. *(c)*	25. *(a)*	26. *(b)*	27. *(a)*	28. *(c)*	29. *(a)*	30. *(b)*

For Detailed Solutions
Visit : http://tinyurl.com/y3xpt9fo
Or Scan :

12 April, Shift-I

1 An example of a disproportionation reaction is

(a) $2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O$
(b) $2NaBr + Cl_2 \longrightarrow 2NaCl + Br_2$
(c) $2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$
(d) $2CuBr \longrightarrow CuBr_2 + Cu$

2 The mole fraction of a solvent in aqueous solution of a solute is 0.8. The molality (in mol kg^{-1}) of the aqueous solution is

(a) 13.88×10^{-2} (b) 13.88×10^{-1}
(c) 13.88 (d) 13.88×10^{-3}

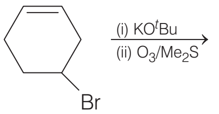
3 An ideal gas is allowed to expand from 1 L to 10 L against a constant external pressure of 1 bar. The work done in kJ is

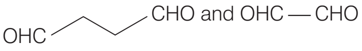
(a) − 9.0 (b) + 10.0 (c) − 0.9 (d) − 2.0

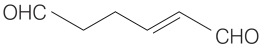
4 Which of the following is a thermosetting polymer?

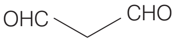
(a) Bakelite (b) Buna-N
(c) Nylon-6 (d) PVC

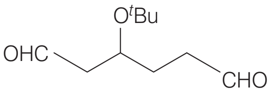
5 The major product(s) obtained in the following reaction is/are



(a) 

(b) 

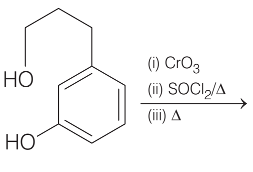
(c) 

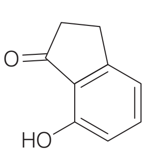
(d) 

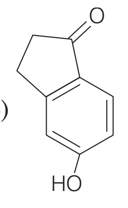
6 The metal that gives hydrogen gas upon treatment with both acid as well as base is

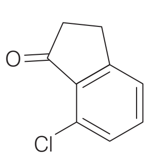
(a) magnesium (b) mercury
(c) zinc (d) iron

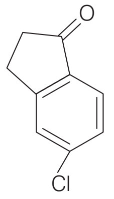
7 The major product of the following reaction is



(a) 

(b) 

(c) 

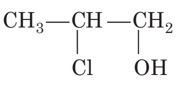
(d) 

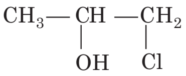
8 Glucose and galactose are having identical configuration in all the positions except position.

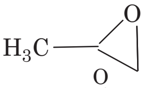
(a) C-3 (b) C-4 (c) C-2 (d) C-5

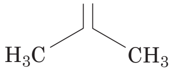
9 The major product of the following addition reaction is

$H_3C—CH = CH_2 \xrightarrow{Cl_2/H_2O}$

(a) 
$CH_3—\underset{Cl}{CH}—\underset{OH}{CH_2}$

(b) 
$CH_3—\underset{OH}{CH}—\underset{Cl}{CH_2}$

(c) 

(d) 

10 Given,

$Co^{3+} + e^- \longrightarrow Co^{2+}; E° = + 1.81 V$
$Pb^{4+} + 2e^- \longrightarrow Pb^{2+}; E° = + 1.67 V$
$Ce^{4+} + e^- \longrightarrow Ce^{3+}; E° = + 1.61 V$
$Bi^{3+} + 3e^- \longrightarrow Bi; E° = + 0.20 V$

Oxidising power of the species will increase in the order

(a) $Ce^{4+} < Pb^{4+} < Bi^{3+} < Co^{3+}$
(b) $Bi^{3+} < Ce^{4+} < Pb^{4+} < Co^{3+}$
(c) $Co^{3+} < Ce^{4+} < Bi^{3+} < Pb^{4+}$
(d) $Co^{3+} < Pb^{4+} < Ce^{4+} < Bi^{3+}$

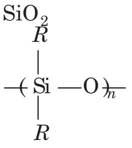
11 Which of the following statement is not true about RNA?

(a) It controls the synthesis of protein
(b) It has always double stranded αhelix structure
(c) It usually does not replicate
(d) It is present in the nucleus of the cell

12 The group number, number of valence electrons and valency of an element with atomic number 15, respectively, are

(a) 16, 5 and 2 (b) 15, 5 and 3
(c) 16, 6 and 3 (d) 15, 6 and 2

13 The basic structural unit of feldspar, zeolites, mica and asbestos is

(a) $(SiO_3)^{2-}$ (b) SiO_2
(c) $(SiO_4)^{4-}$ (d) 
$\left(\underset{R}{\overset{R}{Si}} —O \right)_n$ (R = Me)

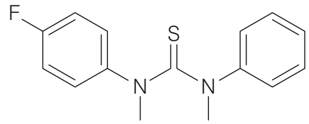
14 In the following reaction; $xA \rightarrow yB$

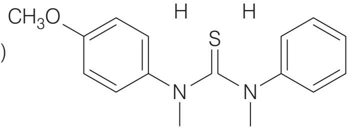
$$\log_{10}\left[-\frac{d[A]}{dt}\right] = \log_{10}\left[\frac{d[B]}{dt}\right] + 0.3010$$

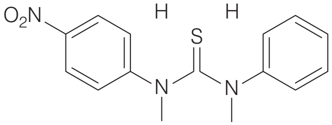
A and B respectively can be

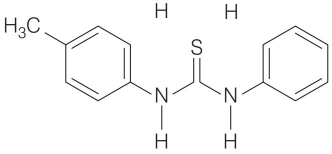
(a) n-butane and iso-butane
(b) C_2H_2 and C_6H_6
(c) C_2H_4 and C_4H_8
(d) N_2O_4 and NO_2

15 The increasing order of the pK_b of the following compound is

(A) 

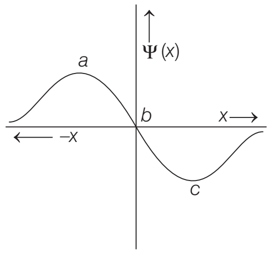
(B) 

(C) 

(D) 

(a) (A) < (C) < (D) < (B)
(b) (C) < (A) < (D) < (B)
(c) (B) < (D) < (A) < (C)
(d) (B) < (D) < (C) < (A)

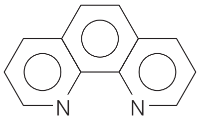
16 The electrons are more likely to be found



17 The correct sequence of thermal stability of the following carbonates is

(a) $BaCO_3 < CaCO_3 < SrCO_3 < MgCO_3$
(b) $MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$
(c) $MgCO_3 < SrCO_3 < CaCO_3 < BaCO_3$
(d) $BaCO_3 < SrCO_3 < CaCO_3 < MgCO_3$

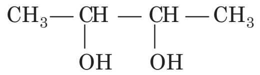
18 The complex ion that will lose its crystal field stabilisation energy upon oxidation of its metal to +3 state is

(Phen = 

Ignore pairing energy

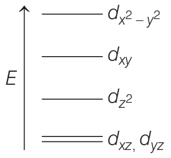
(a) $[Co(phen)_3]^{2+}$
(b) $[Ni(phen)_3]^{2+}$
(c) $[Zn(phen)_3]^{2+}$
(d) $[Fe(phen)_3]^{2+}$

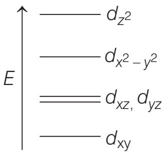
19 But-2-ene on reaction with alkaline $KMnO_4$ at elevated temperature followed by acidification will give

(a)

$CH_3—\underset{OH}{\underset{|}{CH}}—\underset{OH}{\underset{|}{CH}}—CH_3$

(b) one molecule of CH_3CHO and one molecule of CH_3COOH
(c) 2 molecules of CH_3COOH
(d) 2 molecules of CH_3CHO

20 Complete removal of both the axial ligands (along the z-axis) from an octahedral complex leads to which of the following splitting patterns? (relative orbital energies not on scale).

(a)


(b)


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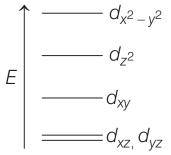

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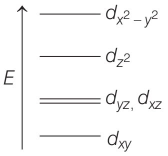


21 An organic compound A is oxidised with Na_2O_2 followed by boiling with HNO_3. The resultant solution is then treated with ammonium molybdate to yield a yellow precipitate.
Based on above observation, the element present in the given compound is

(a) nitrogen (b) phosphorus
(c) fluorine (d) sulphur

22 The correct set of species responsible for the photochemical smog is

(a) N_2, NO_2 and hydrocarbons
(b) CO_2, NO_2, SO_2 and hydrocarbons
(c) NO, NO_2, O_3 and hydrocarbons
(d) N_2, O_2, O_3 and hydrocarbons

23 Peptisation is a

(a) process of bringing colloidal molecule into solution
(b) process of converting precipitate into colloidal solution
(c) process of converting a colloidal solution into precipitate
(d) process of converting soluble particles to form colloidal solution

24 The correct statement among the following is

(a) $(SiH_3)_3N$ is planar and less basic than $(CH_3)_3N$.
(b) $(SiH_3)_3N$ is pyramidal and more basic than $(CH_3)_3N$.
(c) $(SiH_3)_3N$ is pyramidal and less basic than $(CH_3)_3N$.
(d) $(SiH_3)_3N$ is planar and more basic than $(CH_3)_3N$.

25 Enthalpy of sublimation of iodine is 24 cal g^{-1} at 200°C. If specific heat of $I_2(s)$ and I_2(vap.) are 0.055 and 0.031 cal g^{-1} K^{-1} respectively, then enthalpy of sublimation of iodine at 250°C in cal g^{-1} is

(a) 2.85 (b) 5.7
(c) 22.8 (d) 11.4

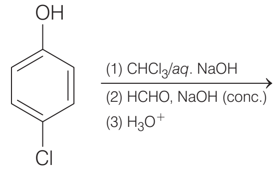
26 An element has a face-centred cubic (fcc) structure with a cell edge of a. The distance between the centres of two nearest tetrahedral voids in the lattice is

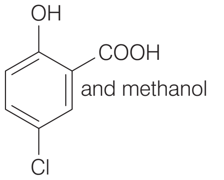
(a) $\sqrt{2}a$ (b) a (c) $\frac{a}{2}$ (d) $\frac{3}{2}a$

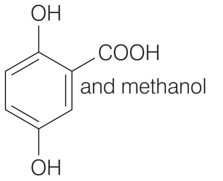
27 What is the molar solubility of $Al(OH)_3$ in 0.2 M NaOH solution? Given that, solubility product of $Al(OH)_3 = 2.4 \times 10^{-24}$

(a) 3×10^{-19} (b) 12×10^{-21}
(c) 3×10^{-22} (d) 12×10^{-23}

28 The major products of the following reaction are



(a)


(b)


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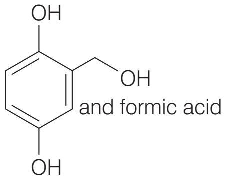

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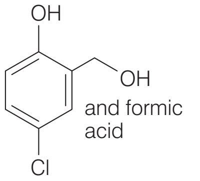

29 5 moles of AB_2 weight 125×10^{-3} kg and 10 moles of A_2B_2 weight 300×10^{-3} kg. The molar mass of $A(M_A)$ and molar mass of $B(M_B)$ in kg mol^{-1} are

(a) $M_A = 10 \times 10^{-3}$ and $M_B = 5 \times 10^{-3}$
(b) $M_A = 50 \times 10^{-3}$ and $M_B = 25 \times 10^{-3}$
(c) $M_A = 25 \times 10^{-3}$ and $M_B = 50 \times 10^{-3}$
(d) $M_A = 5 \times 10^{-3}$ and $M_B = 10 \times 10^{-3}$

30 The idea of froth floatation method came from a person X and this method is related to the process Y of ores. X and Y, respectively, are

(a) fisher woman and concentration
(b) washer woman and concentration
(c) fisher man and reduction
(d) washer man and reduction

ANSWERS

1. *(d)*	2. *(c)*	3. *(c)*	4. *(a)*	5. *(a)*	6. *(c)*	7. *(b)*	8. *(b)*	9. *(b)*	10. *(b)*
11. *(b)*	12. *(b)*	13. *(c)*	14. *(c)*	15. *(c)*	16. *(a)*	17. *(b)*	18. *(d)*	19. *(c)*	20. *(a)*
21. *(b)*	22. *(c)*	23. *(b)*	24. *(d)*	25. *(c)*	26. *(c)*	27. *(c)*	28. *(d)*	29. *(d)*	30. *(b)*

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12 April, Shift-II

1 Thermal decomposition of a Mn compound (X) at 513 K results in compound (Y), MnO_2 and a gaseous product. MnO_2 reacts with NaCl and concentrated H_2SO_4 to give a pungent gas Z. X, Y and Z, respectively, are

(a) K_3MnO_4, K_2MnO_4 and Cl_2
(b) K_2MnO_4, $KMnO_4$ and SO_2
(c) $KMnO_4$, K_2MnO_4 and Cl_2
(d) K_2MnO_4, $KMnO_4$ and Cl_2

2 NO_2 required for a reaction is produced by the decomposition of N_2O_5 in CCl_4 as per the equation,

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

The initial concentration of N_2O_5 is 3.00 mol L^{-1} and it is 2.75 mol L^{-1} after 30 minutes. The rate of formation of NO_2 is

(a) 4.167×10^{-3} mol L^{-1} min^{-1}
(b) 1.667×10^{-2} mol L^{-1} min^{-1}
(c) 8.333×10^{-3} mol L^{-1} min^{-1}
(d) 2.083×10^{-3} mol L^{-1} min^{-1}

3 The pair that has similar atomic radii is

(a) Mn and Re (b) Ti and Hf
(c) Sc and Ni (d) Mo and W

4 The incorrect statement is

(a) lithium is the strongest reducing agent among the alkali metals.
(b) lithium is least reactive with water among the alkali metals.
(c) $LiNO_3$ decomposes on heating to give $LiNO_2$ and O_2.
(d) LiCl crystallise from aqueous solution as $LiCl \cdot 2H_2O$.

5 The C—C bond length is maximum in

(a) graphite (b) C_{70}
(c) C_{60} (d) diamond

6 A solution is prepared by dissolving 0.6 g of urea (molar mass = 60 g mol^{-1}) and 1.8 g of glucose (molar mass = 180 g mol^{-1}) in 100 mL of water at 27°C. The osmotic pressure of the solution is

($R = 0.08206$ L atm K^{-1} mol^{-1})

(a) 8.2 atm (b) 2.46 atm
(c) 4.92 atm (d) 1.64 atm

7 In comparison to boron, berylium has

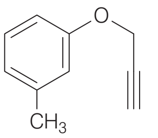
(a) lesser nuclear charge and lesser first ionisation enthalpy
(b) greater nuclear charge and lesser first ionisation enthalpy
(c) greater nuclear charge and greater first ionisation enthalpy
(d) lesser nuclear charge and greater first ionisation enthalpy

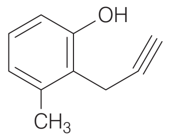
8 The decreasing order of electrical conductivity of the following aqueous solution is

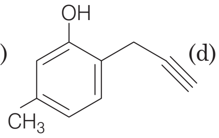
0.1 M formic acid (A),
0.1 M acetic acid (B),
0.1 M benzoic acid (C).

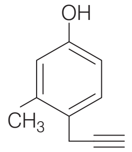
(a) $A > C > B$ (b) $C > B > A$
(c) $A > B > C$ (d) $C > A > B$

9 What will be the major product when m-cresol is reacted with propargyl bromide ($HC\equiv C—CH_2Br$) in presence of K_2CO_3 in acetone?

(a) 

(b) 

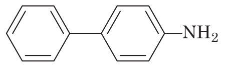
(c) 

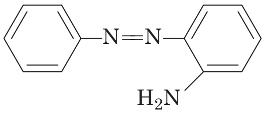
(d) 

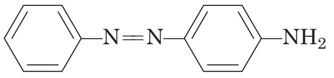
10 The molar solubility of Cd $(OH)_2$ is 1.84×10^{-5} m in water. The expected solubility of $Cd(OH)_2$ in a buffer solution of pH = 12 is

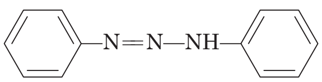
(a) 1.84×10^{-9} M (b) $\frac{2.49}{1.84} \times 10^{-9}$ M
(c) 6.23×10^{-11} M (d) 2.49×10^{-10} M

11 Benzene diazonium chloride on reaction with aniline in the presence of dilute hydrochloric acid gives

(a) 

(b) 

(c) 

(d) 

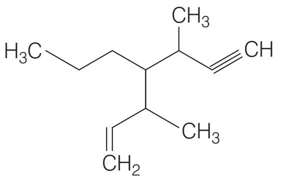
12 The correct statement is

(a) leaching of bauxite using concentrated NaOH solution gives sodium aluminate and sodium silicate.
(b) the hall-heroult process is used for the production of aluminium and iron.
(c) pig iron is obtained from cast iron.
(d) the blistered appearance of copper during the metallurgical process is due to the evolution of CO_2.

13 The primary pollutant that leads to photochemical smog is

(a) acrolein
(b) nitrogen oxides
(c) ozone
(d) sulphur dioxide

14 The IUPAC name for the following compound is

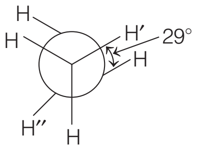


(a) 3-methyl-4-(3-methylprop-1-enyl)-1-heptyne
(b) 3, 5-dimethyl-4-propylhept-6-en-1-yne
(c) 3-methyl-4-(1-methylprop-2-ynyl)-1-heptene
(d) 3, 5-dimethyl-4-propylhept-1-en-6-yne

15 The temporary hardness of a water sample is due to compound X. Boiling this sample converts X to compound Y. X and Y, respectively, are

(a) $Mg(HCO_3)_2$ and $Mg(OH)_2$
(b) $Ca(HCO_3)_2$ and $Ca(OH)_2$
(c) $Mg(HCO_3)_2$ and $MgCO_3$
(d) $Ca(HCO_3)_2$ and CaO

16 In the following skew conformation of ethane, H′—C—C—H″ dihedral angle is



(a) 58° (b) 149°
(c) 151° (d) 120°

17 Among the following, the energy of 2s-orbital is lowest in

(a) K (b) H
(c) Li (d) Na

18 Which one of the following is likely to give a precipitate with $AgNO_3$ solution?

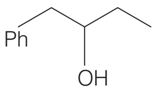
(a) $CH_2=CH—Cl$ (b) CCl_4
(c) $CHCl_3$ (d) $(CH_3)_3CCl$

19 25 g of an unknown hydrocarbon upon burning produces 88 g of CO_2 and 9 g of H_2O.

This unknown hydrocarbon contains

(a) 20 g of carbon and 5 g of hydrogen
(b) 22 g of carbon and 3 g of hydrogen
(c) 24 g of carbon and 1 g of hydrogen
(d) 18 g of carbon and 7 g of hydrogen

20 Heating of 2-chloro-1-phenyl butane with EtOK/EtOH gives X as the major product. Reaction of X with $Hg(OAc)_2 / H_2O$ followed by $NaBH_4$ gives Y as the major product. Y is

(a)


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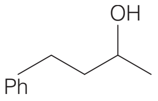

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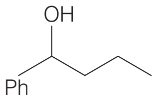

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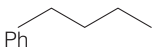


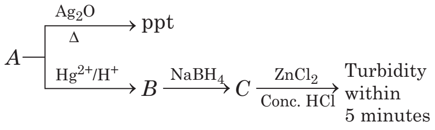
21 The compound used in the treatment of lead poisoning is

(a) D-penicillamine (b) desferrioxime-B
(c) *cis*-platin (d) EDTA

22 Which of the given statements is incorrect about glycogen?

(a) It is straight chain polymer similar to amylose
(b) Only α-linkages are present in the molecule
(c) It is present in animal cells
(d) It is present in some yeast and fungi

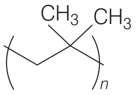
23 Consider the following reactions,



A is

(a) $CH{\equiv}CH$
(b) $CH_3—C{\equiv}C—CH_3$
(c) $CH_3—C{\equiv}CH$
(d) $CH_2{=}CH_2$

24 The correct name of the following polymer is



(a) polyisobutane
(b) polytert-butylene
(c) polyisoprene
(d) polyisobutylene

25 An **Assertion** and a **Reason** are given below. Choose the correct answer from the following options.

Assertion (A) Vinyl halides do not undergo nucleophilic substitution easily.

Reason (R) Even though the intermediate carbocation is stabilised by loosely held π-electrons, the cleavage is difficult because of strong bonding.

(a) Both (A) and (R) are wrong statements.
(b) Both (A) and (R) are correct statements and (R) is correct explanation of (A).
(c) Both (A) and (R) are correct statements but (R) is not the correct explanation of (A).
(d) (A) is a correct statement but (R) is a wrong statement.

26 The ratio of number of atoms present in a simple cubic, body centered cubic and face centered cubic structure are, respectively.

(a) 8 : 1 : 6 (b) 1 : 2 : 4
(c) 4 : 2 : 1 (d) 4 : 2 : 3

27 In which one of the following equilibria, $K_p \neq K_c$?

(a) $2C(s) + O_2(g) \rightleftharpoons 2CO(g)$
(b) $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$
(c) $NO_2(g) + SO_2(g) \rightleftharpoons NO(g) + SO_3(g)$
(d) $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$

28 The coordination numbers of Co and Al in $[CoCl(en)_2]Cl$ and $K_3[Al(C_2O_4)_3]$, respectively, are
(en = ethane-1, 2-diamine)

(a) 5 and 3 (b) 3 and 3
(c) 6 and 6 (d) 5 and 6

29 The incorrect match in the following is

(a) $\Delta G^\circ < 0, K > 1$ (b) $\Delta G^\circ = 0, K = 1$
(c) $\Delta G^\circ > 0, K < 1$ (d) $\Delta G^\circ < 0, K < 1$

30 Among the following, the incorrect statement about colloids is

(a) They can scatter light
(b) They are larger than small molecules and have high molar mass
(c) The osmotic pressure of a colloidal solution is of higher order than the true solution at the same concentration
(d) The range of diameters of colloidal particles is between 1 and 1000 nm

ANSWERS

1. *(c)*	2. *(b)*	3. *(d)*	4. *(c)*	5. *(d)*	6. *(c)*	7. *(d)*	8. *(a)*	9. *(a)*	10. *(d)*
11. *(c)*	12. *(a)*	13. *(b)*	14. *(d)*	15. *(a)*	16. *(b)*	17. *(a)*	18. *(d)*	19. *(c)*	20. *(c)*
21. *(d)*	22. *(a)*	23. *(c)*	24. *(d)*	25. *(c)*	26. *(b)*	27. *(a)*	28. *(d)*	29. *(d)*	30. *(c)*

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JANUARY ATTEMPT

9 January, Shift-I

1 The alkaline earth metal nitrate that does not crystallise with water molecules, is

(a) $Ca(NO_3)_2$ (b) $Sr(NO_3)_2$
(c) $Ba(NO_3)_2$ (d) $Mg(NO_3)_2$

2 0.5 moles of gas A and x moles of gas B exert a pressure of 200 Pa in a container of volume $10 m^3$ at 1000 K. Given R is the gas constant in $JK^{-1}\ mol^{-1}$, x is

(a) $\frac{2R}{4-R}$ (b) $\frac{4-R}{2R}$ (c) $\frac{4+R}{2R}$ (d) $\frac{2R}{4+R}$

3 According to molecular orbital theory, which of the following is true with respect to Li_2^+ and Li_2^-?

(a) Both are unstable
(b) Li_2^+ is unstable and Li_2^- is stable
(c) Both are stable
(d) Li_2^+ is stable and Li_2^- is unstable

4 The major product of following reaction is

$$R—C \equiv N \xrightarrow[\text{(ii) } H_2O]{\text{(i) } AlH(i\text{-}Bu)_2} ?$$

(a) $RCHO$ (b) $RCONH_2$
(c) $RCOOH$ (d) RCH_2NH_2

5 The correct decreasing order for acid strength is

(a) $FCH_2COOH > NCCH_2COOH > NO_2CH_2COOH > ClCH_2COOH$
(b) $CNCH_2COOH > O_2NCH_2COOH > FCH_2COOH > ClCH_2COOH$
(c) $NO_2CH_2COOH > NCCH_2COOH > FCH_2COOH > ClCH_2COOH$
(d) $NO_2CH_2COOH > FCH_2COOH > CNCH_2COOH > ClCH_2COOH$

6 The one that is extensively used as a piezoelectric material is

(a) quartz (b) tridymite
(c) amorphous silica (d) mica

7 The ore that contains both iron and copper is

(a) malachite (b) azurite
(c) dolomite (d) copper pyrites

8 For emission line of atomic hydrogen from $n_i = 8$ to $n_f = n$, the plot of wave number (ν) against $\left(\frac{1}{n^2}\right)$ will be (The Rydberg constant, R_H is in wave number unit)

(a) non linear
(b) linear with slope $-R_H$
(c) linear with slope R_H
(d) linear with intercept $-R_H$

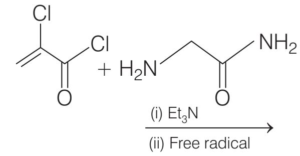
9 Aluminium is usually found in +3 oxidation state. In contrast, thallium exists in +1 and +3 oxidation states. This is due to

(a) lattice effect
(b) lanthanoid contraction
(c) inert pair effect
(d) diagonal relationship

10 A water sample has ppm level concentration of the following metals: Fe = 0.2; Mn = 5.0 ; Cu = 3.0; Zn = 5.0. The metal that makes the water sample unsuitable for drinking is

(a) Cu (b) Fe (c) Mn (d) Zn

11 Major product of the following reaction is



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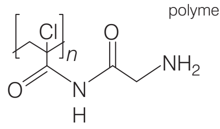

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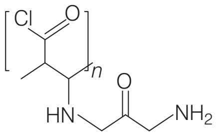

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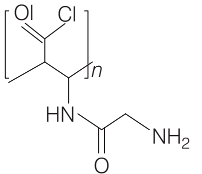

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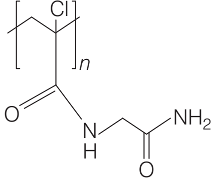
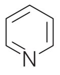
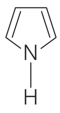
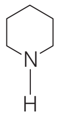


12 Arrange the following amines in the decreasing order of basicity:


(I)


(II)

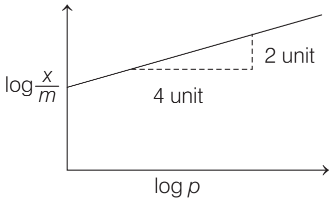

(III)

(a) I > II > III (b) III > II > I
(c) I > III > II (d) III > I > II

13 In general, the properties that decrease and increase down a group in the periodic table, respectively are

(a) electronegativity and atomic radius
(b) electronegativity and electron gain enthalpy
(c) electron gain enthalpy and electronegativity
(d) atomic radius and electronegativity

14 Adsorption of a gas follows Freundlich adsorption isotherm. In the given plot, x is the mass of the gas adsorbed on mass m of the adsorbent at pressure $p \cdot \frac{x}{m}$ is proportional to



(a) p^2 (b) $p^{1/4}$
(c) $p^{1/2}$ (d) p

15 The anodic half-cell of lead-acid battery is recharged using electricity of 0.05 Faraday. The amount of $PbSO_4$ electrolysed in g during the process is (Molar mass of $PbSO_4 = 303 g\ mol^{-1}$)

(a) 11.4 (b) 7.6 (c) 15.2 (d) 22.8

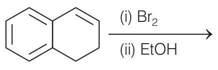
16 The isotopes of hydrogen are

(a) deuterium and tritium only
(b) protium and deuterium only
(c) protium, deuterium and tritium
(d) tritium and protium only

17 A solution of sodium sulphate contains 92 g of Na^+ ions per kilogram of water.
The molality of Na^+ ions in that solution in mol kg^{-1} is

(a) 16 (b) 4 (c) 132 (d) 8

18 The major product of the following reaction is



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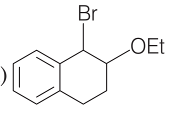

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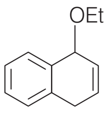

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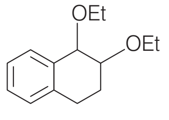

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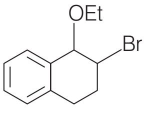
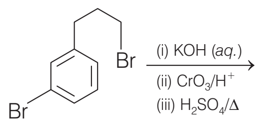


19 Two complexes $[Cr(H_2O)_6]Cl_3$ (A) and $[Cr(NH_3)_6]Cl_3$ (B) are violet and yellow coloured, respectively.
The incorrect statement regarding them is

(a) Δ_o value for (A) is less than that of (B)
(b) both absorb energies corresponding to their complementary colours
(c) Δ_o values of (A) and (B) are calculated from the energies of violet and yellow light, respectively
(d) both are paramagnetic with three unpaired electrons

20 The major product of the following reaction is



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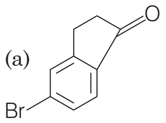

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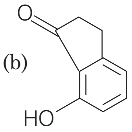

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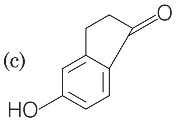
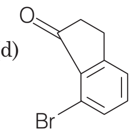
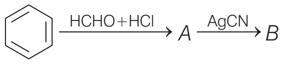


(d)


21 The compounds A and B in the following reaction are, respectively



(a) A = Benzyl alcohol, B = Benzyl isocyanide
(b) A = Benzyl alcohol, B = Benzyl cyanide
(c) A = Benzyl chloride, B = Benzyl isocyanide
(d) A = Benzyl chloride, B = Benzyl cyanide

22 20 mL of 0.1 M H_2SO_4 solution is added to 30 mL of 0.2 M NH_4OH solution. The pH of the resultant mixture is [pK_b of $NH_4OH = 4.7$]

(a) 9.3 (b) 5.0
(c) 9.0 (d) 5.2

23 Which one of the following statements regarding Henry's law is not correct?

(a) Different gases have different K_H (Henry's law constant) values at the same temperature
(b) Higher the value of K_H at a given pressure, higher is the solubility of the gas in the liquids
(c) The value of K_H increases with increase of temperature and K_H is function of the nature of the gas
(d) The partial pressure of the gas in vapour phase is proportional to the mole fraction of the gas in the solution

24 The correct match between Item - I and Item - II is

Item I (Drug)	**Item II** (Test)
A. Chloroxylenol	P. Carbylamine test
B. Norethindrone	Q. Sodium hydrogen carbonate test
C. Sulphapyridine	R. Ferric chloride test
D. Penicillin	S. Bayer's test

(a) A → R ; B → P ; C → S ; D → Q
(b) A → R ; B → S ; C → P ; D → Q
(c) A → Q ; B → P ; C → S ; D → R
(d) A → Q ; B → S ; C → P ; D → R

25 Correct statements among (I) to (IV) regarding silicones are:

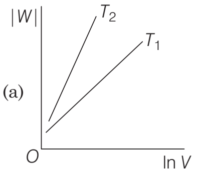
I. They are polymers with hydrophobic character.
II. They are biocompatible.
III. In general, they have high thermal stability and low dielectric strength.
IV. Usually, they are resistant to oxidation and used as greases.

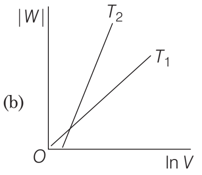
(a) I and II only
(b) I, II, III only
(c) I, II, III and IV
(d) I, II and IV only

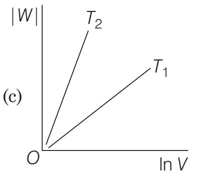
26 The highest value of the calculated spin only magnetic moment (in BM) among all the transition metal complexes is

(a) 5.92 (b) 3.87
(c) 6.93 (d) 4.90

27 Consider the reversible isothermal expansion of an ideal gas in a closed system at two different temperatures T_1 and T_2 ($T_1 < T_2$). The correct graphical depiction of the dependence of work done (W) on the final volume (V) is

(a)


(b)


(c)


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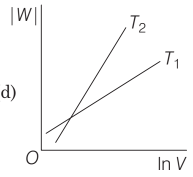


28 The following results were obtained during kinetic studies of the reaction;

$$2A + B \longrightarrow \text{Products}$$

Experiment	$[A]$ (in mol L^{-1})	$[B]$ (in mol L^{-1})	Initial rate of reaction (in mol L^{-1} min^{-1})
I.	0.10	0.20	6.93×10^{-3}
II.	0.10	0.25	6.93×10^{-3}
III.	0.20	0.30	1.386×10^{-2}

The time (in minutes) required to consume half of A is

(a) 5 (b) 10
(c) 100 (d) 1

29 Which amongst the following is the strongest acid?

(a) $CHBr_3$ (b) CHI_3
(c) $CHCl_3$ (d) $CH(CN)_3$

30 The increasing order of pK_a of the following amino acids in aqueous solution is Gly, Asp, Lys, Arg

(a) Asp < Gly < Arg < Lys
(b) Arg < Lys < Gly < Asp
(c) Gly < Asp < Arg < Lys
(d) Asp < Gly < Lys < Arg

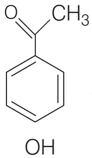
ANSWERS

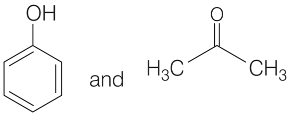
1. *(c)*	2. *(b)*	3. *(d)*	4. *(a)*	5. *(c)*	6. *(a)*	7. *(d)*	8. *(c)*	9. *(c)*	10. *(c)*
11. *(d)*	12. *(d)*	13. *(a)*	14. *(c)*	15. *(b)*	16. *(c)*	17. *(b)*	18. *(d)*	19. *(c)*	20. *(a)*
21. *(c)*	22. *(a)*	23. *(b)*	24. *(b)*	25. *(d)*	26. *(a)*	27. *(c)*	28. *(b)*	29. *(d)*	30. *(d)*

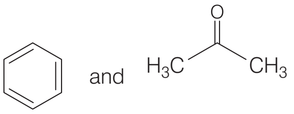
For Detailed Solutions
Visit : http://tinyurl.com/y4qlj9l5
Or Scan :

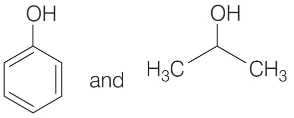
9 January, Shift-II

1 The products formed in the reaction of cumene with O_2 followed by treatment with dil. HCl are

(a)  and CH_3—OH

(b) 

(c) 

(d) 

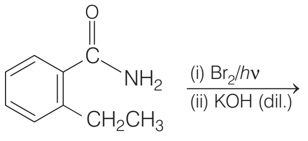
2 Which of the salt-solution is most effective for coagulation of arsenious sulphide?

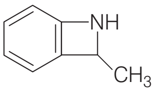
(a) $BaCl_2$ (b) $AlCl_3$
(c) Na_3PO_4 (d) NaCl

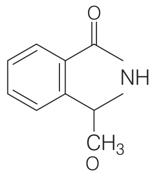
3 In which of the following processes, the bond order has increased and paramagnetic character has changed to diamagnetic?

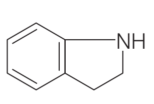
(a) $O_2 \rightarrow O_2^+$ (b) $N_2 \rightarrow N_2^+$
(c) $O_2 \rightarrow O_2^{2-}$ (d) $NO \rightarrow NO^+$

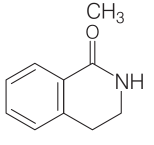
4 The major product of the following reaction is



(a) 

(b) 

(c) 

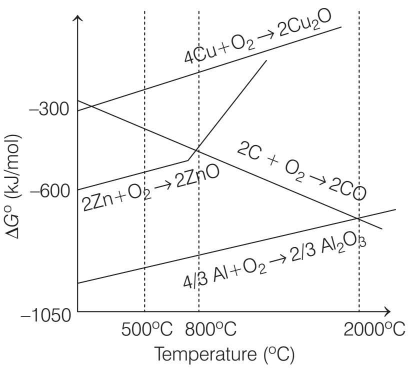
(d) 

5 The correct match between item-I and Item-II is

A. Benzaldehyde	P. Dynamic phase
B. Alumina	Q. Adsorbent
C. Acetonitrile	R. Adsorbate

(a) (A) → (R) ; (B) → (Q); (C) → (P)
(b) (A) → (P); (B) → (R); (C) → (Q)
(c) (A) → (Q); (B) → (P); (C) → (R)
(d) (A) → (Q); (B) → (R); (C) → (P)

6 The correct statement regarding the given Ellingham diagram is

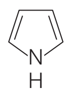


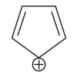
(a) At 800°C, Cu can be used for the extraction of Zn from ZnO
(b) At 1400°C, Al can be used for the extraction of Zn from ZnO
(c) At 500°C, coke can be used for the extraction of Zn from ZnO
(d) Coke cannot be used for the extraction of Cu from Cu_2O

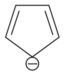
7 What is reason of temporary hardness of water?

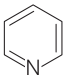
(a) Na_2SO_4 (b) $CaCl_2$
(c) NaCl (d) $Ca(HCO_3)_2$

8 Which of the following compounds is not aromatic?

(a) 

(b) 

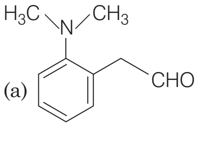
(c) 

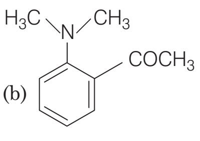
(d) 

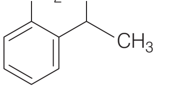
9 The tests performed on compound X and their inferences are :

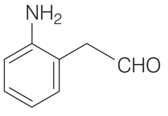
Test	Inference
(a) 2, 4- DNP test	Coloured precipitate
(b) Iodoform test	Yellow precipitate
(c) Azo-dye test	No dye formation

Compound 'X' is

(a) 

(b) 

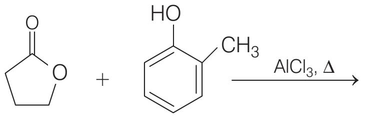
(c) 

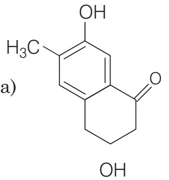
(d) 

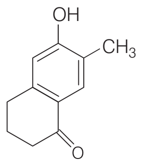
10 Good reducing nature of H_3PO_2 is attributed to the presence of

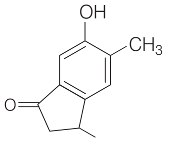
(a) two P— H bonds
(b) one P— H bond
(c) two P— OH bonds
(d) one P — OH bond

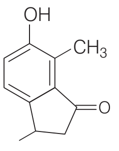
11 The major product of the following reaction is



(a) 

(b) 

(c) 

(d) 

12 The complex that has highest crystal field splitting energy (Δ), is

(a) $[Co(NH_3)_5Cl]\,Cl_2$
(b) $[Co(NH_3)_5(H_2O)]Cl_3$
(c) $K_3[Co(CN)_6]$
(d) $K_2[CoCl_4]$

13 The condition for methemoglobinemia by drinking water is

(a) > 50 ppm nitrate (b) > 50 ppm chloride
(c) > 50 ppm lead (d) > 100 ppm sulphate

14 Consider the following reversible chemical reactions,

$$A_2(g) + B_2(g) \overset{K_1}{\rightleftharpoons} 2AB(g) \quad \text{...(i)}$$

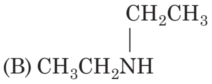
$$6AB(g) \overset{K_2}{\rightleftharpoons} 3A_2(g) + 3B_2(g) \quad \text{...(ii)}$$

The relation between K_1 and K_2 is

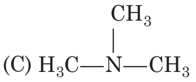
(a) $K_2 = K_1^3$ (b) $K_1K_2 = 3$
(c) $K_2 = K_1^{-3}$ (d) $K_1K_2 = \frac{1}{3}$

15 The increasing basicity order of the following compounds is

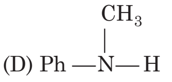
(A) $CH_3CH_2NH_2$



(B) $CH_3CH_2\overset{\overset{\large CH_2CH_3}{|}}{N}H$



(C) $H_3C—\overset{\overset{\large CH_3}{|}}{N}—CH_3$



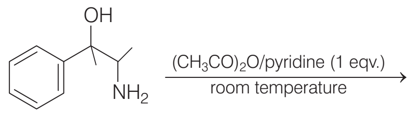
(D) $Ph—\overset{\overset{\large CH_3}{|}}{N}—H$

(a) $(D) < (C) < (B) < (A)$
(b) $(A) < (B) < (C) < (D)$
(c) $(A) < (B) < (D) < (C)$
(d) $(D) < (C) < (A) < (B)$

16 When the first electron gain enthalpy $(\Delta_{eg}H)$ of oxygen is – 141 kJ / mol, its second electron gain enthalpy is

(a) a positive value
(b) a more negative value than the first
(c) almost the same as that of the first
(d) negative, but less negative than the first

17 The major product obtained in the following reaction is



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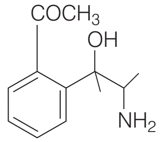

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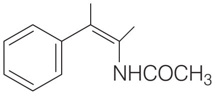

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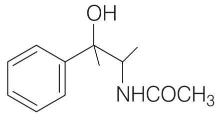
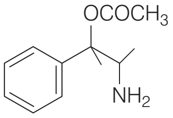


(d)


18 For the reaction, $2A + B \rightarrow$ products

When concentration of both (A and B) becomes double, then rate of reaction increases from 0.3 mol L^{-1} s^{-1} to 2.4 mol L^{-1} s^{-1}.

When concentration of only A is doubled, the rate of reaction increases from 0.3 mol L^{-1} s^{-1} to 0.6 mol L^{-1} s^{-1}.

Which of the following is true?

(a) The whole reaction is of 4th order
(b) The order of reaction w.r.t. B is one
(c) The order of reaction w.r.t. B is 2
(d) The order of reaction w.r.t. A is 2

19 The entropy change associated with the conversion of 1 kg of ice at 273 K to water vapours at 383 K is

(Specific heat of water liquid and water vapour are 4.2 $kJK^{-1}kg^{-1}$ and 2.0 kJK^{-1} kg^{-1}; heat of liquid fusion and vapourisation of water are 334 kJ kg^{-1} and 2491 $kJkg^{-1}$ respectively).($\log 273 = 2.436$, $\log 373 = 2.572$, $\log 383 = 2.583$)

(a) 9.26 kJ kg^{-1} K^{-1} (b) 8.49 kJ $kg^{-1}K^{-1}$
(c) 7.90 kJ $kg^{-1}K^{-1}$ (d) 2.64 kJ $kg^{-1}K^{-1}$

20 The transition element having least enthalpy of atomisation is

(a) Zn (b) V (c) Fe (d) Cu

21 For the following reaction, the mass of water produced from 445 g of $C_{57}H_{110}O_6$ is :

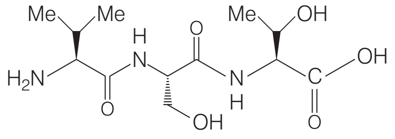
$$2C_{57}H_{110}O_6(s) + 163O_2(g) \rightarrow 114CO_2(g) + 110\,H_2O\,(l)$$

(a) 490 g (b) 495 g (c) 445 g (d) 890 g

22 The metal that forms nitride by reacting directly with N_2 of air, is

(a) Rb (b) K (c) Cs (d) Li

23 The correct sequence of amino acids present in the tripeptide given below is

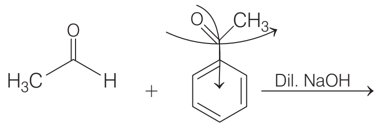


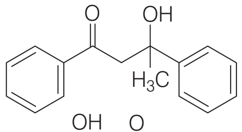
(a) Thr - Ser - Leu (b) Leu - Ser - Thr
(c) Val - Ser - Thr (d) Thr - Ser - Val

24 A solution contain 62 g of ethylene glycol in 250 g of water is cooled upto –10° C. If K_f for water is 1.86 K kg mol^{-1}, then amount of water (in g) separated as ice is

(a) 32 (b) 48 (c) 64 (d) 16

25 The major product formed in the following reaction is



(a)


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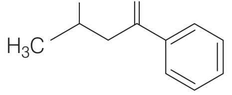
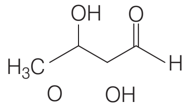


(c)


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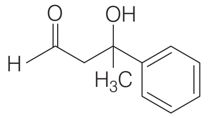

26 If the standard electrode potential for a cell is 2V at 300 K, the equilibrium constant (K) for the reaction,

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$$

at 300 K is approximately

($R = 8\ JK^{-1}mol^{-1}$, $F = 96000\ C\ mol^{-1}$)

(a) e^{-160} (b) e^{160}
(c) e^{-80} (d) e^{320}

27 Which of the following combination of statements is true regarding the interpretation of the atomic orbitals?

I. An electron in an orbital of high angular momentum stays away from the nucleus than an electron in the orbital of lower angular momentum.
II. For a given value of the principal quantum number, the size of the orbit is inversely proportional to the azimuthal quantum number.
III. According to wave mechanics, the ground state angular momentum is equal to $\frac{h}{2\pi}$.
IV. The plot of ψ *vs* r for various azimuthal quantum numbers, shows peak shifting towards higher r value.

(a) I, III (b) II, III
(c) I, II (d) I, IV

28 The pH of rain water, is approximately

(a) 7.5 (b) 6.5
(c) 5.6 (d) 7.0

29 At 100°C, copper (Cu) has FCC unit cell structure with cell edge length of x Å. What is the approximate density of Cu (in g cm^{-3}) at this temperature?

[Atomic mass of Cu = 63.55 u]

(a) $\frac{211}{x^3}$ (b) $\frac{205}{x^3}$
(c) $\frac{105}{x^3}$ (d) $\frac{422}{x^3}$

30 Homoleptic octahedral complexes of a metal ion 'M^{3+}' with three monodentate ligands L_1, L_2 and L_3 absorb wavelengths in the region of green, blue and red respectively. The increasing order of the ligand strength is

(a) $L_1 < L_2 < L_3$ (b) $L_2 < L_1 < L_3$
(c) $L_3 < L_1 < L_2$ (d) $L_3 < L_2 < L_1$

ANSWERS

1 *(b)*	2 *(b)*	3 *(d)*	4 *(a)*	5 *(a)*	6 *(b)*	7 *(d)*	8 *(b)*	9 *(b)*	10 *(a)*
11 *(c)*	12 *(c)*	13 *(a)*	14 *(c)*	15 *(d)*	16 *(a)*	17 *(b)*	18 *(c)*	19 *(a)*	20 *(a)*
21 *(b)*	22 *(d)*	23 *(c)*	24 *(c)*	25 *(c)*	26 *(b)*	27 *(d)*	28 *(c)*	29 *(d)*	30 *(c)*

For Detailed Solutions
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Or Scan :

10 January, Shift-I

1 Which of the following is not an example of heterogeneous catalytic reaction?

(a) Haber's process
(b) Combustion of coal
(c) Hydrogenation of vegetable oils
(d) Ostwald's process

2 Hall-Heroult's process is given by

(a) $ZnO + C \xrightarrow{\text{Coke, 1673 K}} Zn + CO$
(b) $Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$
(c) $2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2$
(d) $Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2H^+(aq)$

3 The chemical nature of hydrogen peroxide is

(a) oxidising and reducing agent in both acidic and basic medium
(b) oxidising and reducing agent in acidic medium, but not in basic medium
(c) reducing agent in basic medium, but not in acidic medium
(d) oxidising agent in acidic medium, but not in basic medium

4 Consider the following reduction processes:

$Zn^{2+} + 2e^- \longrightarrow Zn(s);\ E° = -0.76\,V$
$Ca^{2+} + 2e^- \longrightarrow Ca(s);\ E° = -2.87\,V$
$Mg^{2+} + 2e^- \longrightarrow Mg(s);\ E° = -2.36\,V$
$Ni^{2+} + 2e^- \longrightarrow Ni(s);\ E° = -0.25\,V$

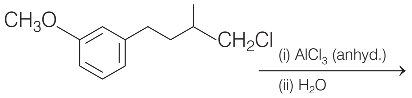
The reducing power of the metals increases in the order

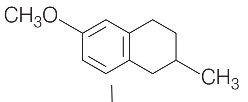
(a) Zn < Mg < Ni < Ca
(b) Ni < Zn < Mg < Ca
(c) Ca < Zn < Mg < Ni
(d) Ca < Mg < Zn < Ni

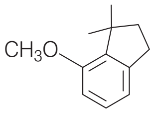
5 The total number of isomers for a square planar complex $[M(F)(Cl)(SCN)(NO_2)]$ is

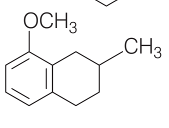
(a) 12 (b) 16 (c) 4 (d) 8

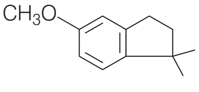
6 The major product of the following reaction is



(a) 

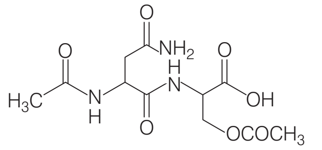
(b) 

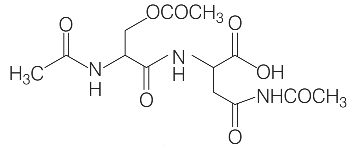
(c) 

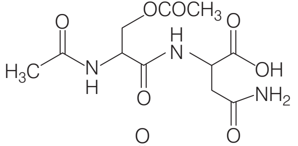
(d) 

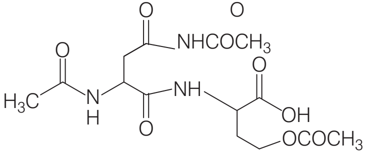
7 The correct structure of product '*P*' in the following reaction is

$Asn - Ser + \underset{\text{(Excess)}}{(CH_3CO)_2O} \xrightarrow{NEt_3} P$

(a) 

(b) 

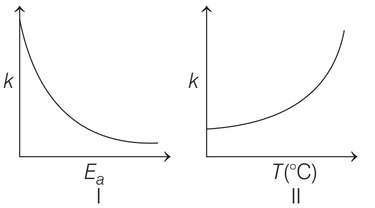
(c) 

(d) 

8 The metal used for making X-ray tube window is

(a) Na (b) Be (c) Mg (d) Ca

9 Consider the given plots for a reaction obeying Arrhenius equation (0°C < T < 300°C) : (k and E_a are rate constant and activation energy, respectively)



Choose the correct option.

(a) Both I and II are wrong
(b) Both I and II are correct
(c) I is wrong but II is right
(d) I is right but II is wrong

10 The values of $\frac{K_p}{K_C}$ for the following reactions at 300 K are, respectively (At 300 K, $RT = 24.62\,dm^3\ atm\ mol^{-1}$)

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(a) $1,\ 24.62\ dm^3\ atm\ mol^{-1},\ 606.0\ dm^6\ atm^2\ mol^{-2}$
(b) $1,\ 24.62\ dm^3\ atm\ mol^{-1},\ 1.65 \times 10^{-3}\ dm^{-6}\ atm^{-2}\ mol^2$
(c) $24.62\ dm^3\ atm\ mol^{-1},\ 606.0\ dm^6\ atm^{-2}\ mol^2,\ 1.65 \times 10^{-3}\ dm^{-6}\ atm^{-2}\ mol^2$
(d) $1,\ 4.1 \times 10^{-2}\ dm^{-3} atm^{-1}\ mol,\ 606\ dm^6\ atm^2\ mol^{-2}$

11 The type of hybridisation and number of lone pair(s) of electrons of Xe in $XeOF_4$, respectively, are

(a) sp^3d^2 and 1 (b) sp^3d and 2
(c) sp^3d and 1 (d) sp^3d^2 and 2

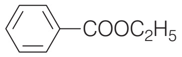
12 Liquids *A* and *B* form an ideal solution in the entire composition range. At 350 K, the vapour pressures of pure *A* and pure *B* are 7×10^3 Pa and 12×10^3 Pa, respectively. The composition of the vapour in equilibrium with a solution containing 40 mole percent of *A* at this temperature is

(a) $x_A = 0.76;\ x_B = 0.24$
(b) $x_A = 0.28;\ x_B = 0.72$
(c) $x_A = 0.4;\ x_B = 0.6$
(d) $x_A = 0.37;\ x_B = 0.63$

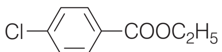
13 The total number of isotopes of hydrogen and number of radioactive isotopes among them, respectively, are

(a) 2 and 1 (b) 3 and 2
(c) 2 and 0 (d) 3 and 1

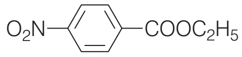
14 The decreasing order of ease of alkaline hydrolysis for the following esters is



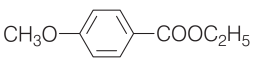
I



II



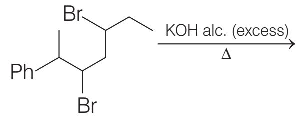
III

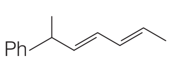


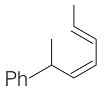
IV

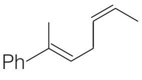
(a) III > II > IV > I (b) III > II > I > IV
(c) II > III > I > IV (d) IV > II > III > I

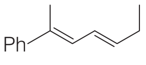
15 The major product of the following reaction is



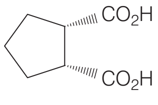
(a) 

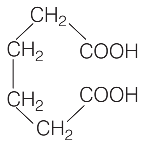
(b) 

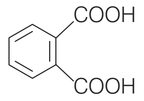
(c) 

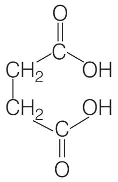
(d) 

16 Which dicarboxylic acid in presence of a dehydrating agent is least reactive to give an anhydride?

(a) 

(b) 

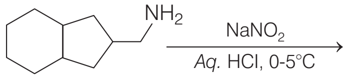
(c) 

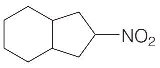
(d) 

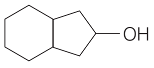
17 A process has $\Delta H = 200\,\text{J mol}^{-1}$ and $\Delta S = 40\,\text{JK}^{-1}\,\text{mol}^{-1}$. Out of the values given below, choose the minimum temperature above which the process will be spontaneous

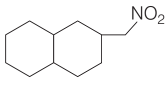
(a) 20 K (b) 4 K (c) 5 K (d) 12 K

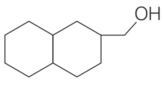
18 The major product formed in the reaction given below will be



(a) 

(b) 

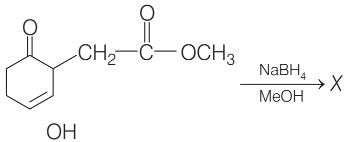
(c) 

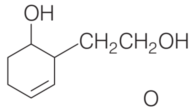
(d) 

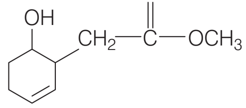
19 If dichloromethane (DCM) and water (H_2O) are used for differential extraction, which one of the following statements is correct?

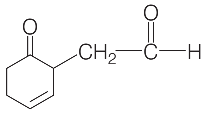
(a) DCM and H_2O would stay as lower and upper layer respectively in the S.F.
(b) DCM and H_2O would stay as upper and lower layer respectively in the separating funnel (S.F.)
(c) DCM and H_2O will be miscible clearly
(d) DCM and H_2O will make turbid/colloidal mixture

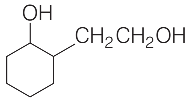
20 The major product '*X*' formed in the following reaction is



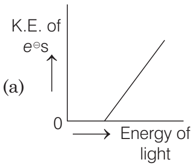
(a) 

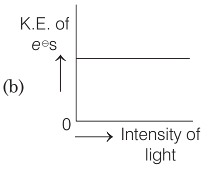
(b) 

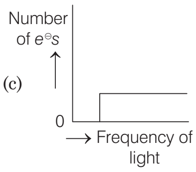
(c) 

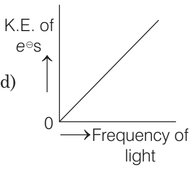
(d) 

21 Which of the graphs shown below does not represent the relationship between incident light and the electron ejected from metal surface?

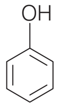
(a) 

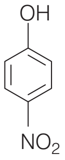
(b) 

(c) 

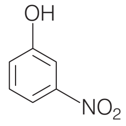
(d) 

22 The increasing order of the pK_a values of the following compounds is

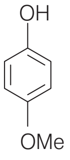

A



B



C



D

(a) $D < A < C < B$ (b) $B < C < A < D$
(c) $C < B < A < D$ (d) $B < C < D < A$

23 A mixture of 100 mmol of $Ca(OH)_2$ and 2 g of sodium sulphate was dissolved in water and the volume was made upto 100 mL.

The mass of calcium sulphate formed and the concentration of OH^- in resulting solution, respectively, are : (Molar mass of $Ca(OH)_2$, Na_2SO_4 and $CaSO_4$ are74, 143 and 136 g mol^{-1}, respectively; K_{sp} of $Ca(OH)_2$ is 5.5×10^{-6})

(a) 13.6 g, 0.28 mol L^{-1}
(b) 1.9 g, 0.28 mol L^{-1}
(c) 13.6 g, 0.14 mol L^{-1}
(d) 1.9 g, 0.14 mol L^{-1}

24 Wilkinson catalyst is

(a) $[(Et_3P)_3RhCl]$
(b) $[(Et_3P)_3IrCl](Et = C_2H_5)$
(c) $[(Ph_3P)_3RhCl]$
(d) $[(Ph_3P)_3IrCl]$

25 Two pi and half sigma bonds are present in

(a) O_2^+ (b) N_2
(c) N_2^+ (d) O_2

26 The effect of lanthanoid contraction in the lanthanoid series of elements by and large means

(a) increase in atomic radii and decrease in ionic radii
(b) decrease in both atomic and ionic radii
(c) increase in both atomic and ionic radii
(d) decrease in atomic radii and increase in ionic radii

27 The electronegativity of aluminium is similar to

(a) lithium (b) carbon
(c) beryllium (d) boron

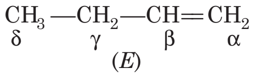
28 Which primitive unit cell has unequal edge lengths ($a \neq b \neq c$) and all axial angles different from 90°?

(a) Hexagonal (b) Monoclinic
(c) Tetragonal (d) Triclinic

29 Water filled in two glasses *A* and *B* have BOD values of 10 and 20, respectively. The correct statement regarding them, is

(a) *A* is more polluted than *B*
(b) *A* is suitable for drinking, wherease *B* is not
(c) Both *A* and *B* are suitable for drinking
(d) *B* is more polluted than *A*

30 Which hydrogen in compound (*E*) is easily replaceable during bromination reaction in presence of light?



$$\underset{\delta}{CH_3}-\underset{\gamma}{CH_2}-\underset{\beta}{CH}=\underset{\alpha}{CH_2}$$

(*E*)

(a) β-hydrogen
(b) δ-hydrogen
(c) γ-hydrogen
(d) α-hydrogen

ANSWERS

1 (b)	2 (c)	3 (a)	4 (b)	5 (a)	6 (d)	7 (a)	8 (b)	9 (b)	10 (b)
11 (a)	12 (b)	13 (d)	14 (b)	15 (d)	16 (b)	17 (c)	18 (*)	19 (a)	20 (b)
21 (d)	22 (b)	23 (b)	24 (c)	25 (c)	26 (b)	27 (c)	28 (d)	29 (d)	30 (c)

For Detailed Solutions
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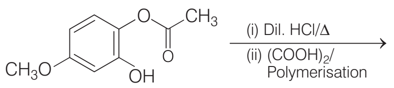
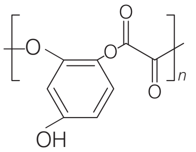
Or Scan :

10 January, Shift-II

1 The major product of the following reaction is



(a)


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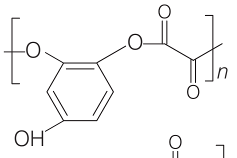

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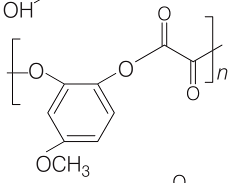
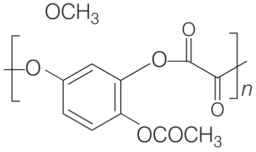
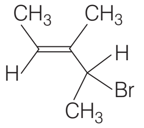


(d)


2 What is the IUPAC name of the following compound ?

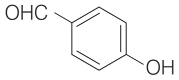


(a) 3-bromo-3-methyl-1,2-dimethylprop-1-ene
(b) 3-bromo-1,2-dimethylbut-1-ene
(c) 2-bromo-3-methylpent-3-ene
(d) 4-bromo-3-methylpent-2-ene

3 A compound of formula A_2B_3 has the hcp lattice. Which atom forms the hcp lattice and what fraction of tetrahedral voids is occupied by the other atoms ?

(a) hcp lattice- A, $\frac{2}{3}$ tetrahedral voids-B
(b) hcp lattice-A, $\frac{1}{3}$ tetrahedral voids-B
(c) hcp lattice-B, $\frac{1}{3}$ tetrahedral voids-A
(d) hcp lattice-B, $\frac{2}{3}$ tetrahedral voids-A

4 An aromatic compound 'A' having molecular formula $C_7H_6O_2$ on treating with aqueous ammonia and heating forms compound 'B'. The compound 'B' on reaction with molecular bromine and potassium hydroxide provides compound 'C' having molecular formula C_6H_7N. The structure of 'A' is

(a)


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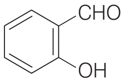

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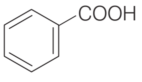

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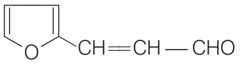


5 In the cell, $Pt(s)|H_2(g, 1\text{ bar})|HCl(aq)|AgCl(s)|Ag(s)|Pt(s)$ the cell potential is 0.92 V when a 10^{-6} molal HCl solution is used. The standard electrode potential of $(AgCl/Ag, Cl^-)$ electrode is

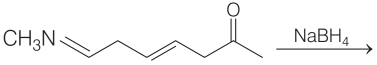
$$\left\{\text{Given, } \frac{2.303RT}{F} = 0.06\text{ V at } 298\text{ K}\right\}$$

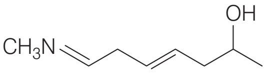
(a) 0.40 V (b) 0.20 V
(c) 0.94 V (d) 0.76 V

6 For an elementary chemical reaction, $A_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2A$, the expression for $\frac{d[A]}{dt}$ is

(a) $2k_1[A_2] - k_{-1}[A]^2$
(b) $k_1[A_2] - k_{-1}[A]^2$
(c) $2k_1[A_2] - 2k_{-1}[A]^2$
(d) $k_1[A_2] + k_{-1}[A]^2$

7 The major product of the following reaction is



(a)


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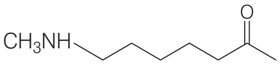

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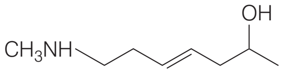

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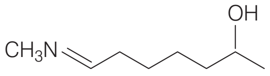


8 The reaction that is not involved in the ozone layer depletion mechanism in the stratosphere is

(a) $CH_4 + 2O_3 \longrightarrow 3CH_2=O + 3H_2O$
(b) $Cl\dot{O}(g) + O(g) \longrightarrow \dot{C}l(g) + O_2(g)$
(c) $HOCl(g) \xrightarrow{h\nu} \dot{O}H(g) + \dot{C}l(g)$
(d) $CF_2Cl_2(g) \xrightarrow{h\nu} \dot{C}l(g) + \dot{C}F_2Cl(g)$

9 The 71st electron of an element X with an atomic number of 71 enters into the orbital

(a) $4f$ (b) $6p$ (c) $5d$ (d) $6s$

10 The amount of sugar $(C_{12}H_{22}O_{11})$ required to prepare 2 L of its 0.1 M aqueous solution is

(a) 17.1 g (b) 68.4 g
(c) 136.8 g (d) 34.2 g

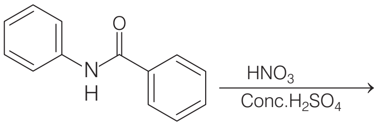
11 The pair that contains two P—H bonds in each of the oxoacids is

(a) $H_4P_2O_5$ and $H_4P_2O_6$
(b) H_3PO_3 and H_3PO_2
(c) $H_4P_2O_5$ and H_3PO_3
(d) H_3PO_2 and $H_4P_2O_5$

12 An ideal gas undergoes isothermal compression from 5 m^3 to 1 m^3 against a constant external pressure of 4 Nm^{-2}. Heat released in this process is used to increase the temperature of 1 mole of Al. If molar heat capacity of Al is 24 J $mol^{-1}K^{-1}$, the temperature of Al increases by

(a) $\frac{3}{2}$ K (b) 1 K (c) 2 K (d) $\frac{2}{3}$ K

13 What will be the major product in the following mononitration reaction ?



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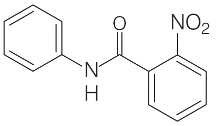

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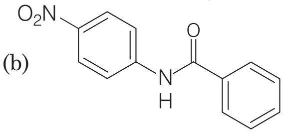

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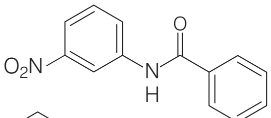

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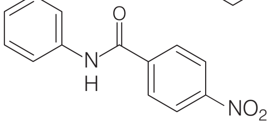


14 Haemoglobin and gold sol are examples of

(a) negatively and positively charged sols, respectively
(b) negatively charged sols
(c) positively charged sols
(d) positively and negatively charged sols, respectively

15 The process with negative entropy change is

(a) synthesis of ammonia from N_2 and H_2
(b) dissociation of $CaSO_4$(s) to CaO(s) and $SO_3(g)$
(c) dissolution of iodine in water
(d) sublimation of dry ice

16 5.1 g NH_4SH is introduced in 3.0 L evacuated flask at 327° C. 30% of the solid NH_4SH decomposed to NH_3 and H_2S as gases. The K_p of the reaction at 327° C is (R = 0.082 atm $mol^{-1}K^{-1}$, molar mass of S = 32 g mol^{-1}, molar mass of N = 14 g mol^{-1})

(a) 0.242×10^{-4} atm^2
(b) 0.242 atm^2
(c) 4.9×10^{-3} atm^2
(d) 1×10^{-4} atm^2

17 In the reaction of oxalate with permanganate in acidic medium, the number of electrons involved in producing one molecule of CO_2 is

(a) 2 (b) 5
(c) 1 (d) 10

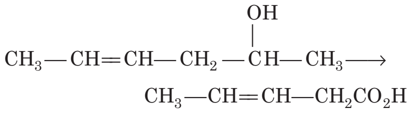
18 Among the following reactions of hydrogen with halogens, the one that requires a catalyst is

(a) $H_2 + Cl_2 \longrightarrow 2HCl$
(b) $H_2 + I_2 \longrightarrow 2HI$
(c) $H_2 + F_2 \longrightarrow 2HF$
(d) $H_2 + Br_2 \longrightarrow 2HBr$

19 Sodium metal on dissolution in liquid ammonia gives a deep blue solution due to the formation of

(a) sodium ammonia complex
(b) sodium ion-ammonia complex
(c) sodamide
(d) ammoniated electrons

20 Which is the most suitable reagent for the following transformation ?



$$CH_3-CH=CH-CH_2-\overset{OH}{\overset{|}{C}}H-CH_3 \longrightarrow CH_3-CH=CH-CH_2CO_2H$$

(a) Tollen's reagent
(b) I_2 / NaOH
(c) Alkaline $KMnO_4$
(d) CrO_2Cl_2 / CS_2

21 The correct match between item 'I' and item 'II' is

	Item 'I' (Compound)		Item 'II' (Reagent)
(A)	Lysine	(P)	1-naphthol
(B)	Furfural	(Q)	Ninhydrin
(C)	Benzyl alcohol	(R)	$KMnO_4$
(D)	Styrene	(S)	Ceric ammonium nitrate

Codes

	A	B	C	D
(a)	Q	R	S	P
(b)	R	P	Q	S
(c)	Q	P	S	R
(d)	Q	P	R	S

22 The difference in the number of unpaired electrons of a metal ion in its high-spin and low-spin octahedral complexes is two. The metal ion is

(a) Mn^{2+} (b) Fe^{2+}
(c) Ni^{2+} (d) Co^{2+}

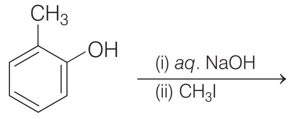
23 The ground state energy of hydrogen atom is -13.6 eV. The energy of second excited state of He^+ ion in eV is

(a) -54.4 (b) -3.4
(c) -6.04 (d) -27.2

24 A reaction of cobalt (III) chloride and ethylene diamine in a 1 : 2 mole ratio generates two isomeric products *A* (violet coloured) and *B* (green coloured). *A* can show optical activity, but *B* is optically inactive. What type of isomers does *A* and *B* represent ?

(a) Ionisation isomers
(b) Coordination isomers
(c) Geometrical isomers
(d) Linkage isomers

25 The major product of the following reaction is



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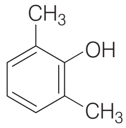

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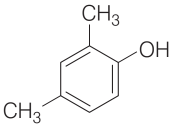

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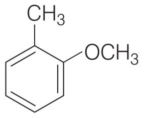

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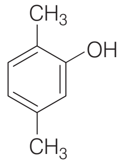
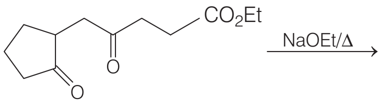
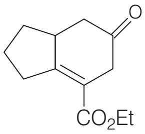


26 The major product obtained in the following reaction is



(a)


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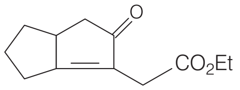

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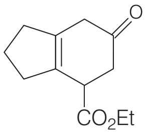

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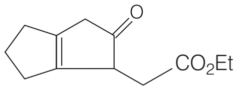

27 The electrolytes usually used in the electroplating of gold and silver, respectively, are

(a) $[Au(OH)_4]^-$ and $[Ag(OH)_2]^-$
(b) $[Au(NH_3)_2]^+$ and $[Ag(CN)_2]^-$
(c) $[Au(CN)_2]^-$ and $[Ag(CN)_2]^-$
(d) $[Au(CN)_2]^-$ and $[AgCl_2]^-$

28 Which of the following tests cannot be used for identifying amino acids ?

(a) Barfoed test (b) Ninhydrin test
(c) Xanthoproteic test (d) Biuret test

29 The number of 2-centre-2-electron and 3-centre-2-electron bonds in B_2H_6, respectively, are

(a) 4 and 2 (b) 2 and 4
(c) 2 and 2 (d) 2 and 1

30 Elevation in the boiling point for 1 molal solution of glucose is 2 K . The depression in the freezing point for 2 molal solution of glucose in the same solvent is 2 K. The relation between K_b and K_f is

(a) $K_b = 1.5\ K_f$ (b) $K_b = 0.5\ K_f$
(c) $K_b = K_f$ (d) $K_b = 2K_f$

ANSWERS

1. (c)	2. (d)	3. (c)	4. (c)	5. (b)	6. (c)	7. (c)	8. (a)	9. (c)	10. (b)
11. (d)	12. (d)	13. (b)	14. (d)	15. (a)	16. (b)	17. (c)	18. (b)	19. (d)	20. (b)
21. (c)	22. (d)	23. (c)	24. (c)	25. (c)	26. (b)	27. (c)	28. (a)	29. (a)	30. (d)

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11 January, Shift-I

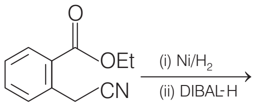
1 An example of solid sol is

(a) gem stones (b) hair cream
(c) butter (d) paint

2 NaH is an example of

(a) metallic hydride
(b) electron-rich hydride
(c) saline hydride
(d) molecular hydride

3 The major product of the following reaction is



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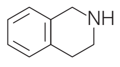

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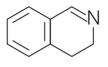

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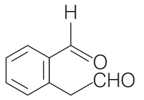

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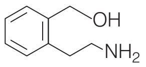
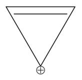


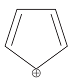
4 The concentration of dissolved oxygen (DO) in cold water can go upto

(a) 14 ppm (b) 10 ppm
(c) 8 ppm (d) 16 ppm

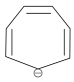
5 Which compound(s) out of the following is/are not aromatic?



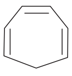
(*A*)



(*B*)



(*C*)



(*D*)

(a) (*B*), (*C*) and (*D*) (b) (*C*) and (*D*)
(c) (*B*) (d) (*A*) and (*C*)

6 An organic compound is estimated through Dumas method and was found to evolved 6 moles of CO_2, 4 moles of H_2O and 1 mole of nitrogen gas. The formula of the compound is

(a) C_6H_8N (b) $C_{12}H_8N$
(c) $C_{12}H_8N_2$ (d) $C_6H_8N_2$

7 Match the metals (Column I) with the coordination compound(s)/enzyme(s) (Column II).

Column I	Column II
(A) Co	(i) Wilkinson catalyst
(B) Zn	(ii) Chlorophyll
(C) Rh	(iii) Vitamin B_{12}
(D) Mg	(iv) Carbonic anhydrase

	A	B	C	D
(a)	(i)	(ii)	(iii)	(iv)
(b)	(iv)	(iii)	(i)	(ii)
(c)	(iii)	(iv)	(i)	(ii)
(d)	(ii)	(i)	(iv)	(iii)

8 A 10 mg effervescent tablet containing sodium bicarbonate and oxalic acid releases 0.25 mL of CO_2 at $T = 298.15$ K and $p = 1$ bar. If molar volume of CO_2 is 25.0 L under such condition, what is the percentage of sodium bicarbonate in each tablet? [Molar mass of $NaHCO_3$ = 84 g mol^{-1}]

(a) 8.4 (b) 0.84
(c) 16.8 (d) 33.6

9 The correct statements among (a) to (d) regarding H_2 as a fuel are :

I. It produces less pollutants than petrol.
II. A cylinder of compressed dihydrogen weights ~ 30 times more than a petrol tank producing the same amount of energy.
III. Dihydrogen is stored in tanks of metal alloys like $NaNi_5$.
IV. On combustion, values of energy released per gram of liquid dihydrogen and LPG are 50 and 142 kJ, respectively.

(a) I, II and III only (b) II, III and IV only
(c) II and IV only (d) I and III only

10 Consider the reaction,

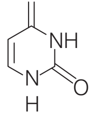
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

The equilibrium constant of the above reaction is K_p. If pure ammonia is left to dissociate, the partial pressure of ammonia at equilibrium is given by (Assume that $p_{NH_3} << p_{total}$ at equilibrium)

(a) $\dfrac{3^{3/2}K_p^{1/2}P^2}{4}$ (b) $\dfrac{3^{3/2}K_p^{1/2}P^2}{16}$

(c) $\dfrac{K_p{}^{1/2}P^2}{16}$ (d) $\dfrac{K_p{}^{1/2}P^2}{4}$

11 Among the following compounds, which one is found in RNA?

(a)


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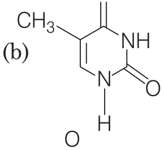

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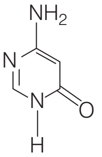
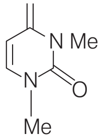
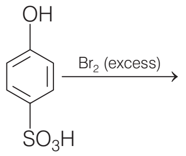


(d)


12 The major product of the following reaction is



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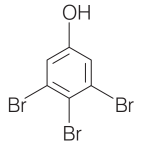

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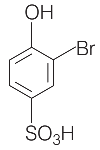

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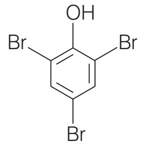

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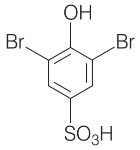


13 Heat treatment of muscular pain involves radiation of wavelength of about 900 nm. Which spectral line of H-atom is suitable for this purpose? [$R_H = 1\times10^5$ cm^{-1}, $h = 6.6\times10^{-34}$ Js, $c = 3\times10^8$ ms^{-1}]

(a) Paschen, 5 → 3 (b) Paschen, ∞ → 3
(c) Lyman, ∞ → 1 (d) Balmer, ∞ → 2

14 The freezing point of a diluted milk sample is found to be –0.2° C, while it should have been –0.5°C for pure milk. How much water has been added to pure milk to make the diluted sample?

(a) 2 cups of water to 3 cups of pure milk
(b) 1 cup of water to 3 cups of pure milk
(c) 3 cups of water to 2 cups of pure milk
(d) 1 cup of water to 2 cups of pure milk

15 The correct order of the atomic radii of C, Cs, Al and S is

(a) C < S < Al < Cs (b) C < S < Cs < Al
(c) S < C < Cs < Al (d) S < C < Al < Cs

16 The amphoteric hydroxide is

(a) $Be(OH)_2$ (b) $Ca(OH)_2$
(c) $Sr(OH)_2$ (d) $Mg(OH)_2$

17 The correct match between items I and II is

Item - I (Mixture)	Item II (Separation method)
A. H_2O : Sugar	P. Sublimation
B. H_2O : Aniline	Q. Recrystallisation
C. H_2O : Toluene	R. Steam distillation
	S. Differential extraction

(a) (A) → (Q); (B) → (R); (C) → (S)
(b) (A) → (Q); (B) → (R); (C) → (P)
(c) (A) → (S); (B) → (R); (C) → (P)
(d) (A) → (R); (B) → (P); (C) → (S)

18 Match the ores (Column A) with the metals (Column B).

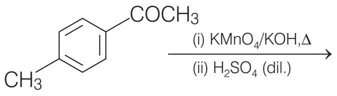
Column A	Column B
Ores	**Metals**
A. Siderite	P. Zinc
B. Kaolinite	Q. Copper
C. Malachite	R. Iron
D. Calamine	S. Aluminium

(a) A - P; B- Q; C - R; D- S
(b) A - R; B- S; C - P; D- Q
(c) A - Q; B- R; C - S; D- P
(d) A - R; B- S; C - Q; D- P

19 The element that usually does not show variable oxidation states is

(a) Sc (b) Cu
(c) Ti (d) V

20 The major product of the following reaction is



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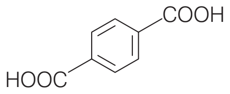

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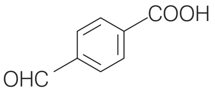

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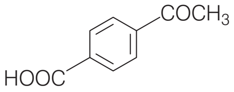

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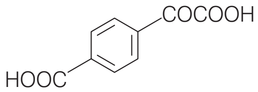


21 The correct match between item (I) and item (II) is

	Item - I		Item - II
(A)	Norethindrone	(P)	Antibiotic
(B)	Ofloxacin	(Q)	Antifertility
(C)	Equanil	(R)	Hypertension
		(S)	Analgesics

(a) (A) → (Q); (B) → (R); (C) → (S)
(b) (A) → (Q); (B) → (P); (C) → (R)
(c) (A) → (R); (B) → (P); (C) → (S)
(d) (A) → (R); (B) → (P); (C) → (R)

22 Peroxyacetyl nitrate (PAN), an eye irritant is produced by

(a) organic waste
(b) acid rain
(c) classical smog
(d) photochemical smog

23 A solid having density of $9\times10^3\ \text{kg m}^{-3}$ forms face centred cubic crystals of edge length $200\sqrt{2}$ pm. What is the molar mass of the solid? [Avogadro constant $= 6\times10^{23}\ \text{mol}^{-1}$, $\pi = 3$]

(a) $0.03050\ \text{kg mol}^{-1}$
(b) $0.4320\ \text{kg mol}^{-1}$
(c) $0.0432\ \text{kg mol}^{-1}$
(d) $0.0216\ \text{kg mol}^{-1}$

24 The chloride that cannot get hydrolysed is

(a) $SnCl_4$ (b) CCl_4
(c) $PbCl_4$ (d) $SiCl_4$

25 For the chemical reaction, $X \rightleftharpoons Y$, the standard reaction Gibbs energy depends on temperature T (in K) as

$$\Delta_r G^\circ\ (\text{in kJ mol}^{-1}) = 120 - \frac{3}{8}T$$

The major component of the reaction mixture at T is

(a) Y if $T = 280$ K (b) X if $T = 350$ K
(c) X if $T = 315$ K (d) Y if $T = 300$ K

26 Two blocks of the same metal having same mass and at temperature T_1 and T_2 respectively, are brought in contact with each other and allowed to attain thermal equilibrium at constant pressure. The change in entropy, ΔS, for this process is

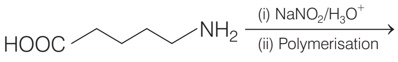
(a) $^2C_p \ln\left[\dfrac{(T_1+T_2)^{\frac{1}{2}}}{T_1T_2}\right]$

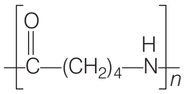
(b) $^2C_p \ln\left[\dfrac{T_1+T_2}{4T_1T_2}\right]$

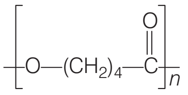
(c) $C_p \ln\left[\dfrac{(T_1+T_2)^2}{4T_1T_2}\right]$

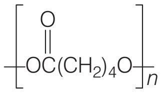
(d) $^2C_p \ln\left[\dfrac{T_1+T_2}{2T_1T_2}\right]$

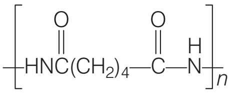
27 The polymer obtained from the following reaction is:



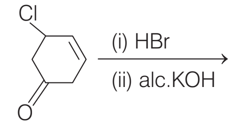
(a)

$\left[\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{H}{N} \right]_n$

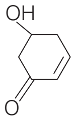
(b)

$\left[O-(CH_2)_4-\overset{O}{\overset{\|}{C}} \right]_n$

(c)

$\left[O\overset{O}{\overset{\|}{C}}(CH_2)_4O \right]_n$

(d)

$\left[HN\overset{O}{\overset{\|}{C}}(CH_2)_4-\overset{O}{\overset{\|}{C}}-\overset{H}{N} \right]_n$

28 The major product of the following reaction is



(a)


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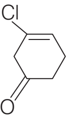

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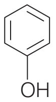

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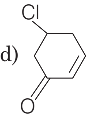

29 If a reaction follows the Arrhenius equation, the plot $\ln k$ *vs* $1/(RT)$ gives straight line with a gradient $(-y)$ unit. The energy required to activate the reactant is

(a) $\dfrac{y}{R}$ unit (b) $-y$ unit
(c) yR unit (d) y unit

30 For the cell, $Zn(s)\,|\,Zn^{2+}(aq)\,||\,M^{x+}(aq)\,|\,M(s)$, different half cells and their standard electrode potentials are given below.

$M^{x+}(aq)/$ $M(s)$	$Au^{3+}(aq)$ / $Au(s)$	$Ag^{+}(aq)/$ $Ag(s)$	$Fe^{3+}(aq)/$ $Fe^{2+}(aq)$	$Fe^{2+}(aq)$ /$Fe(s)$
$E^\circ_{M^{x+}/M}/V$	1.40	0.80	0.77	– 0.44

If $E^\circ_{Zn^{2+}/Zn} = -0.76$ V, which cathode will give a maximum value of E°_{cell} per electron transferred?

(a) $\dfrac{Ag^+}{Ag}$ (b) $\dfrac{Fe^{2+}}{Fe}$
(c) $\dfrac{Au^{3+}}{Au}$ (d) $\dfrac{Fe^{3+}}{Fe^{2+}}$

ANSWERS

1 (a)	2 (c)	3 (b)	4 (b)	5 (a)	6 (d)	7 (c)	8 (a)	9 (a)	10 (b)
11 (a)	12 (c)	13 (b)	14 (c)	15 (a)	16 (a)	17 (a)	18 (d)	19 (a)	20 (a)
21 (b)	22 (d)	23 (a)	24 (b)	25 (c)	26 (c)	27 (b)	28 (c)	29 (d)	30 (a)

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11 January, Shift-II

1 The relative stability of + 1oxidation state of group 13 elements follows the order

(a) Al < Ga < Tl < In
(b) Al < Ga < In < Tl
(c) Tl < In < Ga < Al
(d) Ga < Al < In < Tl

2 The hydride that is not electron deficient is

(a) AlH_3 (b) B_2H_6
(c) SiH_4 (d) GaH_3

3 The higher concentration of which gas in air can cause stiffness of flower buds?

(a) SO_2 (b) CO
(c) CO_2 (d) NO_2

4 The correct match between Item I and Item II is

Item I		Item II	
A.	Ester test	P.	Tyr
B.	Carbylamine test	Q.	Asp
C.	Phthalein dye test	R.	Ser
		S.	Lys

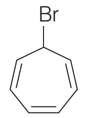
(a) A → Q; B → S; C → R
(b) A → R, B → Q; C → P
(c) A → R; B → S; C → Q
(d) A → Q; B → S; C → P

5 The correct match between Item I and Item II is

Item I		Item II	
A.	Allosteric effect	P.	Molecule binding to the active site of enzyme.
B.	Competitive inhibitor	Q.	Molecule crucial for communication in the body.
C.	Receptor	R.	Molecule binding to a site other than the active site of enzyme.
D.	Poison	S.	Molecule binding to the enzyme covalently.

(a) A → P; B → R; C → S; D → Q
(b) A → P, B → R; C → Q; D → S
(c) A → R; B → P; C → S; D → Q
(d) A → R; B → P; C → Q; D → S

6 Which of the following compounds will produce a precipitate with $AgNO_3$?

(a)


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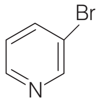

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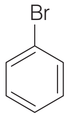

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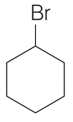


7 The coordination number of Th in $K_4[Th(C_2O_4)_4(OH_2)_2]$ is ($C_2O_4^{2-}$ = Oxalato)

(a) 14 (b) 10
(c) 8 (d) 6

8 The reaction, $2X \rightarrow B$ is a zeroth order reaction. If the initial concentration of X is 0.2 M, the half-life is 6 h. When the initial concentration of X is 0.5 M, the time required to reach its final concentration of 0.2 M will be

(a) 7.2 h (b) 18.0 h (c) 12.0 h (d) 9.0 h

9

$$\underline{A} \xrightarrow{4\,KOH,\,O_2} \underset{\text{(Green)}}{2\underline{B}} + 2H_2O$$

$$3\underline{B} \xrightarrow{4\,HCl} \underset{\text{(Purple)}}{2\underline{C}} + MnO_2 + 2H_2O$$

$$2\underline{C} \xrightarrow{H_2O,\,KI} 2\underline{A} + 2KOH + \underline{D}$$

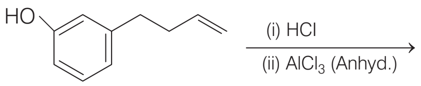
In the above sequence of reactions, $\underline{A}$ and $\underline{D}$, respectively, are

(a) KI and $KMnO_4$
(b) MnO_2 and KIO_3
(c) KI and K_2MnO_4
(d) KIO_3 and MnO_2

10 25 mL of the given HCl solution requires 30 mL of 0.1 M sodium carbonate solution. What is the volume of this HCl solution required to titrate 30 mL of 0.2 M aqueous NaOH solution?

(a) 75 mL (b) 25 mL
(c) 12.5 mL (d) 50 mL

11 The major product of the following reaction is



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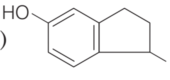

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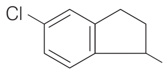

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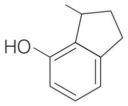

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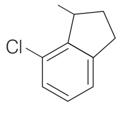
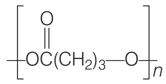
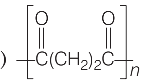


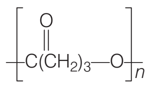
12 The homopolymer formed from 4-hydroxybutanoic acid is

(a)


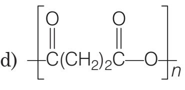
$\left[-O\overset{\overset{O}{\|}}{C}(CH_2)_3-O-\right]_n$

(b)


$\left[-\overset{\overset{O}{\|}}{C}(CH_2)_2\overset{\overset{O}{\|}}{C}-\right]_n$

(c)


$\left[-\overset{\overset{O}{\|}}{C}(CH_2)_3-O-\right]_n$

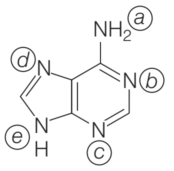
(d)


$\left[-\overset{\overset{O}{\|}}{C}(CH_2)_2\overset{\overset{O}{\|}}{C}-O-\right]_n$

13 Among the colloids cheese (*C*), milk (*M*) and smoke (*S*), the correct combination of the dispersed phase and dispersion medium, respectively is

(a) *C* : liquid in solid; *M* : liquid in liquid; *S* : solid in gas
(b) *C* : solid in liquid; *M* : liquid in liquid; *S* : gas in solid
(c) *C* : liquid in solid; *M* : liquid in solid; *S* : solid in gas
(d) *C* : solid in liquid; *M* : solid in liquid; *S* : solid in gas

14 In the following compound,



the favourable site/s for protonation is/are

(a) (*a*) and (*e*) (b) (*b*), (*c*) and (*d*)
(c) (*a*) and (*d*) (d) (*a*)

15 Given the equilibrium constant (K_C) of the reaction :

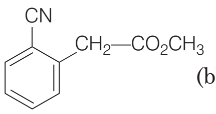
$$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$$

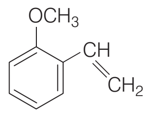
is 10×10^{15}, calculate the E°_{cell} of this reaction at 298 K.

$$\left[2.303\,\frac{RT}{F} \text{ at } 298\text{ K} = 0.059\text{ V}\right]$$

(a) 0.4736 V
(b) 0.04736 mV
(c) 0.4736 mV
(d) 0.04736 V

16 Which of the following compounds reacts with ethyl magnesium bromide and also decolourises bromine water solution

(a)


(b)


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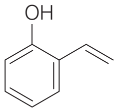

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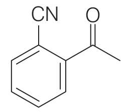
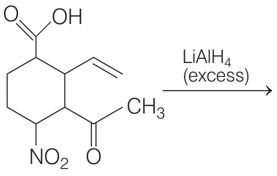
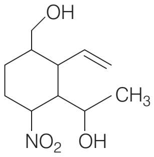
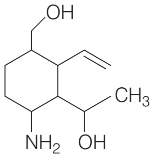
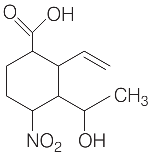


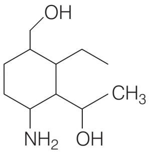
17 The major product obtained in the following reaction is



(a) 

(b) 

(c) 

(d) 

18 The reaction, $MgO(s) + C(s) \rightarrow Mg(s) + CO(g)$, for which $\Delta_r H^\circ = + 491.1 \text{ kJ mol}^{-1}$ and $\Delta_r S^\circ = 198.0 \text{ JK}^{-1}\text{mol}^{-1}$, is not feasible at 298 K. Temperature above which reaction will be feasible is

(a) 2040.5 K (b) 1890.0 K
(c) 2380.5 K (d) 2480.3 K

19 Taj Mahal is being slowly disfigured and discoloured. This is primarily due to

(a) water pollution
(b) soil pollution
(c) global warming
(d) acid rain

20 The standard reaction Gibbs energy for a chemical reaction at an absolute temperature T is given by,

$\Delta_r G^\circ = A - BT$

Where A and B are non-zero constants.

Which of the following is true about this reaction?

(a) Endothermic if, $A < 0$ and $B > 0$
(b) Exothermic if, $B < 0$
(c) Exothermic if, $A > 0$ and $B < 0$
(d) Endothermic if, $A > 0$

21 The correct option with respect to the Pauling electronegativity values of the elements is

(a) $P > S$ (b) $Si < Al$
(c) $Te > Se$ (d) $Ga < Ge$

22 The de-Broglie wavelength (λ) associated with a photoelectron varies with the frequency (ν) of the incident radiation as, [ν_0 is threshold frequency]

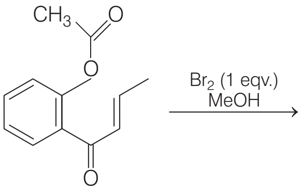
(a) $\lambda \propto \dfrac{1}{(\nu - \nu_0)^{\frac{1}{4}}}$ (b) $\lambda \propto \dfrac{1}{(\nu - \nu_0)^{\frac{3}{2}}}$

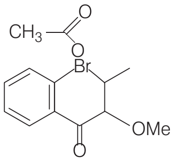
(c) $\lambda \propto \dfrac{1}{(\nu - \nu_0)}$ (d) $\lambda \propto \dfrac{1}{(\nu - \nu_0)^{\frac{1}{2}}}$

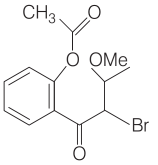
23 A compound '*X*' on treatment with Br_2 / NaOH, provided C_3H_9N, which gives positive carbylamine test. Compound '*X*' is

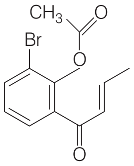
(a) $CH_3COCH_2NHCH_3$
(b) $CH_3CH_2CH_2CONH_2$
(c) $CH_3CON(CH_3)_2$
(d) $CH_3CH_2COCH_2NH_2$

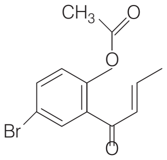
24 The major product obtained in the following conversion is



(a) 

(b) 

(c) 

(d) 

25 The reaction that does not define calcination is

(a) $Fe_2O_3 \cdot XH_2O \xrightarrow{\Delta} Fe_2O_3 + XH_2O$

(b) $ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$

(c) $CaCO_3 \cdot MgCO_3 \xrightarrow{\Delta} CaO + MgO + 2CO_2$

(d) $2Cu_2S + 3O_2 \xrightarrow{\Delta} 2Cu_2O + 2SO_2$

26 K_2HgI_4 is 40% ionised in aqueous solution. The value of its van't Hoff factor (i) is

(a) 1.6 (b) 1.8
(c) 2.2 (d) 2.0

27 The number of bridging CO ligand(s) and Co—Co bond(s) in $Co_2(CO)_8$, respectively are

(a) 2 and 0 (b) 0 and 2
(c) 4 and 0 (d) 2 and 1

28 For the equilibrium,

$2H_2O \rightleftharpoons H_3O^+ + OH^-$, the value of ΔG° at 298 K is approximately

(a) -80 kJ mol^{-1}
(b) 100 kJ mol^{-1}
(c) 80 kJ mol^{-1}
(d) -100 kJ mol^{-1}

29 Match the following items in Column I with the corresponding items in Column II.

	Column I		Column II
(i)	$Na_2CO_3 \cdot 10H_2O$	A.	Portland cement ingredient
(ii)	$Mg(HCO_3)_2$	B.	Castner-Kellner process
(iii)	NaOH	C.	Solvay process
(iv)	$Ca_3Al_2O_6$	D.	Temporary hardness

(a) (i) - (D); (ii) - (A); (iii) - (B); (iv) - (C)
(b) (i) - (B); (ii) - (C); (iii) - (A); (iv) - (D)
(c) (i) - (C); (ii) - (B); (iii) - (D); (iv) - (A)
(d) (i) - (C); (ii) - (D); (iii) - (B); (iv) - (A)

30 The radius of the largest sphere which fits properly at the centre of the edge of a body centred cubic unit cell is (Edge length is represented by 'a')

(a) 0.134 a (b) 0.027 a
(c) 0.047 a (d) 0.067 a

ANSWERS

1. *(b)*	2. *(c)*	3. *(a)*	4. *(d)*	5. *(d)*	6. *(a)*	7. *(b)*	8. *(b)*	9. *(b)*	10. *(b)*
11. *(a)*	12. *(c)*	13. *(a)*	14. *(b)*	15. *(a)*	16. *(c)*	17. *(b)*	18. *(d)*	19. *(d)*	20. *(d)*
21. *(d)*	22. *(d)*	23. *(b)*	24. *(b)*	25. *(d)*	26. *(b)*	27. *(d)*	28. *(c)*	29. *(d)*	30. *(d)*

For Detailed Solutions
Visit : http://tinyurl.com/yy76oka5
Or Scan :

12 January, Shift-I

1 What is the work function of the metal, if the light of wavelength 4000 Å generates photoelectron of velocity 6×10^5 ms^{-1} from it?

(Mass of electron = 9×10^{-31} kg

Velocity of light = 3×10^8 ms^{-1}

Planck's constant = 6.626×10^{-34} Js

Charge of electron = 1.6×10^{-19} JeV^{-1})

(a) 4.0 eV (b) 2.1 eV
(c) 0.9 eV (d) 3.1 eV

2 Given, Gas : H_2, CH_4, CO_2, SO_2

Critical temperature/K 33 190 304 630

On the basis of data given above, predict which of the following gases shows least adsorption on a definite amount of charcoal?

(a) CH_4 (b) SO_2
(c) CO_2 (d) H_2

3 $Mn_2(CO)_{10}$ is an organometallic compound due to the presence of

(a) Mn—C bond
(b) Mn—O bond
(c) C—O bond
(d) Mn—Mn

4 The hardness of a water sample (in terms of equivalents of $CaCO_3$) containing 10^{-3} M $CaSO_4$ is

(Molar mass of $CaSO_4$ = 136 g mol^{-1})

(a) 100 ppm (b) 10 ppm
(c) 50 ppm (d) 90 ppm

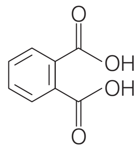
5 A metal on combustion in excess air forms X. X upon hydrolysis with water yields H_2O_2 and O_2 along with another product. The metal is

(a) Li (b) Mg
(c) Rb (d) Na

6 Among the following compounds, most basic amino acid is

(a) serine (b) asparagine
(c) lysine (d) histidine

7 Among the following four aromatic compounds, which one will have the lowest melting point?

(a)


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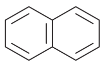

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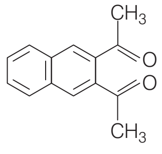

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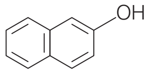


8 The correct order for acid strength of compounds

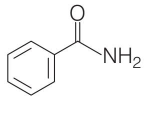
CH ≡ CH, CH_3—C ≡ CH and CH_2 = CH_2 is as follows :

(a) $CH_3—C\equiv CH > CH_2=CH_2 > HC\equiv CH$
(b) $CH_3—C\equiv CH > CH\equiv CH > CH_2=CH_2$
(c) $HC\equiv CH > CH_3—C\equiv CH > CH_2=CH_2$
(d) $CH\equiv CH > CH_2=CH_2 > CH_3—C\equiv CH$

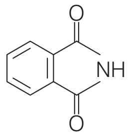
9 Decomposition of X exhibits a rate constant of 0.05 μg/year. How many years are required for the decomposition of 5 μg of X into 2.5 μg?

(a) 20 (b) 25
(c) 40 (d) 50

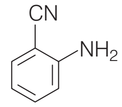
10 The increasing order of reactivity of the following compounds towards reaction with alkyl halides directly is



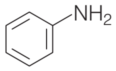
(A)



(B)



(C)



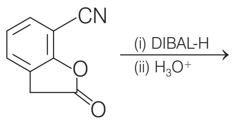
(D)

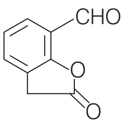
(a) (A) < (C) < (D) < (B)
(b) (B) < (A) < (C) < (D)
(c) (B) < (A) < (D) < (C)
(d) (A) < (B) < (C) < (D)

11 The element with Z = 120 (not yet discovered) will be an/a

(a) transition metal
(b) inner-transition metal
(c) alkaline earth metal
(d) alkali metal

12 The major product of the following reaction is



(a)


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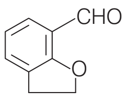

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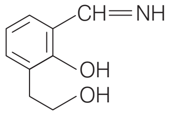

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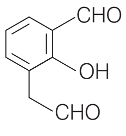
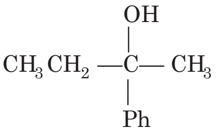


13

$CH_3CH_2—\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle Ph}{|}}{C}}—CH_3$ cannot be prepared by

(a) $CH_3CH_2COCH_3$ + PhMgX
(b) $PhCOCH_3$ + CH_3CH_2MgX
(c) $PhCOCH_2CH_3$ + CH_3MgX
(d) HCHO + PhCH(CH_3) CH_2MgX

14 The standard electrode potential $E^\ominus$ and its temperature coefficient $\left(\frac{dE^\ominus}{dT}\right)$ for a cell are 2V and -5×10^{-4} VK^{-1} at 300 K respectively. The cell reaction is

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

The standard reaction enthalpy ($\Delta_r H^\ominus$) at 300 K in kJ mol^{-1} is,

[Use, R = 8 JK^{-1} mol^{-1} and F = 96,000 C mol^{-1}]

(a) – 412.8 (b) – 384.0
(c) 206.4 (d) 192.0

15 In the following reaction,

$$\text{Aldehyde} + \text{Alcohol} \xrightarrow{HCl} \text{Acetal}$$

Aldehyde	Alcohol
HCHO	^{t}BuOH
CH_3CHO	MeOH

The best combination is

(a) CH_3CHO and MeOH
(b) CH_3CHO and ^{t}BuOH
(c) HCHO and MeOH
(d) HCHO and ^{t}BuOH

16 The molecule that has minimum/no role in the formation of photochemical smog, is

(a) N_2 (b) $CH_2 = O$
(c) NO (d) O_3

17 Poly-β-hydroxybutyrate-Co-β-hydroxyvalerate (PHBV) is a copolymer of ......

(a) 3-hydroxybutanoic acid and 2-hydroxypentanoic acid
(b) 2-hydroxybutanoic acid and 3-hydroxypentanoic acid
(c) 3-hydroxybutanoic acid and 4-hydroxypentanoic acid
(d) 3-hydroxybutanoic acid and 3-hydroxypentanoic acid

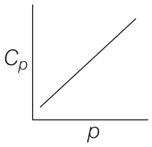
18 In the Hall-Heroult process, aluminium is formed at the cathode. The cathode is made out of

(a) platinum
(b) carbon
(c) pure aluminium
(d) copper

19 Iodine reacts with concentrated HNO_3 to yield Y along with other products. The oxidation state of iodine in Y, is

(a) 1 (b) 3
(c) 7 (d) 5

20 For a diatomic ideal gas in a closed system, which of the following plots does not correctly describe the relation between various thermodynamic quantities?

(a)


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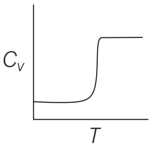

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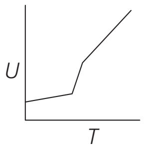

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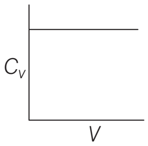


21 Two solids dissociate as follows:

$$A(s) \rightleftharpoons B(g) + C(g);\ K_{p_1} = x\ \text{atm}^2$$
$$D(s) \rightleftharpoons C(g) + E(g);\ K_{p_2} = y\ \text{atm}^2$$

The total pressure when both the solids dissociate simultaneously is

(a) $\sqrt{x+y}$ atm (b) $x^2 + y^2$ atm
(c) $(x+y)$ atm (d) $2(\sqrt{x+y})$ atm

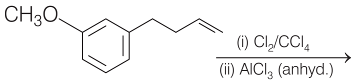
22 The metal d-orbitals that are directly facing the ligands in $K_3[Co(CN)_6]$ are

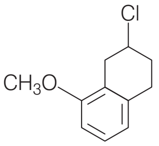
(a) d_{xz}, d_{yz} and d_{z^2}
(b) $d_{x^2-y^2}$ and d_{z^2}
(c) d_{xy}, d_{xz} and d_{yz}
(d) d_{xz} and $d_{x^2-y^2}$

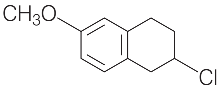
23 Water samples with BOD values of 4 ppm and 18 ppm, respectively, are

(a) clean and clean
(b) highly polluted and clean
(c) highly polluted and highly polluted
(d) clean and highly polluted

24 The major product of the following reaction is



(a)


(c)


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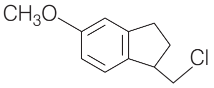
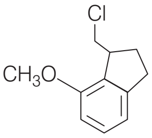


(d)


25 50 mL of 0.5 M oxalic acid is needed to neutralise 25 mL of sodium hydroxide solution. The amount of NaOH in 50 mL of the given sodium hydroxide solution is

(a) 40 g (b) 80 g
(c) 20 g (d) 10 g

26 Freezing point of a 4% aqueous solution of X is equal to freezing point of 12% aqueous solution of Y. If molecular weight of X is A, then molecular weight of Y is

(a) 4A (b) 2A
(c) 3A (d) A

27 The pair of metal ions that can given a spin-only magnetic moment of 3.9 BM for the complex $[M(H_2O)_6]Cl_2$, is

(a) Co^{2+} and Fe^{2+}
(b) Cr^{2+} and Mn^{2+}
(c) V^{2+} and Co^{2+}
(d) V^{2+} and Fe^{2+}

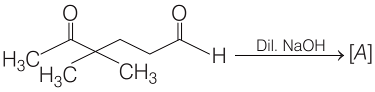
28 In a chemical reaction, $A + 2B \overset{K}{\rightleftharpoons} 2C + D$, the initial concentration of B was 1.5 times of the concentration of A, but the equilibrium concentrations of A and B were found to be equal. The equilibrium constant (K) for the aforesaid chemical reaction is

(a) $\frac{1}{4}$ (b) 16
(c) 1 (d) 4

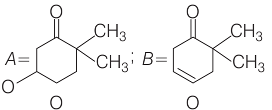
29 The volume of gas A is twice than that of gas B. The compressibility factor of gas A is thrice than that of gas B at same temperature. The pressures of the gases for equal number of moles are

(a) $p_A = 2p_B$ (b) $2p_A = 3p_B$
(c) $p_A = 3p_B$ (d) $3p_A = 2p_B$

30 In the following reactions, products A and B are



$$[A] \xrightarrow[\Delta]{H_3O^+} [B]$$

(a)


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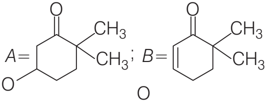

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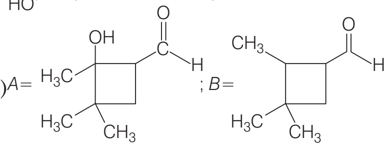

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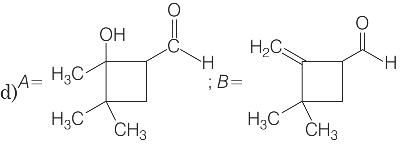


ANSWERS

1. *(b)*	2. *(d)*	3. *(a)*	4. *(a)*	5. *(c)*	6. *(c)*	7. *(b)*	8. *(c)*	9. *(d)*	10. *(b)*
11. *(c)*	12. *(d)*	13. *(d)*	14. *(a)*	15. *(c)*	16. *(a)*	17. *(d)*	18. *(b)*	19. *(d)*	20. *(a)*
21. *(d)*	22. *(b)*	23. *(d)*	24. *(c)*	25. *(*)*	26. *(c)*	27. *(c)*	28. *(d)*	29. *(b)*	30. *(b)*

For Detailed Solutions
Visit : http://tinyurl.com/y6c7dhlt
Or Scan :

12 January, Shift-II

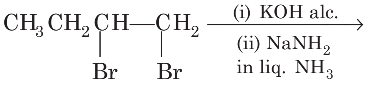
1 The two monomers for the synthesis of nylon 6, 6 are

(a) $HOOC(CH_2)_4COOH$, $H_2N(CH_2)_4NH_2$
(b) $HOOC(CH_2)_6COOH$, $H_2N(CH_2)_4NH_2$
(c) $HOOC(CH_2)_4COOH$, $H_2N(CH_2)_6NH_2$
(d) $HOOC(CH_2)_6COOH$, $H_2N(CH_2)_6NH_2$

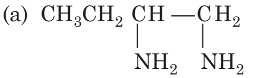
2 The volume strength of 1 M H_2O_2 is (Molar mass of $H_2O_2 = 34\ g\ mol^{-1}$)

(a) 16.8 (b) 22.4 (c) 11.35 (d) 5.6

3 The major product of the following reaction is



$$CH_3CH_2\underset{Br}{CH}-\underset{Br}{CH_2} \xrightarrow[\text{(ii) NaNH}_2 \text{ in liq. NH}_3]{\text{(i) KOH alc.}}$$

(a) 

$CH_3CH_2\underset{NH_2}{CH}-\underset{NH_2}{CH_2}$

(b) $CH_3CH=CHCH_2NH_2$
(c) $CH_3CH=C=CH_2$
(d) $CH_3CH_2C\equiv CH$

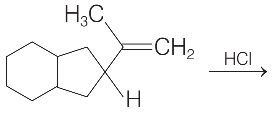
4 The element that shows greater ability to form $p\pi$-$p\pi$ multiple bonds, is

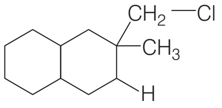
(a) Ge (b) Si (c) Sn (d) C

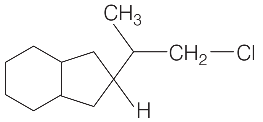
5 If K_{sp} of Ag_2CO_3 is 8×10^{-12}, the molar solubility of Ag_2CO_3 in 0.1 M $AgNO_3$ is

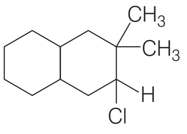
(a) 8×10^{-12} M (b) 8×10^{-13} M
(c) 8×10^{-10} M (d) 8×10^{-11} M

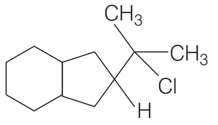
6 The major product of the following reaction is



(a) 

(b) 

(c) 

(d) 

7 Chlorine on reaction with hot and concentrated sodium hydroxide gives

(a) Cl^- and ClO^- (b) Cl^- and ClO_3^-
(c) ClO_3^- and ClO_2^- (d) Cl^- and ClO_2^-

8 The magnetic moment of an octahedral homoleptic Mn(II) complex is 5.9 BM. The suitable ligand for this complex is

(a) CN^- (b) ethylenediamine
(c) NCS^- (d) CO

9 An open vessel at 27°C is heated until two fifth of the air (assumed as an ideal gas) in it has escaped from the vessel. Assuming that the volume of the vessel remains constant, the temperature at which the vessel has been heated is

(a) 750 K (b) 500 K (c) 750°C (d) 500°C

10 Given :

(i) $C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)$; $\Delta_rH^\ominus = x$ kJ mol^{-1}

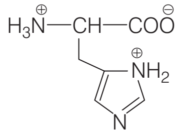
(ii) $C(\text{graphite}) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$; $\Delta_rH^\ominus = y$ kJ mol^{-1}

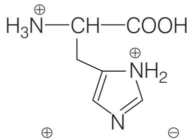
(iii) $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$; $\Delta_rH^\ominus = z$ kJ mol^{-1}

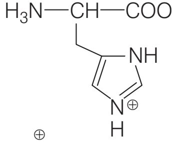
Based on the above thermochemical equations, find out which one of the following algebraic relationships is correct?

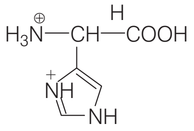
(a) $y = 2z - x$ (b) $x = y - z$
(c) $z = x + y$ (d) $x = y + z$

11 The correct structure of histidine in a strongly acidic solution (pH = 2) is

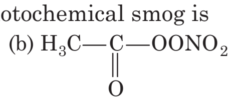
(a) 

(b) 

(c) 

(d) 

12 The compound that is not a common component of photochemical smog is

(a) CF_2Cl_2 (b) 

$H_3C-\underset{\underset{O}{\|}}{C}-OONO_2$

(c) $CH_2=CHCHO$ (d) O_3

13 The pair that does not require calcination is

(a) ZnO and MgO
(b) ZnO and $Fe_2O_3 \cdot xH_2O$
(c) $ZnCO_3$ and CaO
(d) Fe_2O_3 and $CaCO_3 \cdot MgCO_3$

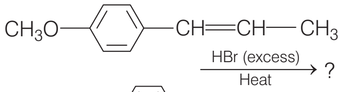
14 The element that does not show catenation is

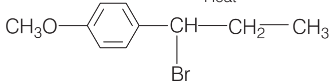
(a) Ge (b) Sn (c) Si (d) Pb

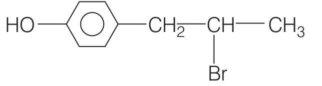
15 8 g of NaOH is dissolved in 18 g of H_2O. Mole fraction of NaOH in solution and molality (in mol kg^{-1}) of the solution respectively are

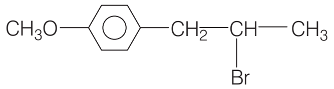
(a) 0.2, 11.11 (b) 0.167, 22.20
(c) 0.2, 22.20 (d) 0.167, 11.11

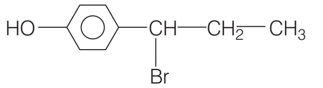
16 The major product in the following conversion is



(a) 

(b) 

(c) 

(d) 

17 Among the following, the false statement is

(a) Tyndall effect can be used to distinguish between a colloidal solution and a true solution
(b) It is possible to cause artificial rain by throwing electrified sand carrying charge opposite to the one on clouds from an aeroplane
(c) Lyophilic sol can be coagulated by adding an electrolyte
(d) Latex is a colloidal solution of rubber particles which are positively charged

18 The correct statement(s) among I to III with respect to potassium ions that are abundant within the cell fluids is/are

I. They activate many enzymes.
II. They participate in the oxidation of glucose to produce ATP.
III. Along with sodium ions, they are responsible for the transmission of nerve signals.

(a) I, and III only (b) I, II and III
(c) I and II only (d) III only

19 The upper stratosphere consisting of the ozone layer protects us from the sun's radiation that falls in the wavelength region of

(a) 600- 750 nm (b) 400- 550 nm
(c) 0.8- 1.5 nm (d) 200- 315 nm

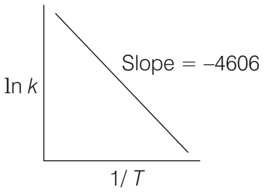
20 The correct order of atomic radii is

(a) Ho > N > Eu > Ce
(b) N > Ce > Eu > Ho
(c) Eu > Ce > Ho > N
(d) Ce > Eu > Ho > N

21 Molecules of benzoic acid (C_6H_5COOH) dimerise in benzene. 'w' g of the acid dissolved in 30 g of benzene shows a depression in freezing point equal to 2 K. If the percentage association of the acid to form dimer in the solution is 80, then w is (Given that K_f = 5 K kg mol^{-1}, molar mass of benzoic acid = 122 g mol^{-1})

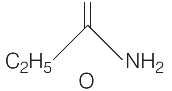
(a) 1.8 g (b) 1.0 g (c) 2.4 g (d) 1.5 g

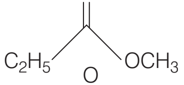
22 For a reaction, consider the plot of ln k *versus* $1/T$ given in the figure. If the rate constant of this reaction at 400 K is 10^{-5} s^{-1}, then the rate constant at 500 K is

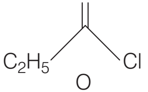


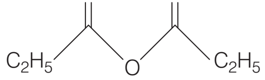
(a) 4×10^{-4} s^{-1} (b) 10^{-6} s^{-1}
(c) 10^{-4} s^{-1} (d) 2×10^{-4} s^{-1}

23 The increasing order of the reactivity of the following with $LiAlH_4$ is

(*A*)


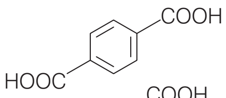
(*B*)


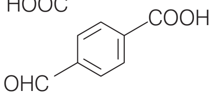
(*C*)


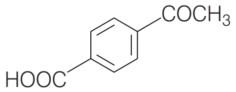
(*D*)


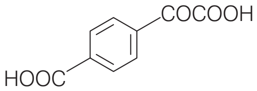
(a) (A) < (B) < (D) < (C)
(b) (A) < (B) < (C) < (D)
(c) (B) < (A) < (D) < (C)
(d) (B) < (A) < (C) < (D)

24 The aldehydes which will not form Grignard product with one equivalent Grignard reagents are

(a)


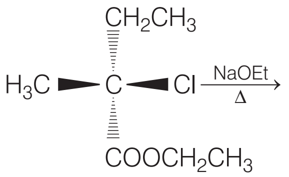
(c)


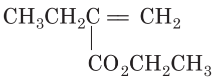
(b)


(d)


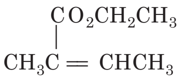
(a) (C), (D) (b) (B), (D)
(c) (B), (C), (D) (d) (B), (C)

25 The major product of the following reaction is

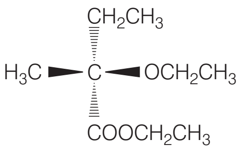


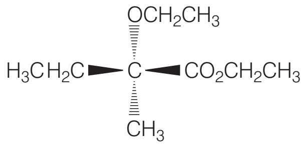
(a)


$CH_3CH_2\underset{\substack{|\\ CO_2CH_2CH_3}}{C} = CH_2$

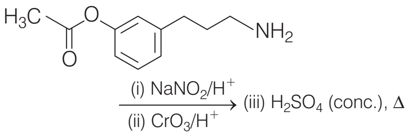
(b)


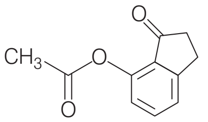
$CH_3\overset{\substack{CO_2CH_2CH_3\\ |}}{C} = CHCH_3$

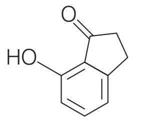
(c)


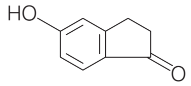
(d)


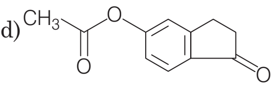
26 The major product of the following reaction is



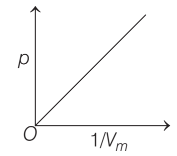
(a)


(b)


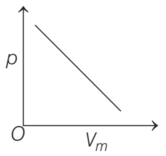
(c)


(d)


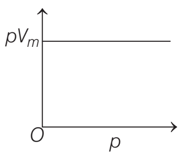
27 The combination of plots which does not represent isothermal expansion of an ideal gas is



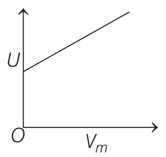
(*A*)



(*B*)



(*C*)



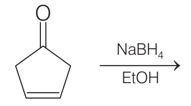
(*D*)

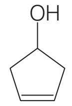
(a) (A) and (C) (b) (B) and (C)
(c) (B) and (D) (d) (A) and (D)

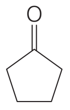
28 If the de-Broglie wavelength of the electron in n^{th} Bohr orbit in a hydrogenic atom is equal to $1.5\ \pi a_0$ (a_0 is Bohr radius), then the value of n/Z is

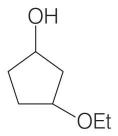
(a) 1.0 (b) 0.75 (c) 0.40 (d) 1.50

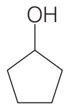
29 The major product of the following reaction is



(a)


(b)


(c)


(d)


30 Λ°_m for NaCl, HCl and NaA are 126.4, 425.9 and 100.5 S cm^2 mol^{-1}, respectively. If the conductivity of 0.001 M HA is 5×10^{-5} S cm^{-1}, degree of dissociation of HA is

(a) 0.25 (b) 0.50 (c) 0.75 (d) 0.125

ANSWERS

1. (c)	2. (c)	3. (d)	4. (d)	5. (c)	6. (d)	7. (b)	8. (c)	9. (b)	10. (d)
11. (d)	12. (a)	13. (a)	14. (d)	15. (d)	16. (d)	17. (d)	18. (b)	19. (d)	20. (c)
21. (c)	22. (c)	23. (a)	24. (b)	25. (b)	26. (c)	27. (c)	28. (b)	29. (a)	30. (d)

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